On the Question of Cyclopropylidene Intermediates in Cyclopropene-to-Allene Rearrangements – Tetrakis(trimethylsilyl)cyclopropene, 3-Alkenyl-1,2,3tris(trimethylsilyl)cyclopropenes, and Related Model Compounds

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Dedicated to Professor Jürgen Troe on the occasion of his 60th birthday

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Several tetrasubstituted cyclopropenes have been prepared and their pyrolyses and photolyses have been investigated. Tetrakis(trimethylsilyl)cyclopropene (10), which was obtained in 25% yield from tris(trimethylsilyl)cyclopropenylium hexachloroantimonate (9), gave tetrakis(trimethylsilyl)allene (12) as the sole product both thermally and photochemically. Kinetic studies in [D₈]toluene indicated first-order behavior with Arrhenius parameters $log(A/s^{-1}) = 11.75 \pm 1.20$ and $E_a =$ (37.5 ± 2.5) kcal mol⁻¹. All three new 3-alkenyl-1,2,3-tris(trimethylsilyl)cyclopropenes (17a-c, with C1-, C2-, and C3-alkenyl groups as tethers, respectively) gave allenes upon irradiation, but thermally only two (17a, 17c) gave allenes, whilst 17b yielded a bicyclo[4.1.0]hept-3-ene derivative 22 as a result of an intramolecular ene reaction. Photolyses of two further cyclopropenes (33a,b) bearing 1,2-bis(alkenyldimethylsilyl) substituents also gave the corresponding allenes as the sole products. For none of these tethered cyclopropenes was a product found that could have originated from intramolecular trapping of a cyclopropylidene intermediate. Quantum mechanical (ab initio) calculations have been carried out on the silyl-substituted cyclopropene model compounds 3,3-dimethyl-1-silyl- (36a), 3,3-dimethyl-1,2-disilyl- (37), and tetra-

silylcyclopropene (38) at the QCISD(T)/6-311G*//B3LYP/6-311G* + ZPVE level of theory, and on 3,3-dimethyl-1-(trimethylsilyl)cyclopropene (36b) at the B3LYP/6-311G*//B3LYP/ 6-311G* + ZPVE level. These calculations provided us with detailed energy surfaces for the potential pyrolysis pathways. Although the potential cyclopropylidene species in these rearrangements are significantly stabilized, for none of the systems was this sufficient to permit isomerization via these intermediates. 36b is calculated to rearrange via a vinylidene intermediate to give 3-methyl-1-trimethylsilyl-1-butyne (47), in agreement with experiment. Comparison of the calculations for 36a and 36b shows that H₃Si- is a poor model for an Me₃Si- substituent in these rearrangements. When an appropriate correction is applied, the calculations on disilyl-(37) and tetrasilylcyclopropenes (38) are consistent with the experimental findings that the trimethylsilyl-substituted cyclopropenes 48 and 10 form allenes 49 and 12, respectively, via vinylcarbene-type intermediates. These findings considerably extend our understanding of silyl group substituent effects on the various intermediates involved in cyclopropene rearrangements.

Introduction

Due to their inherent ring strain, cyclopropenes readily undergo ring-opening reactions upon moderate heating or

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irradiation to yield dienes, acetylenes, or allenes.^[1-3] The kinetics of these rearrangements, the product compositions, and even the mechanisms by which these products are formed, have been found to depend on the substitution pattern and the nature of the substituents on the cyclopropene ring.^[2,3]

The originally suggested ring-opening mode for a cyclopropene 2, particularly that of the parent hydrocarbon, involves the formation of a diradical 1, which is a valence isomer of a vinylcarbene **4**,^[4] and can be either a singlet or a triplet species. With appropriate alkyl substituents on 1/4, the diradical/vinylcarbene can undergo a 1,2- or a 1,4-H migration to yield dienes 7. However, when at least one of the substituents R^1 or R^2 on **2** is a hydrogen atom, it has since been shown^[3c,5] that the alkyne product 6 is not formed via the diradical 1, but rather via a synchronous process of ring-opening accompanied by 1,3-H migration (extrusion) to yield an alkenylidene (a substituted vinylidene) intermediate 3. This is then followed by a 1,2-shift of the substituent \mathbb{R}^2 to yield the alkyne 6 (Scheme 1).



When trimethylsilyl substituents are introduced, some intriguing variations are observed. If one of the vinylic substituents is still a hydrogen, the rearrangement proceeds normally. Thus, **2** ($R^1 = Me_3Si$, $R^2 = H$, $R^3 = R^4 = Me$) yields the corresponding alkyne 6 with > 99% selectivity.^[3b] However, when $R^1 = Me_3Si$ and $R^2 \neq H$, the reaction leads exclusively to allenes 8.^{[3a][3e,6]} Bearing in mind that cyclopropylidenes such as 5, when generated from a diazocyclopropane^[7] or a 1,1-dihalocyclopropane via a carbenoid,^[8] are prone to undergo ring opening to allenes, we conceived the possibility that in a 1-silyl-substituted cyclopropene 2, a fast 1,2-silyl shift^[9,10] might occur in the first step leading to a cyclopropylidene 5,^[11] which could then rearrange to the observed allene 8. An example of a 1,2-silyl shift leading to a carbene has been reported by Barton et al.,^[12] who found that heating of 1,1,3,3-tetramethyl-2,4-dimethylene-1,3-disilacyclobutane results in its rearrangement by consecutive 1,2-silvl and 1,2-H shifts via 1,1,3,3-tetramethyl-2methylene-1,3-disilacyclopent-4-ylidene to 1,1,3,3-tetramethyl-2-methylene-1,3-disilacyclopent-4-ene. Of course, an allene 8 would also result from a fast 1,2-silvl shift in the vinylcarbene 4. The existence of vinylcarbene intermediates formed by ring opening of substituted cyclopropenes^[4] has been proved by very efficient trapping with alkenes in the case of tetrachlorovinylcarbene,^{[13a][13b]} (2',2'-dialkyloxyvinyl)carbenes,^[13c] 1,2-dihalo-3,3-dimethylvinylcarbenes,^[13d] and more recently for 3,3-dialkyloxy-1-(trimethylsilyl)vinylcarbenes.^[13e] We have mentioned the two possibilities for the formation of allenes from silyl-substituted cyclopropenes in a previous report^[3e] and, in order to pursue them further, we have now combined an experimental investigation of some specifically designed tetrasubstituted cyclopropenes with quantum mechanical calculations on closely related model compounds.

For the experimental study, tetrakis(trimethylsilyl)cyclopropene **10**, a set of three 3- ω -alkenyl-1,2,3-tris(trimethylsilyl)cyclopropenes, **17a**-c, and a pair of 1,2-bis(ω -alkenyldimethylsilyl)-3,3-dimethylcyclopropenes **33a**,b were designed. The logic behind the choice of **10** was based on the well-known ability of a β -silyl group to stabilize a carbocation,^[14] which should also apply to a carbene center. We reasoned that if a cyclopropylidene **5** were to be involved in the formation of the allene 8, the best chance of observing it (or at least of generating the example with the lowest activation energy for its formation) should be manifested in the case of tetrakis(trimethylsilyl)cyclopropylidene 11 (Scheme 2), which has the maximum possible stabilization by four β -silyl groups. Compounds 17a-c and 33a,b were studied with a view to possible intramolecular trapping of the cyclopropylidene intermediate, if formed, by means of a tethered double bond. Skattebøl et al.^[15] showed some 30 years ago that a cyclopropylidene (or at least a cyclopropylidenoid 15) generated from a 2-alkenyl-1,1-dibromocyclopropane 14 (n = 1, 2) with methyllithium, is very efficiently trapped by the intramolecular double bond to give the spiropentane 16, especially with a two-carbon tether. This suggests that 19 would be a reasonable product of 17 if the cyclopropylidene 18 were involved as an intermediate in its thermal or photochemical rearrangement (Scheme 3).



Scheme 2



Computationally, we have studied the thermal rearrangement of 3,3-dimethyl-1-silylcyclopropene **36a**, its trimethylsilyl-substituted analogue **36b**, the 3,3-dimethyl-1,2-disilylcyclopropene **37**, and the tetrasilyl-substituted cyclopropene **38**. In addition to shedding light on the general mechanism of breakdown for each of these compounds, which will reveal whether or not cyclopropylidene intermediates are involved, the comparison of **36a** and **36b** allows us to probe the frequently made assumption that a silyl group can be used to computationally model the experimentally more convenient trimethylsilyl substituent.

Experimental Studies and Results

To probe the aforementioned hypothesis, the hitherto unknown cyclopropene **10** had to be synthesized. Several attempts to prepare **10** by reductive silylation of the readily available tetrachlorocyclopropene with magnesium and chlorotrimethylsilane in tetrahydrofuran were unsuccessful.^[16] In the presence of hexamethylphosphoric triamide (HMPA), however, the hexakis(trimethylsilyl)-3,3'-bicyclopropenyl was formed, as reported by two groups shortly thereafter.^[17,18] Under these conditions, *tert*-butylchlorodimethylsilane and tetrachlorocyclopropene gave, besides the corresponding bicyclopropenyl, a 1.8% yield of tetrakis-(*tert*-butyldimethylsilyl)cyclopropene (**2**, R¹, R², R³, R⁴ = Si-Me₂*t*Bu).

Tetrakis(trimethylsilyl)cyclopropene (10) could, however, readily be prepared by the reaction of tris(trimethylsilyl)cyclopropenylium hexachloroantimonate (9)^[19] with tris(trimethylsilyl)aluminum,^[20] which has previously been shown to be an excellent donor reagent of a trimethylsilyl anion equivalent.^[21] In this way, cyclopropene 10 was obtained as a colorless solid (m.p. 196 °C) in 25% yield.

Upon heating at 252 °C, as well as on irradiation with a low-pressure mercury lamp ($\lambda = 254$ nm), 10 underwent clean and quantitative rearrangement to tetrakis(trimethylsilvl)allene (12) (Scheme 2).^[22] The UV absorption of 10 has a rather long wavelength maximum at 296.2 nm ($\varepsilon = 5592$), similar to that observed for tetrakis(tert-butyldimethylsilyl)cyclopropene,^[16] while the allene 12 has its longest wavelength absorption at just 273.3 nm ($\varepsilon = 36066$).^[22] The thermal rearrangement of 10 to 12 in solution could easily be monitored by ¹H NMR spectroscopy. Good linear firstorder plots [log (% reactant) versus time] were obtained at all temperatures in the range 200-252 °C. Rate constants were calculated by least-mean-squares fitting (Table 1). The data were fitted to the Arrhenius equation to give the following parameters: $E_a = 37.3 \pm 2.5 \text{ kcal mol}^{-1}$, $\log(A/$ s^{-1}) = 11.75 ± 1.2.

Table 1. Rate constants for the isomerization of tetrakis(trimethyl-silyl)cyclopropene (10)

$\begin{array}{c} T \ [^{\circ}C] \\ k \ [10^{-5} \ s^{-1}] \end{array} \qquad \begin{array}{c} 200 \\ 0.30 \end{array}$	215	230	252
	1.10	3.73	15.16

The Arrhenius activation energy for the rearrangement of **10** was found to be 6.8 kcal mol⁻¹ lower than that for 3,3-dimethyl-1,2-bis(trimethylsilyl)cyclopropene **2** (R¹,R² = SiMe₃; R³,R⁴ = Me).^[3e,23] Moreover, the rate constant for the rearrangement of **10** was evaluated as being ca. 15 times greater than that in the case of **2** (R¹,R² = SiMe₃; R³,R⁴ = Me) at 500 K. This clearly shows that the replacement of the 3-methyl group by trimethylsilyl has a significant effect on the relative energies of the transition state and ground state of such species. We can infer that the ground state is less stabilized (or more destabilized) than the transition state as compared to the rearrangement of $2 (R^1, R^2 = SiMe_3; R^3, R^4 = Me)$. The steric bulk of the trimethylsilyl groups is almost certainly at least partially responsible for this, although the kinetic effect alone does not allow any conclusion to be drawn as to whether the intermediate is a cyclopropylidene 11 or a vinylcarbene 13. This question was therefore addressed by computational methods (see below).

