JOC The Journal of Organic Chemistry

Article

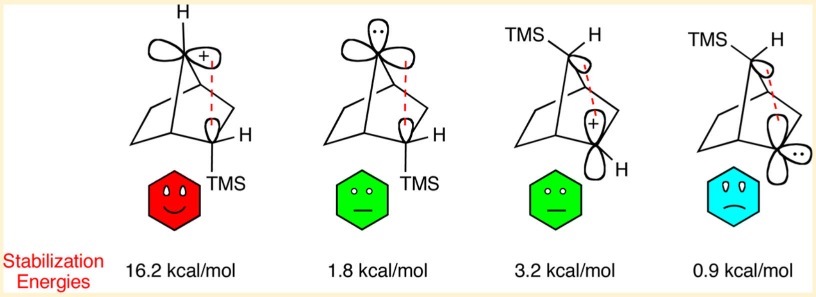
pubs.acs.org/joc

γ-Silyl-Substituted Norbornyl Carbocations and Carbenes

Xavier Creary* and Anna Heffron

Department of Chemistry and Biochemistry University of Notre Dame, Notre Dame, Indiana 46556, United States

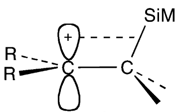
Supporting Information



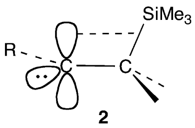
ABSTRACT: *endo*-2-Trimethylsilyl-*anti*-7-norbornyl triflate undergoes solvolysis reactions 1.8 × 10^4 faster than 7-norbornyl triflate in CD_3CO_2D and 1.3 × 10^5 times faster in CF_3CH_2OH. The exclusive substitution products with retained stereochemistry point to a significantly stabilized γ-trimethylsilyl carbocation intermediate. The *endo*-2-trimethylsilyl-7-norbornyl carbene gives a major rearrangement product where the trimethylsilyl-activated hydrogen migrates to the carbenic center. This rearrangement product implies stabilization of the carbene by the γ-trimethylsilyl group. Isodesmic computational studies (M062X/6-311+G**) indicate that the *endo*-2-trimethylsilyl-7-norbornyl cation is stabilized by 16.2 kcal/mol and that the *endo*-2-trimethylsilyl-7-norbornyl carbene is stabilized by a smaller factor of 1.8 kcal/mol. By way of contrast, *anti*-7-trimethylsilyl-*endo*-2-norbornyl mesylate undergoes solvolysis in CD_3CO_2D only 2.6 times faster than *endo*-2-norbornyl mesylate and 9.4 times faster in CF_3CH_2OH. The substitution products have only partially retained stereochemistry, and significant rearrangements are observed. The *anti*-7-trimethylsilyl-2-norbornyl carbene gives a rearrangement product via 1,3-hydrogen migration of the C6 hydrogen, which is completely analogous to the behavior of the unsubstituted 2-norbornyl carbene. Isodesmic calculations show that the *anti*-7-trimethylsilyl-2-norbornyl cation is stabilized by only 3.2 kcal/mol relative to the 2-norbornyl cation, and the corresponding *anti*-7-trimethylsilyl-2-norbornyl carbene is stabilized by a negligible 0.9 kcal/mol.

INTRODUCTION

We have been interested in the chemistry of carbenes and carbocations that contain the trimethylsilyl group. We have studied a variety of carbocations[1] and carbenes[2] that contain a silyl group in the β-position. The so-called β-effect of a silyl group on carbocations **1** is well understood[3] and is attributed to an interaction of the cation vacant orbital with the C−Si σ-bond. This β-effect can lead to carbocation formation at rates up to 10^{11} times faster than from unsilylated analogs.[4] Computational studies[5] support this mode of carbocation stabilization and argue against potential silicon bridged intermediates. An X-ray crystallographic study[6] on an isolable β-silyl vinyl carbocation confirms the preferred alignment of the C−Si σ-bond. Our studies have shown that β-silyl carbenes **2** are stabilized by a similar mechanism.[2] Moreover, these carbenes are prone to rearrange by migration of the silyl group to the carbenic center. In addition, the silyl group also increases the propensity for adjacent hydrogen to migrate.