For the intramolecular trapping experiments, three 3-alkenvlcyclopropenes 17a-c with C1-, C2-, and C3-tethers, respectively (n = 1, 2, 3) were readily prepared from tris(trimethylsilyl)cyclopropenylium hexachloroantimonate (9) and the appropriate alkenylmagnesium bromide in diethyl ether (Scheme 4). All three compounds 17a - c were purified by preparative gas chromatography and were obtained as colorless oils in yields of 40%, 45%, and 51%, respectively. Upon irradiation with a low-pressure mercury lamp ($\lambda =$ 254 nm) in n-pentane solution at 20 °C, all three tris(trimethylsilyl)cyclopropenes 17a-c underwent clean rearrangement to the corresponding allenes 21a-c, which were isolated by preparative gas chromatography (Scheme 4). Even the C₂-tethered compound 17b did not give any of the C₂bridged spiropentane derivative 19b, which might have been expected from a cyclopropylidene intermediate of type 18.



Scheme 4

Upon heating to 380 °C in *cis*-decalin solution in a pressurized thick-walled glass ampoule, however, only **17a** and **17c** gave the respective allenes **21a** and **21c**. On the other hand, the C₂-tethered cyclopropene **17b** underwent clean rearrangement to a new product upon heating to 210 °C in toluene solution. On the basis of its ¹H, ¹³C, and ¹H-¹H NOESY NMR spectra, the structure of the new product

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was assigned 1,6,7exo-tris(trimethylsilyl)bicyas clo[4.1.0]hept-3-ene (22) (Scheme 4). The only reasonable mechanism to account for its formation would be an intramolecular ene reaction, whereby one of the two allylic hydrogen atoms from the side chain in 17b ends up as the 7endo hydrogen atom in 22. Indeed, thermal rearrangement of the labeled cyclopropene 17b-D with two deuterium atoms in the allylic position gave 3,7endo-dideuterio-1,6,7*exo*-tris(trimethylsilyl)bicyclo[4.1.0]hept-3-ene (22-D) as the sole product. Again, no bridged spiropentane derivatives of type 19 were obtained, strongly indicating that cyclopropylidenes of type 18 are not intermediates in either the photochemical or thermal reactions of compounds 17.

The labeled compound 17b-D was obtained from 9 and the Grignard reagent derived from 4-bromo-3,3-dideuteriobut-1-ene (29) (Scheme 5), which, in turn, was prepared from the Diels-Alder adduct 23 of methyl acrylate and anthracene.^[24] Reduction of 23 with lithium aluminum deuteride yielded the deuterated hydroxymethyl derivative 24 (quant.),^[24] which was converted into the bromide 25 (85%). Chain extension was achieved by treating the Grignard reagent derived from 25 with methyl chloroformate (52%); reduction of the ester 26 with $LiAlH_4$ gave the hydroxymethyl derivative 27 (quant.), which was cleaved by flash vacuum pyrolysis to yield the 3,3-dideuteriobut-1-en-4-ol (28) (100%). The latter was then converted into the deuterated homoallyl bromide (29) (65%). The Grignard reagent derived from 29 was finally added to the cyclopropenylium salt 9 to yield 17b-D (46%).



Scheme 5

As a second type of model substrate for intramolecular trapping of a cyclopropylidene intermediate, the pair of 1,2bis(silyl)-substituted cyclopropenes **33a** and **33b**, having tethered ω -vinyl groups on the silicon atoms, were straightforwardly prepared (Scheme 6). 1-Lithio-3,3-dimethylcyclopropene (**31**), generated from 1,1-dibromo-2-chloro-3,3-dimethylcyclopropane (**30**) by treatment with methyllithium according to Baird et al.,^[25] was electrophilically substituted with allylchlorodimethylsilane^[26] or but-3-enyl(methylsulfonyloxy)dimethylsilane^[26c,26d] to give the trisubstituted cyclopropenes **32a** (80% yield) and **32b** (63%), respectively. The latter were deprotonated with lithium diisopropylamide in THF and then substituted once more with the alkenylchlorodimethylsilane reagents to yield the bis(silylated) cyclopropenes 33a (45%) – in which one of the allyl groups had apparently undergone a base-catalyzed doublebond shift – and 33b (40%), respectively. Upon irradiation of 33a and 33b in *n*-pentane with a low-pressure mercury lamp ($\lambda = 254$ nm), both were completely isomerized to the corresponding allenes 35a and 35b, respectively (Scheme 6). In neither case could any trace of the expected trapping products 34a,b be detected, which are akin to compounds 19, but have a silicon atom in the chain bridging the spiropentane unit.



Scheme 6

The absence of spiro compounds of types 19 or 34 might be explained if they were too unstable and thus undergo further rearrangement under the applied experimental conditions. Indeed, the parent bridged spiropentane 16 (n = 2) rearranges relatively easily to give a mixture of products.^[27] This would correspond to 19 (n = 2) in our studies, which cannot be involved because of the favored ene pathway leading from 17b to 22. For the other cases, nothing is known about the stabilities of the potential bridged spiropentane derivatives 19 (n = 1, 3). It would appear extremely unlikely, however, that, even if thermally unstable, these compounds would rearrange cleanly to the observed products 21a and 21c. It is also noteworthy that compounds 19 (n = 1, 2, or 3) are not formed under photochemical conditions either.

Although no products characteristic of a cyclopropylidene intermediate could be detected, the observed formation of **22** from **17b** is notable as the first example of an intramolecular ene reaction involving a cyclopropene. This constitutes yet another mechanistic variation to add to the already rich and varied chemistry of cyclopropene rearrangements.

Computational Studies

Methods

All calculations were performed with the Gaussian 94 series of programs.^[28] Initially, the structures of the molecules were fully optimized at the HF/6-31G* level of theory and refined using density functional theory^[29a] employing Becke's three-parameter hybrid method using the LYP correlated functional (B3LYP)^[29b-29d] and the polarized and triply split 6-311G* basis set. Frequency calculations at the B3LYP/6-311G* level were used to characterize the various stationary points as minima or transition states. Transition structures were located using the TS routine of the Gaussian 94 package and the intrinsic reaction coordinate (IRC) method. Schaefer et al.^[30] have recently demonstrated that the hybrid DFT B3LYP method with a sufficiently large basis set represents a valuable alternative to elaborate multi-reference CI calculations for systems related to those under study here, such as the electrocyclic ring opening of cyclopropylidene. Energies were also obtained at the QCISD(T)/6-311G* level of theory^[31] using the B3LYP/6-311G* optimized geometries and were corrected using the B3LYP/6-311G* zero-point energies [denoted as QCISD(T)/6-311G*//B3LYP/6-311G* +ZPVE]. QCISD(T) energies are known to give reliable results, even in difficult cases for which a single-determinant approach might not be sufficiently accurate.^[32] Unless stated otherwise, the relative energies and the energies of the isodesmic reactions quoted in this paper have been calculated at this level. All species were calculated in their lowest singlet state.

Results

Computationally, we have studied the thermolysis of four systems: 3,3-dimethyl-1-silylcyclopropene (36a), its trimethylsilyl analogue 36b, 3,3-dimethyl-1,2-disilylcyclopropene (37), and the tetrasilylcyclopropene (38). While in the calculations on 36a, 37, and 38 an H₃Si group served as a model for the Me₃Si group used in the experiments (e.g. 38 was used as a model for 10), the computational results obtained for 36b can be directly compared with the previously published experimental results for this molecule.^[3b] Moreover, comparison of the potential energy surfaces (PESs) for the decompositions of 36a and 36b allows an estimation of the electronic and steric effects of the trimethylsilyl group in **36b** as opposed to a silvl group in **36a**. This comparison is important since calculations of the PESs of interest and, in particular, of the transition states for the trimethylsilyl analogues of 37 (i.e. 48) and 38 (i.e. 10), are still not feasible due to the size of these molecules. The total energies and zero-point energies of all the species calculated are available as Supporting Information.



Discussion

(a) General Considerations

Multi-reference CI calculations by Yoshimine and coworkers^[33] have shown that the thermal isomerization of the parent cyclopropene does not proceed via a cyclopropylidene intermediate but rather via vinylmethylene and propenylidene intermediates, yielding allene and propyne, respectively (propyne being more stable than allene by just 0.3 kcal mol⁻¹). According to the calculations, the allene is formed in two steps via a vinylmethylene intermediate **4**, $R^1,R^2,R^3,R^4 = H$ (see Figure 1). This reaction path is preferred by 11.1 kcal mol⁻¹ (at the MRCI/DZP level of theory) as compared to the alternative path via cyclopropylidene **5**, $R^1,R^2,R^3,R^4 = H$.^[33] A direct interconversion of allene to propyne by a 1,3-H shift is unlikely in view of the very high calculated barrier of 94.9 kcal mol⁻¹ (at the SCF/ DZP level).



Figure 1. Part of the potential energy surface of C_3H_4 at MRCl/ DZP according to Yoshimine et al.^[33]; relative energies in kcal mol⁻¹

Also by computational methods [at the QCISD(T)/6-311G*//MP2/6-31G* level], Shimizu and Gordon^[34] found some interesting differences regarding the thermal isomerization of 1-silvlcyclopropene (Figure 2) compared to that of the parent cyclopropene (Figure 1). The two-step reaction path by which cyclopropene is converted to allene via the vinylmethylene intermediate (Figure 1) merges for the 1-silyl-substituted cyclopropene into a concerted single-step reaction. However, the barrier associated with the cyclopropylidene path is higher in energy by $11.7 \text{ kcal mol}^{-1}$ for 1silvlcyclopropene as well (Figure 2). Therefore, the authors concluded that cyclopropylidenes are probably not intermediates in the thermal isomerization of 1-trimethylsilylcyclopropenes either. The most stable isomer on the $H_3SiC_3H_3$ PES is 1-silylpropyne, but silylallene is more stable than 3silylpropyne (relative energies: -8.0, 0.0, and 2.9 kcal mol^{-1}). The 1,3-silvl migration by which 3-silvlpropyne is converted to silvlallene has an associated barrier of just 52.9 kcal mol⁻¹, roughly half of the 94.9 kcal mol⁻¹ required for the allene-to-propyne interconversion.

In a recent theoretical study, Goldberg et al.^[35] have shown that alkyl-substituted cyclopropenes (2, $R^1 = R^3 =$ H, $R^2 = R^4 = Me$; 2, $R^1 = R^2 = R^3 = R^4 = Me$) decom-



Figure 2. Part of the calculated potential energy surface of $C_3H_3(SiH_3)$ at the QCISD(T)/6-311G*//MP2/6-31G* level according to Shimizu et al.^[34]; relative energies in kcal mol⁻¹

pose via the corresponding alkyl-substituted vinylidenes **3**. It was also found that although homolytic bond cleavage, giving rise to vinylcarbenes **4**, is in some cases energetically preferred over vinylidene formation, it leads to an energetic dead end, because barriers to subsequent hydrogen shifts leading to allenes or dienes are all higher in energy than those associated with the corresponding vinylidene pathways. It was concluded that for these systems vinylcarbenes are not intermediates in the formation of alkynes from cyclopropenes.

(b) The β-Silyl Stabilization of Cyclopropylidenes

The question central to this study has been whether additional silyl substitution would change the energetics of the competing reaction channels in favor of a cyclopropylidene intermediate making this the preferred pathway. This qualitative expectation was based on the knowledge that silyl groups at the β -position strongly stabilize electron-deficient centers, particularly carbenium ions, through hyperconjugative interaction between the σ -(Si–C) bond and the empty 2p(C⁺) orbital.^[36] For β -silyl-substituted carbocations, the silyl group stabilizing effect is extremely large, of the order of 30 kcal mol⁻¹ (calculated at the MP2/6-31G*//6-31G* level)^[37] to 34 kcal mol⁻¹ (measured in the gas phase)^[38] for a secondary carbocation.

The stabilization of cyclopropylidene by β -silyl groups can be evaluated by the isodesmic Equation (1), which compares the stabilities of di- and tetrasilyl-substituted singlet cyclopropylidenes **39**, **40** with that of the parent singlet cyclopropylidene **42**.



The calculations show that **39a** is stabilized by 8.3 kcal mol^{-1} relative to cyclopropylidene (**42**) [Equation (1), R = H] and that **40**, with four β -silyl groups, is more stable than **42** by 12.5 kcal mol^{-1} [Equation (1), R = SiH₃]. This represents a substantial stabilizing effect, but, as expected, is significantly smaller than that in the corresponding cyclopropyl cations. Thus, the tetrasilylcyclopropyl cation **45** is found to be 37.1 kcal mol^{-1} more stable than the parent cyclopropyl cation **46** [Equation (2)].

The occurrence of hyperconjugative stabilization in 40 is supported by a natural bond orbital (NBO) analysis^[39] of the wavefunction, as well as by the optimized geometry of the molecule (Figure 3). Thus, the occupancy of the formally vacant carbenic 2p orbital is substantially higher in 40 than in 42 (0.15 e and 0.05 e, respectively), in agreement with increased charge transfer from the β -C-Si bonds to the carbonic 2p(C) orbital. In the analogous carbocation, the β -silvl effect is much larger with a calculated $2p(C^+)$ occupancy of 0.36 e in 45 (compared with 0.14 e in 46). As a result of the hyperconjugative interaction, the $C^{1}-C^{2(3)}$ bonds (C¹ is the carbonic carbon atom) in 40 are shortened by 0.031 Å compared to those in 42 (1.502 Å), while the C²⁽³⁾-Si bonds are elongated by 0.016 Å and 0.003 Å compared to the C^3 -Si bonds in cyclopropene **38** (1.890 Å). Concomitant with the shortening of the $C^{1}-C^{2(3)}$ and C^1-C^3 distances, the C^2-C^3 bond in 40 is elongated by 0.066 Å as compared to that in 42 (see Figure 3).



Figure 3. Calculated geometries (at the B3LYP/6-311G* level) of cyclopropylidenes 40 (C_2) and 42 (C_{2v})

The evidence from the trapping experiments presented above indicates that the cyclopropylidene 5 (\mathbb{R}^1 , \mathbb{R}^2 , \mathbb{R}^3 , $R^4 = Me_3Si$) is probably not an intermediate in the rearrangement of 10 to 12. Evidently, the hyperconjugative stabilization of a cyclopropylidene by four silvl groups is insufficient to make it an intermediate along the lowestenergy reaction path leading from 10 to 12. As is shown below, this is also the conclusion that emerges from the computational results. To determine the preferred reaction path, we computed the effect of silvl substitution on the various reaction pathways for the thermal decomposition of the four silvl-substituted cyclopropenes 36a,b, 37, and 38. Compounds 37 and 38 constitute structurally close models for the experimentally studied systems 48^[3e] and 10, respectively (the Me₃Si groups in the experimental systems are replaced by H₃Si in the calculations). On heating, both 48 and 10 undergo isomerization to exclusively afford the corresponding allenes 49 and 12, respectively. In contrast, the monosilyl-substituted cyclopropene 36b isomerizes almost quantitatively to the 1-trimethylsilylalkyne 47.^[3b]



The calculated relative energies of all the computed species, at several levels of theory, are summarized in Table 2. The calculated reaction paths for the isomerization of cyclopropenes **36a,b**, **37**, and **38** are also shown schematically in Figures 4-8.

(c) Calculations on the Thermal Rearrangement Pathways for Silyl-Substituted Cyclopropenes

(i) Monosilyl-Substituted Cyclopropenes: First, the isomerization of 36a will be considered (Figure 4 and Figure 5). The most stable isomer on the $C_5H_{10}Si$ potential energy surface is the butadiene 52a, which is 9.0, 4.4, and 15.1 kcal mol⁻¹ lower in energy than the allene 51a and the isomeric 1-silyl- and 3-silylbutynes 53a and 54a, respectively.

There are three possible reaction channels for the thermal isomerization of 36a. The first of these is a two-step process involving the isomeric vinylcarbene intermediates 50a-H and 50a-Si, which leads to the allene 51a (Path A, Figure 4). The calculations show that both vinylcarbenes, but in particular the α -silvl-substituted vinvlcarbene 50a-Si, lie in relatively flat energy minima, so that the formation of allene 51a from 36a along path A is almost concerted with an overall barrier (via 50a-H) of 44.1 kcal mol^{-1} ; the barrier is higher, at 50.9 kcal mol⁻¹, via **50a-S**i. The α -silyl-substituted vinylcarbene **50a**-Si^[40] is the key intermediate en route to the formation of butadiene 52a. The 1,4-hydrogen shift in 50a-Si leading to 52a is subject to a relatively small barrier of just 8.2 kcal mol⁻¹, but the overall barrier for the formation of **52a** from **36a** is 45.4 kcal mol⁻¹, which is 1.3 kcal mol⁻¹ higher than the barrier associated with allene formation via 50a-H. The formation of alkyne 53a from vinylcarbene 50a-Si through a 1,2-H shift [TS8a(H)] across the double bond is also associated with a high overall barrier of $53.0 \text{ kcal mol}^{-1}$. Thus, the lowest barrier for the isomerization of 36a along path A amounts to 44.1 kcal mol^{-1} , leading via **50a**-H to the allene **51a**.

Reaction path B (Figure 5) involves simultaneous C-C bond breaking and a 1,2-vinylic H or SiH₃ migration across the C–C bond to the adjacent sp³-hybridized carbon atom, yielding a vinylidene intermediate. By both experimental means^[5c,e] and calculations,^[33–35] vinylidenes have been established as being intermediates in the thermolysis of cyclopropene and of alkyl-substituted cyclopropenes. For **36a**, we find that the vinylidene structures **[TS4a(H)** and

Compound	B3LYP/ 6-311G* ^[b]	QCISD(T)/ 6-311G* ^[b]	$\begin{array}{c} \text{QCISD(T)} \\ \text{G-311G*} \\ + \Delta \text{ZPVE}^{[b][c]} \\ \hline 17.4 \\ \text{G3.0} \\ 54.6 \\ 59.0 \\ -4.6 \\ \text{G.1} \\ 0^{[a]} \\ -9.0 \\ \text{G1.1} \\ 54.5 \\ \text{G8.3} \\ \text{G1.5} \\ \text{G2.8} \\ 53.4 \\ 54.9 \\ \text{G6.0} \\ 73.3 \\ 73.2 \\ 55.8 \\ 70.4 \\ \end{array}$	
36a 55 50a-Si 50a-H 53a 54a 51a 52a TS1a(H) TS1a(Si) TS2a(H) TS2a(Si) TS4a(H) TS5a(Si) TS5a(Si) TS5a(Si) TS5a(Si) TS5a(Si) TS5a(H) TS5a(Si) TS5a(H)	$\begin{array}{c} 23.1 \\ 71.3 \\ 54.5 \\ 62.2 \\ -1.4 \\ 13.6 \\ 0^{[a]} \\ -8.0 \\ 65.0 \\ 56.0 \\ 56.0 \\ 68.9 \\ 64.9 \\ 65.0 \\ 63.4 \\ 64.5 \\ 75.2 \\ 82.9 \\ 80.0 \\ 59.1 \\ 74.5 \end{array}$	17.6 64.2 55.7 60.8 -5.5 6.4 0[a] -9.6 63.0 55.7 71.5 63.7 66.2 54.8 57.5 68.4 76.3 74.7 57.3 74.0		
36b 50b-Si 53b \equiv 47 54b 51b ^[a] 52b TS1b(Si) TS2b(H) TS3b TS4b(Si) TS4b(H)	$\begin{array}{c} 22.7\\ 55.7\\ -2.5\\ 14.6\\ 0^{[a]}\\ -7.4\\ 57.0\\ 68.1\\ 65.9\\ 67.8\\ 64.0 \end{array}$		$\begin{array}{c} 22.5^{[d]} \\ 54.9^{[d]} \\ -2.4^{[d]} \\ 14.4^{[d]} \\ 0^{[a]} \\ -6.9^{[d]} \\ 55.9^{[d]} \\ 65.0^{[d]} \\ 62.0^{[d]} \\ 66.8^{[d]} \\ 61.5^{[d]} \end{array}$	
37 60 59 58 TS1c TS4c TS5c TS6c TS7c	$ \begin{array}{r} 19.8 \\ 71.5 \\ 5.8 \\ 0[^{a]} \\ 62.8 \\ 61.1 \\ 72.0 \\ 77.9 \\ 51.4 \\ \end{array} $	$ \begin{array}{c} 14.7 \\ 62.9 \\ 0.6 \\ 0^{[a]} \\ 62.2 \\ 52.0 \\ 63.8 \\ 71.4 \\ 50.7 \\ \end{array} $	14.6 62.2 1.0 0 ^[a] 60.5 51.1 62.9 70.1 49.8	
38 32.3 40 76.9 52 7.8 51 0 ^[a] FS1d 72.6 FS4d 67.7 FS5d 81.0 FS6d 81.0 FS7d 50.3		27.5 69.7 0.8 0 ^[a] 68.8 59.6 71.0 84.4 46.3	26.8 68.6 0.9 0 ^[a] 66.8 58.3 69.5 82.9 45.6	

 [a] Absolute energy of 51a: B3LYP/6-311G*//B3LYP/6-311G*: -486.06098 H, ZPVE: 80.1 kcal mol⁻¹; QCISD(T)/6-311G*// B3LYP/6-311G*: -484.93003 H. Absolute energy of 51b: B3LYP/ 6-311G*//B3LYP/6-311G*: -604.07101 H, ZPVE: 134.3 kcal mol⁻¹. Absolute energy of 58: B3LYP/6-311G*//B3LYP/6-311G*: -776.78441 H, ZPE: 89.8 kcal mol⁻¹; QCISD(T)/6-311G*// B3LYP/6-311G*: -775.13602 H. Absolute energy of 61: B3LYP/6-311G*//B3LYP/6-311G*: -1279.58435 H, ZPE: 74.0 kcal mol⁻¹; QCISD(T)/6-311G*/B3LYP/6-311G*: -1277.14590 H. - ^[b] Using B3LYP/6-311G* geometries. - ^[c] Zero-point energies (ZPE) are unscaled. - ^[d] At B3LYP/6-311G*//B3LYP/6-311G* + ΔZPVE.

TS4a(Si)] are not minima, but are transition states that connect **36a** directly to the silyl-substituted butynes **53a** and **54a**. The barriers associated with these isomerizations are relatively low, amounting to 37.5 and 36 kcal mol⁻¹, re-



Figure 4. Part of the calculated potential energy surface of $C_3HMe_2(SiH_3)$ [at the QCISD(T)/6-311G*//B3LYP/6-311G* + ZVPE level]; relative energies in kcal mol⁻¹; the lowest barrier is highlighted by a box



Figure 5. Part of the calculated potential energy surface of $C_3HMe_2(SiH_3)$ [at the QCISD(T)/6-311G*//B3LYP/6-311G* + ZVPE level]; relative energies in kcal mol⁻¹; the lowest barrier is highlighted by a box

spectively, with formation of the 3-silyl-substituted alkyne **54a** being preferred by $1.5 \text{ kcal mol}^{-1}$.

The third possible mechanism is a two-step process involving migration of either a hydrogen or a silyl group across the C=C bond, yielding cyclopropylidene **55** as an intermediate (path C, Figure 5). The barriers associated with these

1,2-shifts are relatively high, amounting to 48.6 kcal mol⁻¹ [TS5a(Si)] and 55.9 kcal mol⁻¹ [TS5a(H)] for the silyl and the H shift, respectively. Furthermore, the second step, i.e. the electrocyclic ring opening of 55, is even higher in energy than TS5a(Si), being 55.8 kcal mol⁻¹ above the precursor 36a.