1

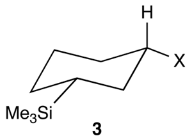


2

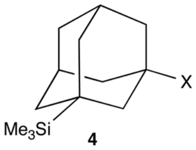
The γ-effect of silicon on carbocations and carbenes has been less appreciated. Shiner[7] observed this phenomenon in solvolysis of brosylate **3**, which reacted 452 times faster than *trans*-4-*t*-butylcyclohexyl brosylate. This rate enhancement was attributed to a γ-silyl effect, where the intermediate carbocation was stabilized by an interaction involving the rear lobe of the C−Si σ-bond in a "W" fashion. A subsequent study by Grob[8] revealed a modest rate enhancement in solvolysis of the adamantyl system **4**, and this was also attributed to the γ-silyl effect. 4-Trimethylsilyl-1-norbornyl triflate, **5**, gave an even larger rate enhancement of 1300 in trifluoroethanol solvent.[9] More recently we have found remarkable rate-enhancing effects in solvolysis reactions that lead to carbocations of type **6**.[10] Cation **6** (R = H) forms even faster than the 2-trimethylsilylcyclobutyl cation in solvolysis reactions. Computational studies also suggest that cation **6** (R = H) is more stable than the 2-trimethylsilylcyclobutyl cation, i.e., the γ-silyl effect leading to cation **6** (R = H) is even greater than the β-silyl effect. A recent experimental and computational study of carbene **7** also reveals a large stabilizing interaction due to the transannular

Received: January 2, 2014
Published: February 18, 2014

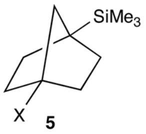
trimethylsilyl group.[11] This interaction leads to preferential formation of 1-trimethylsilylbicyclobutane from 7. A labeling study showed that the source of the bicyclobutane was 1,3-hydrogen migration to the carbene center (and not trimethylsilyl migration).



3

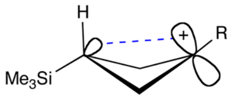


4

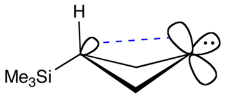


5

Rate Enhancement 450 8.6 1300

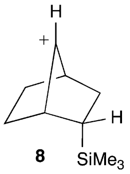


6

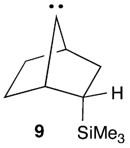


7

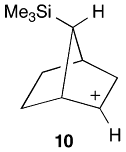
In view of the remarkable carbocation and carbene stabilizing effect of the γ-silyl group on cations of type **6** and carbene **7**, we wanted to further examine the generality of this effect. The norbornyl system was chosen in view of its rigid nature and the ability to control stereochemistry of the trimethylsilyl group relative to the cation/carbene center. We have now generated carbocations **8** and **10** as well as carbenes **9** and **11** and now report on the effect of the trimethylsilyl group on these reactive intermediates.



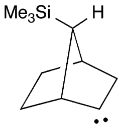
8



9



10



11

■ RESULTS AND DISCUSSION

The synthesis of precursors to cation **8** and carbene **9** (Scheme 1) began with *anti*-7-norbornen-7-ol.[12] Protection of the alcohol as the TBS ether **13**, followed by reaction with phenylselenyl bromide and hydrogen peroxide oxidation, gave the vinyl bromide **14**. Introduction of the trimethylsilyl group was accomplished by lithium-halogen exchange and reaction with trimethylsilyl chloride. Catalytic hydrogenation and subsequent removal of the TBS protection resulted in a mixture of *exo* and *endo*-isomers **16** and **17** from which pure **16** could be separated by chromatography. Conversion of alcohol **16** to triflate **18** was straightforward.