A direct interconversion between allene **51a** and 1-silyl-1-butyne **53a** seems unlikely as all attempts to locate the transition state for the required 1,3-H shift failed and led instead to **TS8a(H)**, which connects the vinylcarbene **50a**-Si with the butyne **53a**. In contrast, the isomerization of allene **51a** to the terminal butyne **54a** proceeds through a concerted 1,3-silyl shift in **TS7a(Si)** (Path D). The calculated activation energy of 49.7 kcal mol⁻¹ for the reverse reaction (i. e. **54a** \rightarrow **51a**) is in excellent agreement with the experimentally measured barrier of 49.9 \pm 0.6 kcal mol⁻¹ for the isomerization of 3-trimethylsilylpropyne (**56**) to trimethylsilylallene (**57**).^[41]



In summary, the calculations on 36a clearly show that the reaction channel via the cyclopropylidene intermediate 55 (path C) can be excluded as this pathway is much higher in energy than the other possibilities. The lowest-energy pathway for the thermal isomerization of 2,2-dimethyl-1-silylcyclopropene (36a) is ring opening via a vinylidene-like transition state TS4a(Si) (path B, Figure 5), yielding the terminal 3-silvl-substituted butyne 54a. This computational result apparently contradicts the experimental finding that pyrolysis of the corresponding trimethylsilyl-substituted cyclopropene 36b leads almost exclusively to the 1-trimethylsilylbutyne 47, along with just 1% of butadiene 52b as the only identifiable by-product.^[3b] However, the calculations were performed for an SiH₃ substituent (i.e. on 36a) while the experiments were carried out with an Me₃Si-substituted cyclopropene (i.e. with 36b). The steric requirements are greater in TS4a(Si), where the migrating group closely approaches the gem-dimethyl group at C³, than in TS4a(H) (leading to the 1-silvl-substituted butyne 53a) and this effect may reverse their relative stabilities, especially in view of the fact that the calculated energy difference between the transition states leading to the isomeric 54a and 53a is only $1.5 \text{ kcal mol}^{-1}$. Adcock et al. have recently pointed out that the common practice of theoretical modeling of Me₃Si by the use of H₃Si to reduce the complexity of the computational problem can be inadequate.^[42]

To test the adequacy of the modeling of Me₃Si by H₃Si in the present case, the competing low-energy reaction pathways A and B for the experimentally studied system **36b** were calculated (see Figure 6). Comparison of the calculations for **36a** and **36b** indeed shows that the Me₃Si substituent considerably destabilizes **TS4b(Si)** compared to **TS4b(H)**, so that the one-step isomerization of **36b** to **53b** through H-migration becomes the most favorable reaction channel. Thus, while **TS4a(Si)** is lower in energy than **TS4a(H)** by 1.5 kcal mol⁻¹, the order is reversed for **36b**, **TS4b(H)** being 5.3 kcal mol⁻¹ lower in energy than **TS4b(Si)**. This leads to the computational prediction that **53b** should be the major product upon thermolysis of **36b**,

e more, the calculated activation energy of 39.0 kcal mol⁻¹ for the process $36b \rightarrow 53b$ is in reasonable agreement with the experimental data $(37.2 \pm 0.4 \text{ kcal mol}^{-1}).^{[3b]}$ Path A, leading to the formation of butadiene 52b via the intermediate vinylcarbene 50b-Si, is calculated to be only 0.5 kcal mol⁻¹ less favorable than the $36b \rightarrow 53b$ process. This theoretical result is also in good agreement with the experimental detection of ca. 1% of 52b as the only thermolysis product besides 53b. The process leading to the allene 51b[via TS2b(H)] is a further 3.0 kcal mol⁻¹ higher in energy (Figure 6) and, in agreement with this theoretical result, 51bis not observed experimentally. Thus, the calculations and the gas-phase experiments^[3b] on the thermolysis of 36b are in very good qualitative and quantitative agreement. Comparison of the calculations on 36a and 36b reveals

in full agreement with the experimental findings. Further-

that the substitution of H₃Si by an Me₃Si group has a very significant effect. As expected, this is especially important for reaction steps for which the transition states are sterically congested. Thus, the activation energy required for the 1,2-shift of the silvl group across the C-C bond is 8.3 kcal mol⁻¹ higher for an Me₃Si group [TS4b(Si), $E_a =$ 44.3 kcal mol⁻¹] than for an H₃Si group [TS4a(Si), $E_a =$ 36.0 kcal mol^{-1}]. As expected, the effect is smaller for the analogous 1,2-H shift and the activation energy of TS4b(H) is only 1.5 kcal mol⁻¹ higher than that of **TS4a(H)**. As a result of these Me₃Si vs. H₃Si effects, the relative energy difference between the two vinylidene-like transition states leading to isomeric butynes decreases from 1.5 kcal mol^{-1} for H₃Si [TS4a(H) vs. TS4a(Si)] to -5.3 kcal mol⁻¹ for Me₃Si [TS4b(H) vs. TS4b(Si); TS4b(H) favored]. Entropy also disfavors the highly crowded transition state for Me₃Si migration, TS4b(Si), relative to the other transition states. Thus, the differences (at 298 K) between the corresponding free energies G are 2.4, 3.8, and 3.3 kcal mol⁻¹ [for TS4b(H), TS2b(H), and TS3b, respectively] larger than the corresponding differences between the enthalpies calculated at 0 K.^[43] On the other hand, the replacement of H₃Si by Me₃Si stabilizes the α -silvl-substituted vinylcarbene 50b-Si relative to 50a-Si by 4.8 kcal mol^{-1} , probably on electronic grounds. As the Me₃Si vs. H₃Si substitution has opposite effects on the α -silylvinylcarbenes and on the TS for silyl group migration along path B, substitution of H₃Si by Me₃Si has a large effect on the relative energies of TS4(Si) vs. 50-Si. While ΔE [TS4a(Si) – 50a-Si] is -1.2 kcal mol⁻¹ [TS4a(Si) being lower in energy], the corresponding ΔE with the Me₃Si group is 11.9 kcal mol⁻¹, with **50b**-Si being lower in energy. This large effect resulting from the substitution of an H₃Si by an Me₃Si group must be taken into consideration whenever an H₃Si group is used as a model for the trimethylated analogue. This is exemplified here by 37 and 38, for which, due to the size of the systems, we could not carry out calculations on the Me₃Si derivatives used in the experimental study.

(ii) Disilyl- and Tetrasilyl-Substituted Cyclopropenes: The $C_3Me_2(SiH_3)_2$ potential energy surface (PES) (Figure 7) is less complex than that of $C_3Me_2H(SiH_3)$, due to the higher symmetry of the precursor **37**. The global minimum on this

Figure 6. Calculated potential energy surface of $C_3HMe_2(SiMe_3)$ (at the B3LYP/6-311G* + Δ ZPVE level); relative energies in kcal mol⁻¹; the lowest barrier is highlighted by a box

PES is the allene 58, which is 1.0 kcal mol^{-1} more stable than the alkyne 59. This stability order is different from that for the monosilylated system, where the alkyne 53a is more stable than the allene **51a** by 4.6 kcal mol^{-1} . The disilylcyclopropene 37 is found to be higher in energy than the allene 58 by 14.6 kcal mol^{-1} . Here, path A has become merged into a single-step process leading to 58 via a vinylmethylene-type transition state (TS1c), with an associated barrier of 45.9 kcal mol $^{-1}$ (Figure 7). The cyclopropylidene 60 is a minimum at the B3LYP/6-311G* level, but the barrier for its back reaction to cyclopropene is extremely small $(0.7 \text{ kcal mol}^{-1})$ and thus path C also practically merges into a single step, the highest point being TS6c, which lies 55.5 kcal mol⁻¹ above 37 – the highest energy among the investigated reaction channels for 37. The lowest-energy reaction channel is path B, leading through a concerted process to the alkyne **59**, with a barrier of $36.5 \text{ kcal mol}^{-1}$. Thus, for 37, the cyclopropylidene path can again be excluded with confidence, as the barriers along this path are significantly higher than those for the other reaction channels. According to the calculations, the preferred isomerization path for 37 is along path B, yielding exclusively the butyne 59. Even in the gas phase, where 59 is generated in a vibrationally excited state, it is unlikely that 59 would isomerize to the allene 58 under normal experimental conditions since the activation energy for this slightly exothermic process, requiring a 1,3-silyl shift, is 48.8 kcal mol^{-1} (path D). Thus, the calculations predict that the thermal rearrangement of 37 should yield exclusively the alkyne 59. As stated above, this is not necessarily the case for the corresponding Me_3Si analogue **48**, which has been studied experimentally (see below).

The overall topologies of the PESs for the tetrasilyl- and disilyl-substituted systems are very similar (see Figure 8). The allene 61 is more stable than the propyne 62 by 0.9 kcal mol^{-1} . However, the cyclopropene **38** is strongly destabilized, being 26.8 kcal mol^{-1} higher in energy than 61. This difference is 12.2 kcal mol⁻¹ larger than that between 37 and 58. The cyclopropylidene 40 lies in a very shallow potential well, but here again reaction via this intermediate (path C) is significantly higher in energy (requiring 56.1) kcal mol⁻¹) than the other two competing reaction channels. The concerted reaction via a vinylcarbene-type transition state (path A via **TS1d**) requires 40.0 kcal mol⁻¹. The lowest-energy path (path B), leading to the propyne 62 via the vinylidene carbene-type transition state (TS4d), requires an activation energy of only $31.5 \text{ kcal mol}^{-1}$. Due to the significant gem-disilyl destabilization of the precursor 38, the activation energies for paths A and B are lower by 5.9 and 5.0 kcal mol^{-1} , respectively, than in the case of the 3,3gem-dimethyl-substituted cyclopropene 37. Thus, on going from 3,3-dimethyl substitution to 3,3-disilyl substitution, the reaction rate is predicted to be significantly enhanced. In agreement with this theoretical prediction, it has been found experimentally that replacement of the 3,3-dimethyl substituents in 48 by 3,3-bis(trimethylsilyl) substituents as in 10 lowers the activation energy by 6.7 kcal mol^{-1} (Table 3).

The calculations reveal interesting differences between the C_3H_4 and the $C_3H_{4-n}(SiH_3)_n$ potential energy surfaces.

Figure 7. Calculated potential energy surface of $C_3Me_2(SiH_3)_2$ [at the QCISD(T)/6-311G*//B3LYP/6-311G* + Δ ZPVE level]; relative energies in kcal mol⁻¹; the lowest barrier is highlighted by a box

Figure 8. Calculated potential energy surface of $C_3(SiH_3)_4$ [at the QCISD(T)/6-311G*//B3LYP/6-311G* level]; relative energies in kcal mol⁻¹; the lowest barrier is highlighted by a box

One important feature is that increasing silyl substitution energetically favors the allene compared to the isomeric alkynes or the precursor cyclopropene. Increased steric demand at the propargylic carbon atom also increases the alkyne–allene energy difference. Thus, at the HF/6-31G*// HF/6-31G* level, the tetrakis(trimethylsilyl)propyne **63** is found to be 12.0 kcal mol⁻¹ higher in energy than the isomeric allene **12**. This compares to an energy difference of just 5.7 kcal mol⁻¹ for the tetrasilyl-substituted analogues **62/61**. Because of the size of these systems, these calcula-

1. 55.9/ 51a this work
this work
1. 55.5/ 58 this work
d. 56.1/ 61 this work
[3b]
[3e]
this work

Table 3. Calculated and experimental Arrhenius activation energies (E_a) [kcal mol⁻¹] of thermal cyclopropene isomerizations

^[a] See text for definition of reaction paths.

tions were only possible at this relatively low level of theory. Furthermore, even at this level it is not practical to search the PES, particularly with a view to locating the various transition states.