Scheme 1. Synthesis of Precursors to Cation 8 and Carbene 9

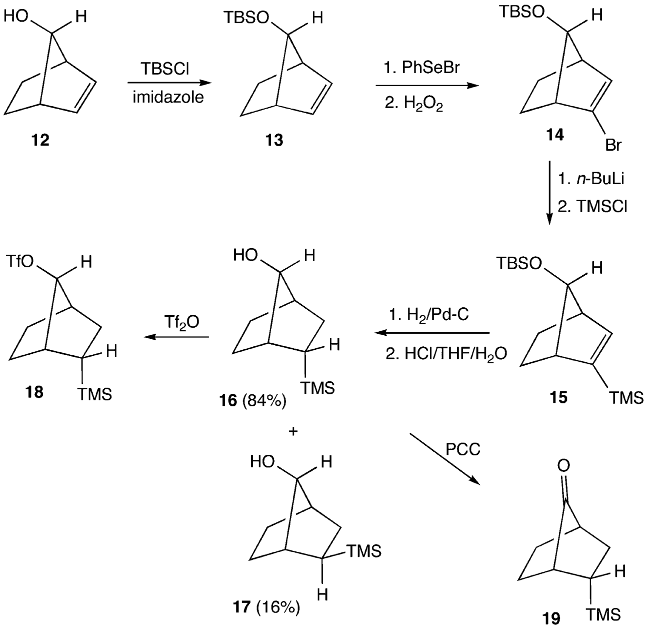
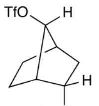
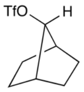
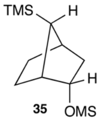
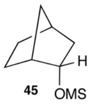


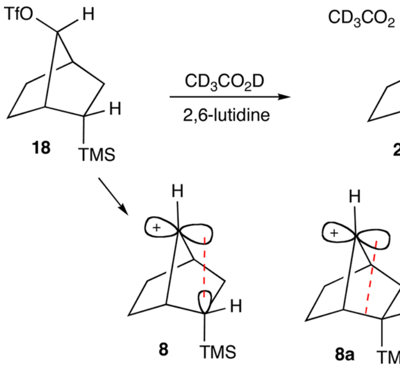
Table 1. Solvolysis Rates for Substrates in CD_3CO_2D and CF_3CH_2OH

Compound	Solvent	T (°C)	k (s^{-1})	k_{rel}
 **18**	CD_3CO_2D	25.0	2.74×10^{-5}	1.75×10^{4}
	CF_3CH_2OH	23.5	1.73×10^{-2}	1.33×10^{5}
 **20**	CD_3CO_2D	100.0	5.51×10^{-5}	
	CD_3CO_2D	80.0	5.19×10^{-6}	
	CD_3CO_2D	25.0	1.56×10^{-9}	1.00
	CF_3CH_2OH	23.5	1.30×10^{-7}	1.00
 **35**	CD_3CO_2D	60.0	3.01×10^{-5}	
	CD_3CO_2D	40.0	2.25×10^{-6}	
	CD_3CO_2D	25.0	2.58×10^{-7}	2.6
	CF_3CH_2OH	25.0	3.39×10^{-5}	9.4
 **45**	CD_3CO_2D	70.0	3.84×10^{-5}	
	CD_3CO_2D	50.0	3.34×10^{-6}	
	CD_3CO_2D	25.0	1.00×10^{-7}	1.00
	CF_3CH_2OH	25.0	3.59×10^{-6}	1.00

The triflate **18** reacted readily at room temperature in CD_3CO_2D. This triflate is much more reactive (1.8×10^4 times) than the desilylated analog, 7-norbornyl triflate, **20** (Table 1). In trifluoroethanol, the rate enhancement relative to 7-norbornyl triflate is an even larger factor of 1.3×10^5. These rate enhancements are substantially greater than in the less rigid cyclohexyl system **3** and also greater than in the rigid systems **4** and **5**. The sole product from acetolysis of **18** is the acetate **21** where the stereochemistry of this substitution product is completely retained. The large rate enhancement as well as the product of complete retention point toward a significant interaction of the trimethylsilyl group with the cationic intermediate in the acetolysis of **18**. The suggested intermediate is the rear lobe stabilized γ-silyl cation **8**, where capture at carbon by acetic acid occurs from the rear of this delocalized cation.

Computational studies[13] at the M062X/6-311+G** level strongly support the suggested involvement of cation **8** in the solvolytic reaction of triflate **18**. Figure 1 shows the M062X/6-311+G** calculated structure of cation **8**. The cation shows a C7−C2 bond distance of only 1.714 Å as well as an elongated

Scheme 2. Solvolysis of Triflate 18 in CD_3CO_2D



C2−Si bond (2.005 Å vs 1.892 Å in the neutral silane **23**). These bond lengths are completely consistent with the proposed carbocation stabilization by a rear lobe interaction of the cationic center with the C2−Si bond. Also of interest is the C1−C2 bond, which is unusually long at 1.651 Å. This suggests another stabilizing interaction between the carbocation vacant orbital and the C1−C2 σ-bond, as represented by **8a**.

The magnitude of the stabilization of cation **8** can be estimated using an isodesmic calculation, as shown in Scheme 3. Cation **8** is stabilized by 16.2 kcal/mol relative to the 7-norbornyl cation, **24**, which itself is a delocalized cation involving σ-bond stabilization. While this stabilization is substantial, it is somewhat less than in the rear-lobe stabilized cation **6** (R = H), where the trimethylsilyl group stabilizes by 22.6 kcal/mol relative to the cyclobutyl cation.

Attention was next turned to the carbene **9**. The ketone **19**, available from oxidation of alcohol **16**, was converted to the tosylhydrazone, which was deprotonated with sodium methoxide to give the salt **26** (Scheme 4). Vacuum pyrolysis of the dry sodium salt **26** generated the carbene **9** via a transient diazocompound **27** that loses nitrogen under the pyrolytic conditions (Bamford−Stevens reaction).[14] Examination of the pyrosylate revealed a major product **28** (96.5%), where hydrogen had migrated to the carbenic center, along with a small amount of the silane **23** (3.5%). The structure of **28** was determined by NMR spectroscopy. Specifically, the proton coupled ^{13}C NMR spectrum shows two cyclopropyl carbons with one bond C−H coupling. The C7 cyclopropyl carbon shows J_{CH} = 181 Hz, which is characteristic of a highly strained cyclopropyl carbon. The structure of the minor product **23** was determined by NMR spectral comparison with an authentic sample. The behavior of carbene **9** therefore contrasts with that of the 7-norbornyl carbene **25**, which was studied many years ago by Moss and Whittle.[15] Carbene **25** gives bicyclo[3.2.0]-hept-1-ene as the major product (74%), along with norbornane (14%), and only 12% of **32**, the hydrocarbon analog of **28**.

Computational studies provide insight into the contrasting behaviors of carbenes **9** and **25**. As can be seen in Figure 1, the carbenic center in **9** tilts slightly toward the hydrogen on C2. The isodesmic reaction in Scheme 3 also suggests that carbene **9** is slightly stabilized (1.8 kcal/mol) relative to the unsubstituted 7-norbornyl carbene. While silyl stabilization of carbene **9** does not approach that of the carbocation **8**, it appears to be a real, albeit small factor. The computational study in Scheme 5 also reveals an increased propensity for migration of the *exo*-2-hydrogen to the carbenic center. There is a rather substantial barrier to migration (11.1 kcal/mol) of the *exo*-2-hydrogen to the carbenic center in **25**. However, the trimethylsilyl group of **9** results in a substantial lowering of the *exo*-2-hydrogen migration barrier to only 5.8 kcal/mol. This is consistent with the observed major product in Scheme 4 and the fact that **32** is only a minor product (12%) from the 7-norbornyl carbene, **25**.

Attention was next turned to reactive intermediates **10** and **11**, where the electron-deficient carbon is at the 2-position. The ketone **33** served as the starting material for generation of these intermediates (Scheme 6). This ketone was previously prepared[16] by the Nef reaction of 2-nitro-*anti*-7-trimethylsilylbicyclo[2.2.1]heptane, where it was proposed that a γ-silyl effect was responsible for the relatively high yield of **33**. While lithium aluminum hydride reduction of **33** gave *endo*-alcohol **34** contaminated with 15% of the *exo*-isomer, lithium tri-*sec*-butylborohydride reduction of **33** gave pure **34**.