Even more important is the finding that the direct interconversion of silylated alkynes and the corresponding allenes can compete energetically with multi-step isomerization via a cyclopropene. The barrier for the 1,3-silyl shift interconverting alkynes and allenes is significantly lower $(45-50 \text{ kcal mol}^{-1})$ for alkynes **54a**, **59**, and **62** as compared with the 95 kcal mol⁻¹ barrier for H-migration in the parent cyclopropene. These computational results are supported by the experimental finding that the isomerization of 3-trimethylsilylalkyne (**56**) to trimethylsilylallene (**57**) proceeds with a relatively low barrier of 49.9 ± 0.6 kcal mol⁻¹.^[41] An analogous rearrangement of tris(trimethylsilyl)propyne (**64**) to tris(trimethylsilyl)allene (**65**) occurs upon prolonged heating of neat **64** at 110 °C, giving an equilibrium mixture of **65** and **64** in a ratio of 60:40.^[22]

One may therefore envisage an overall isomerization of cyclopropenes 37, 38 to allenes 58, 61 via butynes 59, 62 as intermediates (paths B and D, Figure 7 and 8). In principle, when formed, 59 and 62 have sufficient internal energy to undergo the subsequent isomerization to the corresponding allene. While in the gas phase the importance of the subsequent reaction depends on the lifetime of the vibrationally excited species, in practice, under normal pressures (10-50)Torr) and for large molecules such as these, collisional stabilization will be fully effective. Of course, in the condensed phase, the excess energy will likewise be completely transferred to the medium. If the rearrangement of an initially formed alkyne to an allene were to have been the reaction path, then the alkynes 63 and Me₃SiC=CC(SiMe₃)Me₂ (66) should have been detected chromatographically or spectroscopically. Since not even the slightest indication of the formation of alkyne 63 has ever been found in the studies of the solution isomerization $10 \rightarrow 12$, this possibility can be excluded with confidence.

The calculations predict that upon thermolysis the tetrasilyl-substituted model system **38** should undergo exclusive rearrangement to the acetylene 62. In contrast, it is found experimentally that the analogous tetrakis(trimethylsilyl)cyclopropene (10) yields exclusively the allene 12. How can these differences be rationalized? As discussed above, the calculations on the Me₃Si-substituted cyclopropene 36b vs. the H₃Si-substituted cyclopropene 36a showed that replacement of H₃Si by Me₃Si increased the reaction barrier associated with the pathway leading to the corresponding acetylene by ca. 8 kcal mol⁻¹ compared with that for the pathway leading to the corresponding allene [TS2a(Si) vs. TS4a(Si) and TS2b(H) vs. TS4b(Si)]. This effect is expected to be even more pronounced for 38, due to the steric crowding of three large Me₃Si groups in TS4d as compared to two smaller methyl groups and one trimethylsilyl group in 36b. Even a conservative estimate of this additional destabilization of TS4d compared with TS1d of just 3-4 kcal mol⁻¹ would be sufficient to reverse the energy balance between the transition states leading to the acetylene (TS4d) and to the allene (TS1d) so as to favor the latter (the calculated difference between these two reaction channels in the H_3Si system **38** is 8.5 kcal mol⁻¹). Thus, taking into consideration the effect of the Me₃Si groups, the calculations and the experiments for 10 reach agreement. We hope that in the future, with additional computational resources, we will be able to explicitly calculate the thermal isomerization channels for 10 and hence test this analysis.

Conclusions

Our experimental and theoretical results clearly show that cyclopropylidenes are not involved as intermediates in the isomerizations of silylated cyclopropenes. Thus, while the experimental activation energies for the isomerization of these systems are in the range of 37-44 kcal mol⁻¹, the calculations show that isomerization via cyclopropylidenes would require much higher energies of ca. 55 kcal mol⁻¹ (see Table 3). It is difficult to imagine that this striking discrepancy could be wholly attributed to the methyl groups on the silyl residues, which were omitted in the calculations. Furthermore, the calculations point to two alternative lower-energy rearrangement channels, with activation energies of the order of those found experimentally. Although it is difficult to make a definitive statement about the precise mechanisms of these rearrangements on the basis of the calculations, the overall evidence seems to indicate that the thermolysis of 1,2-disilyl- and tetrasilyl-substituted cyclopropenes yields the corresponding substituted allenes in a single-step process involving cleavage of the C^1-C^3 bond in the cyclopropene and proceeding via a vinylcarbene-type TS.

As already discussed, the agreement between calculation and experiment is only good when the calculations include the trimethylsilyl groups actually present in the experiments. Thus, for 36b there is a good agreement between the observed and the theoretically predicted product distribution and activation energies (Table 3) and hence the mechanism of the thermal rearrangement of 36b can be confidently concluded to proceed via a vinylidene-type transition state. The situation is more complex for 10 and 48. Calculations of the potential energy surfaces for these systems at a sufficiently high level of theory are unfortunately beyond our computational means. Thus, we have to make do with the computational results for the model compounds 37 and 38, where the Me₃Si groups used experimentally are replaced by SiH₃ groups. Calculations on the rearrangements of 37 and 38 predict a concerted ring opening via a vinylidenelike transition state in each case, to give the alkynes 59 and 62, respectively, with relatively low associated activation barriers of 36.5 and 31.5 kcal mol^{-1} . This is inconsistent with both the measured activation barriers (which for both 10 and 48 are 6-8 kcal mol⁻¹ higher than calculated) (Table 3) and with the observed allenic products 12 and 49, respectively.

The theoretical conclusions change, however, if we take into consideration the fact that the vinylidene-like transition states TS4e and TS4f (see Scheme 7), which involve silyl group migration, are considerably destabilized by the steric requirements of the trimethylsilyl group as compared to the vinylcarbene-like transition states TS1e and TS1f. Thus, TS4b(Si) is destabilized relative to the corresponding vinylcarbene 50-Si by 13.3 kcal mol^{-1 [44]} when H₃Si is replaced by Me_3Si (Figures 4–6). When the barriers associated with the Me₃Si migration are corrected accordingly by increasing the energies of the vinylidene-type transition states leading to formation of alkynes 59, 62 by ca. 10 kcal mol^{-1} , path A via **TS1e** (which is less sensitive to steric effects), leading exclusively to allenes, becomes the lowestenergy reaction path. Support for this interpretation is the good agreement between the activation energies computed for path A in the cases of 37 and 38 (see Table 3) and those determined experimentally for 48 and 10, respectively. In contrast, the calculated barriers in the H₃Si-substituted model compounds (Figure 7 and 8) for the reaction along path B are too low.

In summary, the combined experimental and theoretical study described herein allows us to confidently conclude that cyclopropylidenes are not intermediates in the thermal isomerizations of silyl-substituted cyclopropenes. The computations predict that 1-trimethylsilylcyclopropene should isomerize to trimethylsilylpropyne via a vinylidene-type transition state, whereas the bis- and tetrakis(trimethylsilyl)cyclopropenes should isomerize to the corresponding allenes via vinylcarbene-like transition states. This difference in mechanism, according to the calculations, is mainly due to steric congestion of the Me_3Si groups in the vinylidenetype transition states. Furthermore, the computations suggest that H_3Si and Me_3Si substitution of cyclopropenes should lead to different pathways. We hope that it will be possible to test this experimentally in the future.

Scheme 7

Experimental Section

General Remarks: Unless otherwise indicated, all reactions were performed in oven- or flame-dried glassware under argon. Solvents were distilled immediately prior to use: Et₂O and THF from sodium/benzophenone ketyl, toluene and acetonitrile from LiAlH₄, and CH₂Cl₂ from CaH₂. - Thin-layer chromatography was performed on Macherey-Nagel Alugram Sil G/UV254 Fertigfolien and spots were visualized under UV light or by exposure to panisaldehyde or molybdatophosphoric acid. - NMR spectra were recorded with Bruker AM 250 or Varian VXR 500 S spectrometers with samples in CDCl3, C6D6, or [D8]toluene solution. Coupling constants are given in Hz. - IR spectra were recorded with a Bruker IFS 66 FT-IR spectrometer. - UV spectra were measured with a Varian Cary 219 spectrophotometer. - Melting points were measured with a Büchi melting point apparatus; values are uncorrected. - The pure compounds were isolated by preparative GC with an Intersmat 131 instrument using a thermal conductivity detector. The column used was $3.5 \text{ m} \times 10 \text{ mm}$, 15% SE 30 on 60-80mesh Chromosorb W-AW-DMCS; carrier gas was H2. - The photolyses were carried out with a low-pressure mercury UV lamp (254 nm, 250 W) from Gräntzel, Karlsruhe. - Mass spectra were obtained with a Finnigan MAT 95 spectrometer. High-resolution mass spectra were obtained with a Varian MAT 311 A spectrometer. Molecular compositions were determined by high-resolution mass spectrometry with pre-selective ion peak matching at $R \approx$ 10000 within ± 2 ppm of the exact masses. – Microanalyses were performed by the staff of the Mikroanalytisches Laboratorium, Institut für Organische Chemie der Georg-August-Universität Göttingen.

Tetrakis(trimethylsily1)cyclopropene (10): To a suspension of the cyclopropenylium salt **9** (354 mg, 0.6 mmol) in Et₂O (13 mL) at -78 °C, a solution of tris(trimethylsily1)aluminum (675 mg, 2.7 mmol) in Et₂O (5 mL) was added over a period of 20 min. The reaction mixture was stirred at -78 °C for 9 h and then diluted with Et₂O (25 mL) and quenched with H₂O (10 mL). The organic layer was separated, washed with brine (10 mL), and dried with Na₂SO₄. The solvent was evaporated under reduced pressure. Purification of the residue by preparative gas chromatography gave 49

mg (25%) of **10** as a colorless solid (m.p. 196 °C). – IR (KBr): $\tilde{v} = 2957, 2900, 1721, 1406, 1249, 1020, 979, 758, 683, 641, 623, 611, 522, 505 cm⁻¹. – ¹H NMR (250 MHz, CDCl₃): <math>\delta = 0.20$ (s, 18 H), –0.11 (s, 18 H). – ¹³C NMR (62.9 MHz, CDCl₃): $\delta = 135.7, 22.3, 0.2, -0.4. - C_{15}H_{36}Si_4$ (328.8): calcd. C 54.80, H 11.04; found C 54.76, H 10.10.

General Procedure for the Preparation of 3-Alkenyl-1,2,3-tris(trimethylsilyl)cyclopropenes: To a suspension of 1 equiv. of the cyclopropenylium salt 9 in Et₂O at 0 °C was added a solution of 10 equiv. of the alkenylmagnesium bromide in Et₂O. After stirring the mixture for 3 h at room temp., the reaction was quenched by the addition of saturated aq. NH_4Cl solution. The organic layer was washed with H_2O and brine and dried with MgSO₄. The solvent was evaporated in vacuo. Purification of the residue by preparative gas chromatography gave a colorless oil in each case.

3-Allyl-1,2,3-tris(trimethylsilyl)cyclopropene (17a): Addition of a solution of allylmagnesium bromide (3.39 mmol) in Et₂O (4 mL) to cyclopropenylium salt **9** (200 mg, 0.34 mmol) in Et₂O (5 mL) gave 40 mg (40%) of **17a**. – IR (film): $\tilde{v} = 3074$, 2956, 2897, 1710, 1636, 1406, 1248, 991, 908, 839, 754, 693, 628, 515 cm⁻¹. – ¹H NMR (250 MHz, CDCl₃): $\delta = 5.60$ (ddt, J = 7, 10, 17 Hz, 1 H), 4.79–4.90 (m, 2 H), 2.05 (dt, J = 1, 7 Hz, 2 H), 0.20 (s, 18 H), –0.09 (s, 9 H). – ¹³C NMR (125 MHz, CDCl₃): $\delta = 141.0$, 138.9, 114.5, 44.3, 16.4, –0.4, –1.2. – HRMS: *m*/*z* calcd. for C₁₅H₃₂Si₃ 296.1812; found 296.1811.