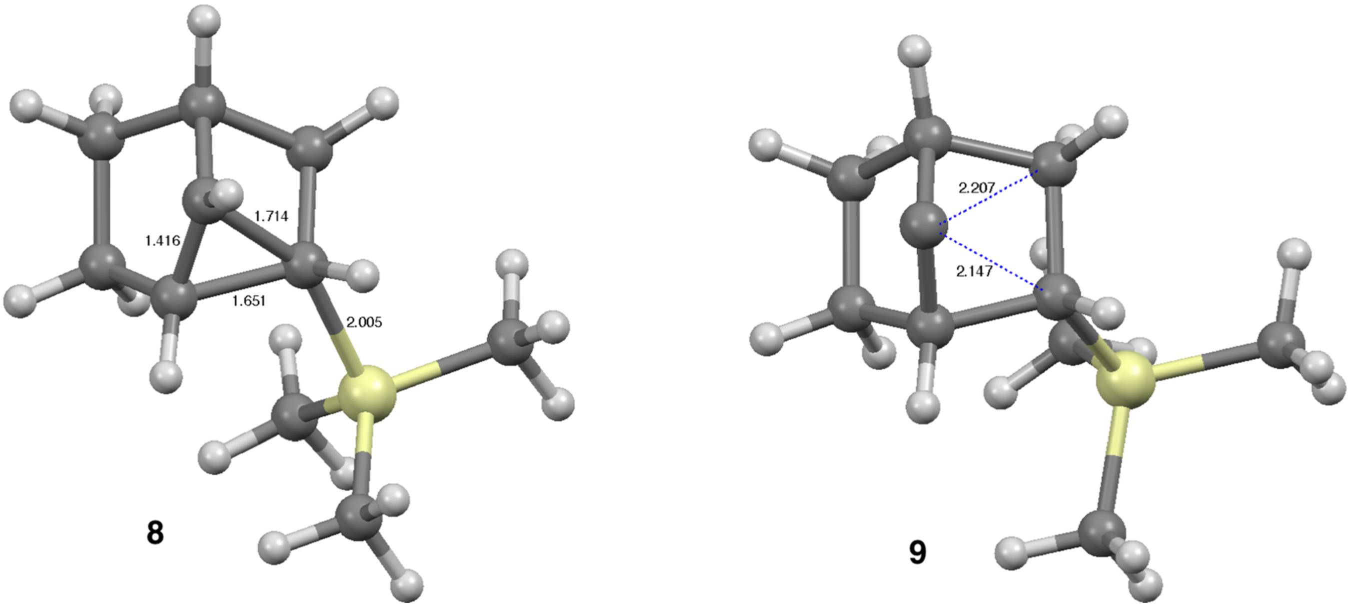
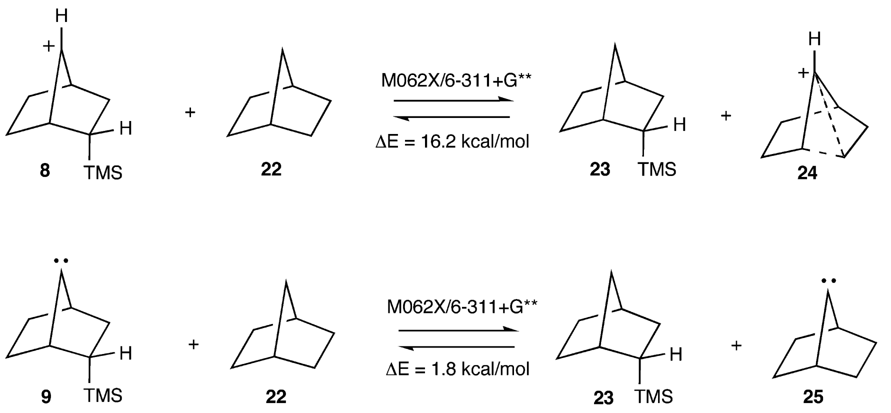
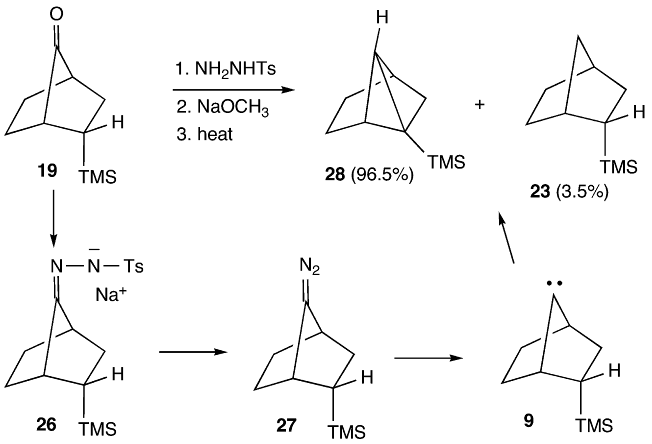


Figure 1. M062X/6-311+G** calculated structures of cation **8** and carbene **9**.