3-(4'-But-1'-enyl)-1,2,3-tris(trimethylsilyl)cyclopropene (17b): Addition of a solution of 4-but-1-enylmagnesium bromide (4.24 mmol) in Et₂O (3 mL) to cyclopropenylium salt **9** (250 mg, 0.42 mmol) in Et₂O (7 mL) gave 59 mg (45%) of **17b.** – IR (film): $\tilde{v} = 2956$, 1708, 1640, 1406, 1249, 906, 840, 755, 693, 631, 516 cm⁻¹. – ¹H NMR (250 MHz, CDCl₃): $\delta = 5.65 - 5.85$ (m, 1 H), 4.82–4.98 (m, 2 H), 1.68–1.80 (m, 2 H), 1.34–1.47 (m, 2 H), 0.17 (s, 18 H), -0.10 (s, 9 H). – ¹³C NMR (62.9 MHz, CDCl₃): $\delta = 142.5$, 141.0, 115.3, 38.4, 34.9, 16.8, -0.3, -1.1. – C₁₆H₃₄Si₃ (310.7): calcd. C 61.85, H 11.03; found C 61.75, H 10.62.

3-(5'-Pent-1'-enyl)-1,2,3-tris(trimethylsilyl)cyclopropene (17c): Addition of a solution of 5-pent-1-enylmagnesium bromide (4.24 mmol) in Et₂O (3 mL) to cyclopropenylium salt **9** (250 mg, 0.42 mmol) in Et₂O (7 mL) gave 70 mg (51%) of **17c.** – IR (film): $\tilde{v} = 2956$, 1700, 1684, 1653, 1558, 1540, 1506, 1457, 1248, 908, 838, 753 cm⁻¹. – ¹H NMR (250 MHz, C₆D₆): $\delta = 5.82$ (ddt, J = 8, 10, 17 Hz, 1 H), 4.94–5.08 (m, 2 H), 1.95–2.07 (m, 2 H), 1.47–1.56 (m, 2 H), 1.23–1.38 (m, 2 H), 0.21 (s, 18 H), 0.07 (s, 9 H). – ¹³C NMR (62.9 MHz, C₆D₆): $\delta = 142.0$, 139.5, 114.8, 38.7, 35.0, 28.6, 17.7, –0.1, –0.8. – HRMS: *m*/*z* calcd. for C₁₇H₃₆Si₃ 324.2125; found 324.2124. – C₁₇H₃₆Si₃ (324.7): calcd. C 62.88, H 11.17; found C 62.18, H 10.91.

General Procedure for the Photolyses of 10 and 17a-c: Under argon, a degassed solution of 10 or one of 17a-c (30 mg) in *n*-pentane (30 mL) was irradiated with a low-pressure mercury UV lamp ($\lambda = 254$ nm) for 3 h in a ring reactor (quartz glass).

General Procedure for the Thermolyses of 10 and 17a–c: A degassed solution of **10** or **17b** (20 mg) in toluene (2 mL) or of **17a** or **17c** (20 mg) in *cis*-decalin (2 mL) was heated in an oil or sand bath until the starting material was no longer detectable by analytical GC.

1,1,3-Tris(trimethylsilyl)-1,2,5-hexatriene (21a): Irradiation of **17a** (30 mg, 0.10 mmol) in *n*-pentane (30 mL) for 2 h with a low-pressure mercury lamp ($\lambda = 254$ nm), evaporation of the solvent, and purification of the residue by preparative gas chromatography gave

28 mg (93%) of the allene **21a** as a colorless oil. Thermolysis of **17a** (20 mg, 0.07 mmol) in *cis*-decalin (2 mL) at 380 °C for 24 h gave, after purification by preparative gas chromatography, 14 mg (70%) of the allene **21a**. – IR (film): $\tilde{v} = 2956$, 2898, 1894, 1734, 1248, 1019, 900, 839, 759, 690, 638 cm⁻¹. – ¹H NMR (300 MHz, C₆D₆): $\delta = 5.82-5.96$ (m, 1 H), 4.94–5.06 (m, 2 H), 2.64–2.68 (m, 2 H), 0.18 (s, 18 H), 0.13 (s, 9 H). – ¹³C NMR (300 MHz, C₆D₆): $\delta = 208.0$, 138.4, 114.6, 79.6, 75.9, 33.2, 0.6, –1.0. – HRMS: *m/z* calcd. for C₁₅H₃₂Si₃ 296.1812; found 296.1811.

1,1,3-Tris(trimethylsily)-1,2,6-heptatriene (21b): Irradiation of **17b** (30 mg, 0.10 mmol) in *n*-pentane (30 mL) for 3 h with a low-pressure mercury lamp ($\lambda = 254$ nm), evaporation of the solvent, and purification of the residue by preparative gas chromatography gave 26 mg (87%) of the allene **21b** as a plastic mass. – IR (film): $\tilde{v} = 2956$, 2899, 1894, 1641, 1402, 1248, 903, 839, 760, 689, 620, 522 cm⁻¹. – ¹H NMR (250 MHz, CD₃CN): $\delta = 5.79-5.97$ (m, 1 H), 4.89–5.07 (m, 2 H), 2.09–2.21 (m, 2 H), 1.30–1.43 (m, 2 H), 0.08 (s, 18 H), 0.04 (s, 9 H). – ¹³C NMR (62.9 MHz, CD₃CN): $\delta = 207.4$, 140.5, 115.2, 82.1, 77.9, 36.1, 23.8, 0.7, –1.1. – HRMS: *m/z* calcd. for C₁₆H₃₄Si₃ 310.1968; found 310.1968.

1,1,3-Tris(trimethylsily)-1,2,7-octatriene (21c): Irradiation of **17c** (30 mg, 0.09 mmol) in *n*-pentane (30 mL) for 2 h with a low-pressure mercury lamp ($\lambda = 254$ nm), evaporation of the solvent, and purification of the residue by preparative gas chromatography gave 27 mg (90%) of the allene **21c** as a colorless oil. Thermolysis of **17c** (20 mg, 0.06 mmol) in *cis*-decalin (2 mL) at 380 °C for 22 h gave, after purification by preparative gas chromatography, 15 mg (75%) of the allene **21c**. – IR (film): $\tilde{v} = 2956$, 1893, 1641, 1402, 1248, 1019, 905, 838, 760, 689, 620, 522 cm⁻¹. – ¹H NMR (250 MHz, CDCl₃): $\delta = 5.81$ (ddt, J = 7, 10, 17 Hz, 1 H), 4.91–5.05 (m, 2 H), 1.43–2.14 (m, 6 H), 0.09 (s, 18 H), 0.05 (s, 9 H). – ¹³C NMR (250 MHz, CDCl₃): $\delta = 207.0$, 138.9, 114.3, 79.0, 76.4, 33.8, 29.3, 27.1, 0.5, –1.2. – HRMS: *m/z* calcd. for C₁₇H₃₆Si₃ 324.2125; found 324.2124.

1,6,7*exo*-**Tris(trimethylsilyl)bicyclo[4.1.0]hept-3-ene (22):** Thermolysis of **17b** (20 mg, 0.06 mmol) in toluene (2 mL) at 210 °C for 14 h gave, after purification by preparative gas chromatography, 17 mg (85%) of the bicycloheptene **22** as colorless plastic crystals. – IR (KBr): $\tilde{v} = 3026$, 2953, 2898, 1406, 1249, 1066, 945, 892, 836, 755, 687, 637, 617, 440 cm⁻¹. – ¹H NMR (500 MHz, C₆D₆): $\delta = 5.46-5.48$ (m, 2 H), 2.16–2.28 (m, 4 H), 0.60 (s, 1 H), 0.21 (s, 9 H), 0.19 (s, 18 H). – ¹³C NMR (125 MHz, C₆D₆): $\delta = 122.6$, 30.5, 18.9, 16.0, 2.2, 1.4. – HRMS: *m/z* calcd. for C₁₆H₃₄Si₃ 310.1968; found 310.1968. – C₁₆H₃₄Si₃ (310.7): calcd. C 61.85, H 11.03; found C 60.38, H 11.10.

9,10-Dihydro-9,10-(bromodideuteriomethylethano)anthracene (25): At 0 °C, a solution of triphenylphosphane (15.1 g, 58 mmol) in CH_2Cl_2 (30 mL) was slowly added to a solution of alcohol 24^[24] (9.3 g, 39 mmol) and CBr₄ (22.9 g, 69 mmol) in CH₂Cl₂ (170 mL). After stirring overnight, the mixture was diluted with pentane until a white precipitate separated. The mixture was filtered, and the filtrate was concentrated to dryness. The crude product was purified by column chromatography (light petroleum ether, b.p. 40-80°C) on 270 g of silica gel ($R_{\rm f} = 0.20$) to yield 10.0 g (85%) of bromide 25 as a colorless solid; m.p. 126 °C. – IR (KBr): \tilde{v} = 3021, 2958, 2940, 2859, 1457, 1284, 1173, 1020, 984, 961, 901, 795, 772, 743, 684, 609, 546 cm⁻¹. - ¹H NMR (250 MHz, CDCl₃): $\delta =$ 7.08-7.42 (m, 8 H), 4.48 (d, J = 2.8 Hz, 1 H), 4.28 (t, J = 2.8 Hz, 1 H), 2.29-2.40 (m, 1 H), 2.08 (ddd, J = 2.8, 9.7, 12.5 Hz, 1 H), 1.19 (ddd, J = 2.8, 4.9, 12.5 Hz, 1 H). $- {}^{13}$ C NMR (125 MHz, $CDCl_3$): $\delta = 143.5, 143.3, 143.1, 139.5, 126.2, 125.9, 125.79,$

125.78, 125.6, 123.8, 123.4, 123.2, 47.1, 44.2, 40.8, 37.4 (quint, J = 20 Hz), 34.7. – HRMS: m/z calcd. for C₁₇H₁₃D₂Br 300.0482; found 300.0482.

9,10-[Dideuterio(methoxycarbonyl)methylethano]-9,10-dihydroanthracene (26): A Grignard solution was generated by adding bromide 25 (5.12 g, 17 mmol) in Et₂O (30 mL) to Mg powder (0.46 g, 19 mmol) in Et₂O (10 mL) under gentle reflux. After a further 2 h, the solution was cooled to room temp. At 0 °C, this Grignard solution (40 mL, 17 mmol) was then slowly added to a solution of methyl chloroformate (3.2 g, 34 mmol) in Et₂O (20 mL). After stirring for 0.5 h at room temp., the mixture was heated under reflux for a further 5 h. The reaction was then quenched by the addition of saturated aq. NH₄Cl solution (20 mL), and the separated organic layer was washed with H₂O (20 mL) and brine (20 mL) and dried with MgSO₄. The solvent was evaporated and the crude product was purified by column chromatography [light petroleum ether (b.p. 40-80 °C)/Et₂O, 10:1] on 160 g of silica gel ($R_{\rm f} = 0.15$) to yield 2.47 g (52%) of the methyl ester 26 as a colorless solid (m.p. 121 °C). – IR (KBr): $\tilde{v} = 3021, 2947, 2866, 1734, 1458, 1434, 1377,$ 1263, 1224, 1018, 747, 619, 565 cm⁻¹. – ¹H NMR (250 MHz, CDCl₃): $\delta = 7.08 - 7.42$ (m, 8 H), 4.27 (d, J = 2.8 Hz, 1 H), 4.21 (t, J = 2.8 Hz, 1 H), 3.67 (s, 3 H), 2.35-2.48 (m, 1 H), 2.12 (ddd, 1)J = 2.8, 9.8, 12.4 Hz, 1 H, 1.23 (ddd, J = 2.8, 4.7, 12.4 Hz, 1 H). - ¹³C NMR (125 MHz, CDCl₃): $\delta = 172.8, 143.62, 143.59, 142.9,$ 140.0, 125.9, 125.7, 125.53, 125.45, 125.3, 123.4, 123.3, 123.0, 51.2, 48.4, 43.9, 39.5 (quint, J = 20 Hz), 34.5, 34.2. – HRMS: m/z calcd. for C₁₉H₁₆D₂O₂ 280.1432; found 280.1432.