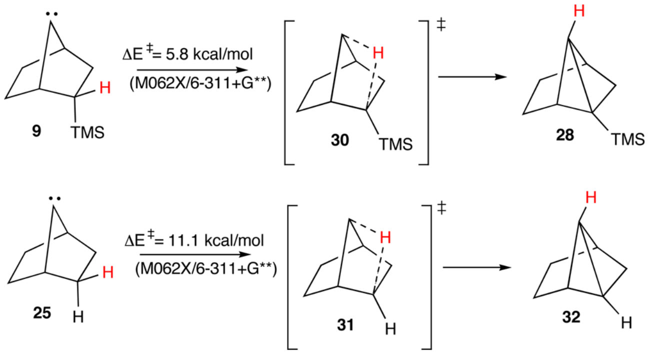
Scheme 3. Isodesmic Reactions of Cation 8 and Carbene 9



Scheme 4. Generation and Rearrangement of Carbene 9



Scheme 5. Calculated Barriers to Rearrangement of Carbenes 9 and 25

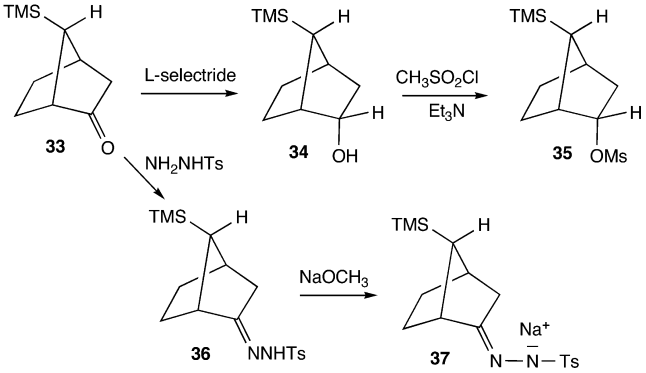


Conversion of **34** to the mesylate **35** was straightforward. The ketone **33** could also be readily converted to the tosylhydrazone **36**. Deprotonation of **36** with sodium methoxide gave the tosylhydrazone salt **37**, which served as the precursor to carbene **11**.

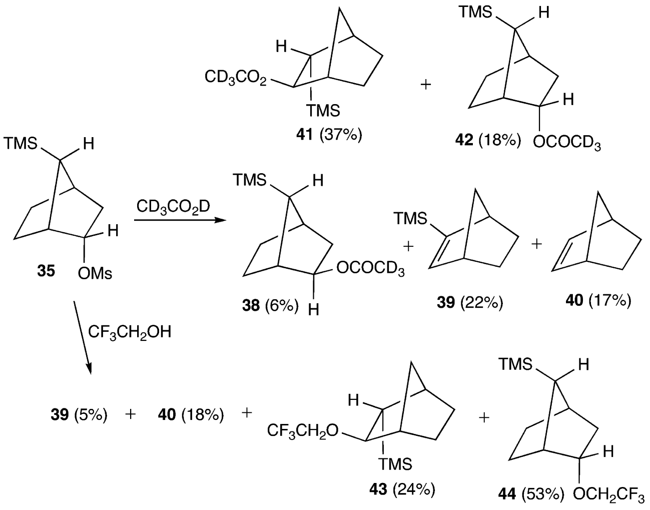
By way of contrast with triflate **18**, the behavior of mesylate **35** under solvolytic conditions is quite complex. Five products are formed (Scheme 7) when **35** reacts in CD_3CO_2D, including **38** and **42** with unrearranged carbon skeleton and structurally rearranged products **39**, **40**, and **41**. Mesylate **35** is only 2.6 times more reactive than the desilylated analog, *endo*-2-norbornyl mesylate, **45** (Table 1) in CD_3CO_2D. In CF_3CH_2OH, a more highly ionizing solvent that favors k_Δ processes, the *endo*-trifluoroethyl ether **44** is the major solvolysis product (53%) derived from **35**. Also formed are smaller amounts of rearranged products **39**, **40**, and **43**. The rate enhancement in CF_3CH_2OH is a modest factor of 9.4 and is slightly larger than one would expect from a purely inductive effect.

On the basis of the negligible rate enhancement in CD_3CO_2D as well as the rearranged products **39-41**, it is suggested that the major reaction pathway is ionization without participation of the silyl group (Path A of Scheme 8).