9,10-[(1',1'-Dideuterio-2'-hydroxyethyl)ethano]-9,10-dihydroanthracene (27): A mixture of the methyl ester **26** (2.28 g, 8.1 mmol) and LiAlH₄ (0.31 g, 8.1 mmol) in THF (25 mL) was heated under reflux for 12 h. After cooling to room temp., the reaction was quenched by the addition of saturated aq. NH₄Cl solution (15 mL), and the separated organic layer was dried with MgSO₄. Evaporation of the solvent gave the alcohol **27** in quantitative yield (2.04 g) as a colorless solid; m.p. 114 °C. – IR (KBr): $\tilde{v} = 3235$, 2932, 2901, 2858, 1653, 1457, 1322, 1261, 1055, 1025, 799, 749, 550 cm⁻¹. – ¹H NMR (250 MHz, CDCl₃): $\delta = 7.03-7.41$ (m, 8 H), 4.28 (d, J = 2.6 Hz, 1 H), 4.15 (t, J = 2.6 Hz, 1 H), 3.66 (m, 2 H), 2.02–2.16 (m, 2 H), 1.15–1.29 (m, 1 H). – ¹³C NMR (125 MHz, CDCl₃): $\delta = 144.3$, 143.8, 143.3, 140.7, 125.8, 125.60, 125.57, 125.4, 125.3, 123.4, 123.3, 123.0, 61.0, 49.0, 44.3, 38.4 (quint, J =20 Hz), 34.7, 34.4. – MS: m/z = 252, 221, 178.

2,2-Dideuteriobut-3-ene-1-ol (28): Flash vacuum pyrolysis of the alcohol **27** (1.86 g, 7.4 mmol) under argon at 350 °C gave butenol **28** in quantitative yield (0.55 g) as a colorless liquid. – ¹H NMR (250 MHz, CDCl₃): δ = 5.80 (dd, *J* = 10, 17 Hz, 1 H), 5.10–5.19 (m, 2 H), 3.68 (s, 2 H). – ¹³C NMR (62.9 MHz, CDCl₃): δ = 134.8, 117.6, 61.2.

4-Bromo-3,3-dideuteriobut-1-ene (29): To a stirred solution of butenol **28** (549 mg, 7.41 mmol) in pyridine (174 mg, 2.20 mmol) at 0 °C was added PBr₃ (812 mg, 3.00 mmol). After allowing the mixture to warm to room temp., the homoallylic bromide **29** was distilled off into a cooled (-78 °C) receiving flask. Yield 657 mg (65%). Compound **29** was used without further purification. – ¹H NMR (250 MHz, CDCl₃): δ = 5.80 (dd, *J* = 10, 17 Hz, 1 H), 5.10–5.19 (m, 2 H), 3.41 (s, 2 H). – ¹³C NMR (62.9 MHz, CDCl₃): δ = 135.1, 117.5, 70.3.

3-[4'-(3',3'-Dideuterio)but-1'-enyl]-1,2,3-tris(trimethylsilyl)cyclopropene (17b-D): A Grignard solution was first generated by adding bromide **29** (360 mg, 2.63 mmol) in Et₂O (2 mL) to Mg powder (64 mg, 2.63 mmol) in Et₂O (1 mL) and heating for 1 h under reflux. This Grignard solution (3 mL, 2.63 mmol) was then added to a suspension of the cyclopropenylium salt **9** (155 mg, 0.26 mmol) in Et₂O (5 mL) at 0 °C. After stirring at room temp. overnight, the reaction was quenched by the addition of saturated aq. NH₄Cl solution (3 mL). The organic layer was washed with H₂O (3 mL) and brine (3 mL) and dried with MgSO₄. The solvent was evaporated in vacuo. Purification of the residue by preparative gas chromatography gave 38 mg (46%) of the cyclopropene **17b**-D as a colorless oil. $^{-1}$ H NMR (250 MHz, CDCl₃): $\delta = 5.76$ (dd, J = 10, 17 Hz, 1 H), 4.83–4.97 (m, 2 H), 1.49 (s, 2 H), 0.18 (s, 18 H), $^{-0.09}$ (s, 9 H). $^{-13}$ C NMR (125 MHz, CDCl₃): $\delta = 141.2$, 139.8, 113.5, 37.7, 32.1 (quint, J = 20 Hz), 16.6, $^{-0.4}$, $^{-0.7}$.

3,7*endo*-Dideuterio-1,6,7-tris(trimethylsilyl)bicyclo[4.1.0]hept-3-ene (**22-D**): A degassed solution of **17b**-D (30 mg, 0.10 mmol) in toluene (2 mL) was heated to 210 °C for 14 h under argon. After purification by preparative gas chromatography, 25 mg (83%) of bicycloheptene **22**-D was obtained as white plastic crystals. – IR (KBr): $\tilde{v} = 2955$, 1408, 1250, 1096, 1048, 911, 835, 756, 687, 636, 440 cm⁻¹. – ¹H NMR (250 MHz, C₆D₆): $\delta = 5.53$ (s, 1 H), 2.23 (s, 4 H), 0.21 (s, 9 H), 0.19 (s, 18 H). – ¹³C NMR (75 MHz, C₆D₆): $\delta = 123.2$, 30.27, 30.20, 18.50, 18.46, 2.2, 1.4. – HRMS: *m/z* calcd. for C₁₆H₃₂D₂Si₃ 312.2094; found 312.2094.

Allylchlorodimethylsilane: To magnesium turnings (5.35 g, 0.220 mol), which had been activated with a crystal of iodine, in diethyl ether (30 mL) was added a solution of freshly distilled allyl chloride (15.31 g, 0.200 mol) in diethyl ether (30 mL) at such a rate that the temperature remained between -5 and 0 °C. The mixture was stirred at ambient temperature for 12 h, then added in small portions to a solution of freshly distilled dichlorodimethylsilane (36.2 mL, 0.300 mol). After stirring the reaction mixture at ambient temperature for 18 h, it was filtered through Celite. The solvent was distilled off through a 50-cm Vigreux column. Distillation of the residue gave 11.72 g (44%) of allylchlorodimethylsilane (b.p. 85-95 °C) as a colorless liquid sensitive to hydrolysis. - ¹H NMR (250 MHz, CDCl₃): $\delta = 5.79$ (ddt, ${}^{3}J = 8.0$, ${}^{3}J = 9.5$, ${}^{3}J = 17.5$ Hz, 1 H, CH₂=CH), 4.93-5.02 (m, 2 H, CH₂=CH), 1.83 (ddd, ${}^{4}J$ = $1.0, {}^{4}J = 1.0, {}^{3}J = 8.0 \text{ Hz}, 2 \text{ H}, \text{ SiCH}_{2}, 0.42 \text{ [s, 6 H, Si(CH_{3})_{2}]}.$ ¹³C NMR (62.9 MHz, CDCl₃): $\delta = 132.0$ (+, CH₂=CH), 115.3 $(-, CH_2 = CH), 26.4 (-, SiCH_2), 1.0 [+, Si(CH_3)_2].$

1-(Allyldimethylsilyl)-3,3-dimethyl-1-cyclopropene (32a): To a solution of 1,1-dibromo-2-chloro-3,3-dimethylcyclopropane (30) (11.9 g, 45.4 mmol) in diethyl ether (60 mL) a 1.61 M solution of methyllithium in diethyl ether (62.0 mL, 99.9 mmol) was added dropwise at -78 °C. After 5 min at -78 °C, the mixture was allowed to warm to room temp. and stirred for a further 1 h. It was then cooled to -78 °C once more, whereupon allylchlorodimethylsilane^[26b] (5.09 g, 37.8 mmol) was added. After 5 min, the mixture was allowed to warm to room temp. once more. After 2 h, H₂O (80 mL) was added. The aqueous phase was extracted with diethyl ether $(3 \times 30 \text{ mL})$, and the combined organic phases were dried (MgSO₄). The solvent was evaporated at -10 °C under reduced pressure (15 Torr), and the residue was subjected to bulb-to-bulb distillation at room temp. (0.1 Torr) to yield 5.05 g (80%) of 32a as a yellow liquid. For characterization, a fraction was isolated by preparative-scale gas chromatography in > 99% purity. - IR (neat): $\tilde{v} = 3079, 2961, 2929, 2857, 1669, 1630 \text{ cm}^{-1}$. - ¹H NMR (250 MHz, CDCl₃): $\delta = 7.96$ (s, 1 H, 2-H), 5.80 (ddt, ${}^{3}J = 8.1$, ${}^{3}J = 10.3, {}^{3}J = 16.8$ Hz, 1 H, 2'-H), 4.90 (ddt, ${}^{4}J = 1.2, {}^{2}J = 2.2,$ ${}^{3}J = 16.8$ Hz, 1 H, 3'-H), 4.88 (ddt, ${}^{4}J = 1.2$, ${}^{2}J = 2.2$, ${}^{3}J =$ 10.3 Hz, 1 H, 3'-H), 1.66 (ddd, ${}^{4}J = 1.2$, ${}^{4}J = 1.2$, ${}^{3}J = 8.1$ Hz, 2 H, 1'-H), 1.14 [s, 6 H, C(CH₃)₂], 0.16 [s, 6 H, Si(CH₃)₂]. - ¹³C NMR (62.9 MHz, CDCl₃, DEPT): $\delta = 138.1 (+, C-2'*), 134.4 (+, -1)$

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C-2*), 132.9 (C_{quat}, C-1), 113.4 (-, C-3'), 28.9 [+, C(CH₃)₂], 23.5 (-, SiCH₂), 16.1 (C_{quat}, C-3), -3.1 [+, Si(CH₃)₂]. - MS (70 eV): *m/z* (%) = 151 (17) [M⁺ - CH₃], 125 (24) [M⁺ - C₃H₅], 99 (10) [Si(CH₃)₂C₃H₅⁺], 98 (100) [Si(CH₃)₂C₃H₄⁺]. - C₁₀H₁₈Si (166.3): calcd. C 72.21, H 10.91; found C 72.07, H 10.86.

2-(Allyldimethylsilyl)-1-[dimethyl-(1E)-propenylsilyl]-3,3-dimethylcyclopropene (33a): To a solution of diisopropylamine (0.51 mL, 3.6 mmol) in THF (10 mL) a 2.36 м solution of n-butyllithium in *n*-hexane (1.17 mL, 2.77 mmol) was added dropwise at -78 °C. After 5 min at -78 °C, the reaction mixture was allowed to warm to room temp. and stirred for a further 45 min. Then, a solution of 32a (0.50 g, 3.00 mmol) in THF (2 mL) was added, the reaction mixture was stirred at room temp. for 12 h, and subsequently added dropwise to a solution of allylchlorodimethylsilane^[26b] (0.486 g, 3.61 mmol) in THF (10 mL) at -78 °C. The resulting mixture was stirred at -78 °C for 1 h and at room temp. for 2 h, then poured into H₂O (30 mL). The aqueous phase was extracted with n-pentane $(3 \times 15 \text{ mL})$, the combined organic phases were dried $(MgSO_4)$, and the solvent was evaporated under reduced pressure. The crude product (950 mg) was filtered through 20 g of silica gel eluting with *n*-pentane and purified by preparative-scale gas chromatography to yield 358 mg (45%) of 33a as a colorless oil. - IR (neat): $\tilde{v} = 2958 \text{ cm}^{-1}$, 2914, 2852, 1697, 1621. – ¹H NMR (250 MHz, CDCl₃): $\delta = 6.13$ (dq, ${}^{3}J = 6.1$, ${}^{3}J = 18.4$ Hz, 1 H, SiCH=CH), 5.64-5.86 (m, 2 H, CH₂=CH, SiCH=CH), 4.83-4.91 (m, 2 H, CH_2 =CH), 1.83 (dd, ${}^{4}J$ = 1.5, ${}^{3}J$ = 6.1 Hz, 3 H, CH₃), 1.64 (ddd, ${}^{4}J = 1.1$, ${}^{4}J = 1.1$, ${}^{3}J = 8.1$ Hz, 2 H, SiCH₂), 1.10 [s, 6 H, C(CH₃)₂], 0.19 [s, 6 H, Si(CH₃)₂], 0.15 [s, 6 H, Si(CH₃)₂]. - ¹³C NMR (62.9 MHz, CDCl₃, DEPT): δ = 149.1 (C_{quat}, C-2**), 147.6 (C_{quat}, C-1**), 143.5 (+, CH₂=CH*), 134.6 (+, SiCH=CH*), 129.0 (+, SiCH=CH), 113.1 (-, CH₂=CH), 29.0 [+, C(CH₃)₂], 23.7 (-, SiCH₂), 22.6 (+, CH₃), 18.3 (C_{quat}, C-3), -1.9 [+, Si(CH₃)₂], -2.9 [+, Si(CH₃)₂]. - MS (70 eV): m/z $(\%) = 264 (2) [M^+], 249 (2) [M^+ - CH_3], 223 (43) [M^+ - C_3H_5],$ 181 (17) $[M^+ - C_6H_{11}]$. - $C_{15}H_{28}Si_2$ (264.6): calcd. 264.1729 (correct HRMS).

1-(But-3'-enyldimethylsilyl)-3,3-dimethyl-1-cyclopropene (32b): To a solution of 1,1-dibromo-2-chloro-3,3-dimethylcyclopropane (30) (10.0 g, 38.1 mmol) in diethyl ether (100 mL) a 1.61 M solution of methyllithium in diethyl ether (52.0 mL, 83.8 mmol) was added dropwise at -78 °C. After 5 min at -78 °C, the mixture was allowed to warm to room temp. and stirred for a further 1 h. It was then cooled to -78 °C once more, whereupon but-3-enyl(methylsulfonyloxy)dimethylsilane^[27a] (7.22 g, 34.6 mmol) was added. After 5 min at -78 °C, the mixture was allowed to warm to room temp., stirred for 2 h, and then treated with H₂O (100 mL). The aqueous phase was extracted with diethyl ether (3 \times 30 mL), and the combined ethereal extracts were dried (MgSO₄). The solvent was evaporated at -10 °C under reduced pressure (15 Torr) and the residue was subjected to bulb-to-bulb distillation (0.1 Torr) to yield 3.94 g (63%) of **32b** as a yellow liquid. – IR (neat): $\tilde{v} = 2964$ cm⁻¹, 2922, 2866, 1667. – ¹H NMR (250 MHz, CDCl₃): δ = 7.92 (s, 1 H, 2-H), 5.91 (m_c, 1 H, 3'-H), 4.99-5.11 (m, 2 H, 4'-H), 2.15 (m_c, 2 H, 2'-H), 1.19 [s, 6 H, C(CH₃)₂], 0.74–0.89 (m, 2 H, SiCH₂), 0.19 [s, 6 H, Si(CH₃)₂]. - ¹³C NMR (50.3 MHz, CDCl₃, APT): $\delta = 141.6 (+, C-3'*), 137.6 (+, C-2*), 133.3 (-, C-1), 112.8 (-, -)$ C-4'), 28.9 [+, C(CH₃)₂], 28.0 (-, C-2'), 16.8 (-, C-3), 14.8 (-, SiCH₂), -2.6 [+, Si(CH₃)₂]. - MS (70 eV): m/z (%) = 180 (< 1) $[M^+]$, 165 (14) $[M^+ - CH_3]$.

But-3'-enylchlorodimethylsilane: $^{[26d]}$ To magnesium turnings (0.63 g, 26.0 mmol) in diethyl ether (10 mL) was added 4-chloro-1-butene (2.36 g, 26 mmol) in diethyl ether (10 mL) at such a rate as

to maintain a gentle reflux. The mixture was then heated under reflux for a further 5 h. Subsequently, this solution was slowly added to a solution of dichloromethylsilane (6.30 mL, 52.3 mmol) at room temp. The resulting mixture was stirred for 18 h at room temp., then filtered through Celite, and the solvent was distilled off through a 15-cm Vigreux column. The residue was purified by bulb-to-bulb distillation to yield 1.19 g (31%) of but-3'-enylchlorodimethylsilane as a colorless liquid, which proved sensitive to hydrolysis. The spectroscopic data are identical to those reported in the literature.^[26c]

1,2-Bis(3'-butenyldimethylsilyl)-3,3-dimethyl-1-cyclopropene (33b): To a solution of diisopropylamine (0.47 mL, 3.3 mmol) in THF (10 mL) a 2.36 M solution of *n*-butyllithium in *n*-hexane (1.17 mL, 2.77 mmol) was added dropwise at -78 °C. After 5 min at -78 °C, the reaction mixture was allowed to warm to room temp. and stirred for a further 45 min. It was then cooled to -78 °C once more, whereupon a solution of 32b (0.50 g, 2.77 mmol) in THF (2 mL) was added. The resulting mixture was stirred at room temp. for 12 h and then added dropwise at -78 °C to a solution of but-3'enylchlorodimethylsilane^[27b] (0.412 g, 2.77 mmol) in THF (10 mL). The reaction mixture was stirred at -78 °C for 1 h and at room temp. for 2 h, then poured into H_2O (30 mL). The aqueous phase was extracted with *n*-pentane $(3 \times 15 \text{ mL})$, the combined organic phases were dried (MgSO₄), and the solvent was evaporated under reduced pressure. The residue (560 mg) was filtered through 15 g of silica gel, eluting with *n*-pentane, and then purified by preparative-scale gas chromatography to yield 325 mg (40%) of 33b as a colorless oil. – IR (neat): $\tilde{v} = 3077 \text{ cm}^{-1}$, 2957, 2919, 1771, 1696, 1640. – ¹H NMR (250 MHz, CDCl₃): $\delta = 5.89$ (ddt, ³J = 6.4, ${}^{3}J = 10.3$, ${}^{3}J = 16.8$ Hz, 2 H, 3'-H), 4.99 (ddt, ${}^{4}J = 1.3$, ${}^{2}J = 1.5$, ${}^{3}J = 16.8$ Hz, 2 H, 4'-H), 4.91 (ddt, ${}^{4}J = 1.3$, ${}^{2}J = 1.5$, ${}^{3}J =$ 10.3 Hz, 2 H, 4'-H), 2.08 (m_c, 4 H, 2'-H), 1.10 [s, 6 H, C(CH₃)₂], 0.73 (m_c, 4 H, 1'-H), 0.15 [s, 12 H, Si(CH₃)₂]. - ¹³C NMR (62.9 MHz, CDCl₃, DEPT): δ = 148.2 [C_{quat}, C-1(2)], 141.6 (+, C-3'), 112.8 (-, C-4'), 29.1 [+, C(CH₃)₂], 28.0 (-, C-2'), 17.9 (C_{quat}, C-3), 14.9 (-, C-1'), -2.4 [+, Si(CH₃)₂]. - MS (70 eV): m/z (%) = 292 (<1) [M⁺], 277 (<1) [M⁺ - CH₃], 113 (67) [Si(CH₃)₂C₄H₇⁺]. - C17H32Si2 (292.6): calcd. C 69.78, H 11.02; found C 69.88, H 10.98.

General Procedure for the Photochemical Isomerization of Cyclopropenes: A solution of the appropriate cyclopropene (50–120 mg) in *n*-pentane (free from unsaturated impurities; 1 L) was irradiated with a low-pressure mercury lamp ($\lambda = 254$ nm). The progress of each reaction was monitored by gas chromatography. When the starting material could no longer be detected, the solvent was evaporated under reduced pressure.

1-(Allyldimethylsilyl)-1-[dimethyl-(1*E***)-propenylsilyl]-3-methyl-1,2-butadiene (35a):** Photolysis of **33a** (50 mg, 0.19 mmol) for 35 min gave 39 mg (78%) of **35a**. – ¹H NMR (250 MHz, CDCl₃): $\delta = 6.00-6.18$ (m, 1 H, SiCH=CH), 5.60-5.88 (m, 2 H, CH₂= CH, SiCH=CH), 4.80-4.97 (m, 2 H, CH₂=CH), 1.86 (dd, ⁴J = 1.5, ³J = 6.1 Hz, 3 H, CH₃), 1.65 [s, 6 H, C(CH₃)₂], 1.59 (ddd, ⁴J = 1.1, ⁴J = 1.1, ³J = 8.1 Hz, 2 H, SiCH₂), 0.16 [s, 6 H, Si(CH₃)₂], 0.08 [s, 6 H, SiC(CH₃)₂]. – ¹³C NMR (62.9 MHz, CDCl₃, DEPT): $\delta = 212.6$ (C_{quat}, C-2), 142.7 (+, CH₂=CH*), 135.3 (+, SiCH= CH*), 130.7 (+, SiCH=CH), 112.6 (-, CH_2 =CH), 85.2 (C_{quat}, C- 3^*), 79.8 (C_{quat}, C-1*), 23.0 (-, SiCH₂), 22.6 (+, CH₃), 19.1 [+, C(CH₃)₂], -1.3 [+, Si(CH₃)₂], -1.7 [+, Si(CH₃)₂].

1,1-Bis(3'-butenyldimethylsilyl)-3-methyl-1,2-butadiene (35b): Photolysis of **33b** (50 mg, 0.17 mmol) for 45 min yielded 45 mg (90%) of **35b.** - ¹H NMR (250 MHz, CDCl₃): $\delta = 5.90$ (ddt, ³J = 6.4, ${}^{3}J = 10.3$, ${}^{3}J = 16.8$ Hz, 2 H, 3'-H), 4.97 (ddt, ${}^{4}J = 1.3$, ${}^{2}J = 1.5$, ${}^{3}J = 16.8$ Hz, 2 H, 4'-H), 4.89 (ddt, ${}^{4}J = 1.3$, ${}^{2}J = 1.5$, ${}^{3}J = 10.3$ Hz, 2 H, 4'-H), 2.02 (m_c, 4 H, 2'-H), 1.60 [s, 6 H, C(CH₃)₂], 0.65 (m_c, 4 H, 1'-H), 0.08 [s, 12 H, Si(CH₃)₂]. $- {}^{13}$ C NMR (62.9 MHz, CDCl₃, DEPT): $\delta = 212.4$ (C_{quat}, C-2), 141.9 (+, C-3'), 112.6 (-, C-4'), 85.2 (C_{quat}, C-3*), 79.3 (C_{quat}, C-1*), 28.1 (-, C-2'), 18.9 [+, C(CH₃)₂], 15.9 (-, C-1'), -1.5 [+, Si(CH₃)₂].

Kinetics of the Rearrangement of Tetrakis(trimethylsilyl)cyclopropene (10) in Solution: A solution of 10 (3 mg) in $[D_8]$ toluene (0.5 mL) in an NMR tube was carefully degassed by three freeze-pump-thaw cycles and then the tube was sealed. The tube was immersed in a well-stirred silicone oil bath for the appropriate length of time and then the reaction was quenched by immersing the tube in ice/water. The temperature was monitored by means of a quartz thermometer. The variation in the temperature during any run was always less than 0.5 °C (Table 4). The ratio of allene 12 to cyclopropene 10 was estimated by ¹H NMR spectroscopy by integrating the signals of the relevant methyl groups of these compounds. As an internal standard, the CD_2H signal of $[D_7]$ toluene was used. The average values of four integrations were used in the ensuing calculations.

Table 4. Rearrangement of cyclopropene 10 to allene 12: proportion of 10 (%) as a function of time t [min] and temperature T [°C]

T =	200	<i>T</i> =	= 215	<i>T</i> =	= 230	<i>T</i> =	= 252
t	10	t	10	t	10	t	10
0 300 780 1140 1590 1920 2280	99.36 96.20 89.07 82.00 78.58 71.83 65.73	0 120 300 420 600 780 990	65.73 61.07 52.61 48.03 42.73 38.56 34.78	0 60 120 180 270 360 510 570 660 750 870	79.85 72.52 66.23 58.76 50.89 41.36 31.42 27.17 21.28 14.69 11.04	30 60 90 120 150 180	84.54 68.31 49.42 34.99 27.59 23.09

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- ^[44] This is the change in the relative energy between TS4a(Si)/50a-Si and TS4b(Si)/50b-Si.

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