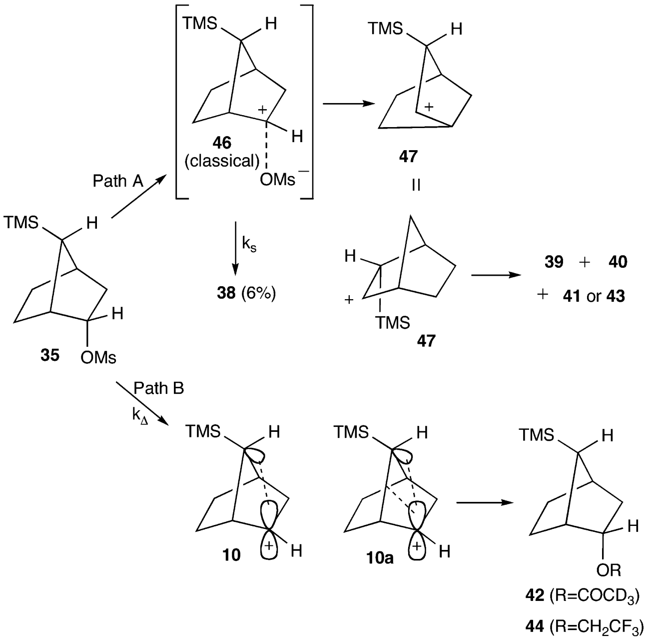
Scheme 6. Synthesis of Precursors to Cation 10 and Carbene 11



Scheme 7. Solvolyses of Mesylate 35 in CD_3CO_2D and CF_3CH_2OH



Scheme 8. Mechanistic Pathways for Solvolyses of Mesylate 34



Ionization of **35** proceeds via the "classical" ion pair **46**, where solvent capture leads to the small amount (6%) of the *exo*-acetate **38**. Cation **46** undergoes rapid rearrangement to give the β-silyl cation **47**, which is the source of rearranged products **39**−**41**, via proton elimination (22%), trimethylsilyl elimination (17%), or solvent capture (37%).

The product that is more difficult to rationalize is the 18% *endo*-acetate **42**, where substitution has occurred with net retention. This type of product (*endo*-substitution) is not formed in solvolysis reactions of *endo*-2-norbornyl derivatives, where only *exo*-substitution products are observed.[17] The unrearranged *endo*-substitution product **44** becomes the major product (53%) in CF_3CH_2OH. A mechanism that would account for the *endo*-substitution products **42** and **44** involves the competing Path B in Scheme 8, where the γ-silyl-stabilized cation **10** is involved. Computationally, with a proper starting geometry, we have been able to locate such a delocalized cation (Figure 2). However, if one starts the calculation with a geometry similar to that expected for a classical cation **46**, then the structure optimizes to give the rearranged β-silyl cation **47**,[18] which lies 6.9 kcal/mol lower energy than **10**. The long C_7−Si bond (1.990 Å) and the long C_1−C_7 bond (1.668 Å) suggest that cation **10** derives stabilization from an interaction with the C−Si rear lobe as well as an interaction with the C_1−C_7 σ-bond, as represented by **10a**.

The lack of a significant rate enhancement in acetolysis of **35** as well as the large amounts of rearranged products indicate that γ-silyl stabilization of cation **10** is not as large as in cations **6** or **8**. Computational studies concur with this assessment and the isodesmic calculation shown in Scheme 9 indicates that **10** is only stabilized by 3.2 kcal/mol relative to the 2-norbornyl cation, **49**. This trimethylsilyl stabilization in **10** does not approach the 22.6 kcal/mol and the 16.2 kcal/mol seen in cations **6** and **8**, where the demand for stabilization in these intrinsically more strained and destabilized cations is much greater.

The generation of carbene **11** from ketone **33** was straightforward using the Bamford−Stevens reaction. The sole product derived from this carbene was the tricyclic product **51**, formed via 1,3-migration of the *endo* C6 hydrogen to the carbenic center (Scheme 10). The structure of this product is based partially on the proton coupled ^{13}C NMR spectrum that shows three cyclopropyl carbons with single bond J_{CH} values of 173−174 Hz. This product **51** is quite analogous to that formed from the 2-norbornyl carbene, **50**, where nortricyclane is the predominant product.[19] Figure 2 shows the calculated structure of carbene **11**, and no unusual bonding interactions are apparent in this structure. The isodesmic reaction shown in Scheme 8 shows negligible stabilization of this carbene by the 7-trimethylsilyl group relative to the unsubstituted 2-norbornyl carbene, **50**. The product **51** also argues against any large interaction of the carbenic center in **11** with the silyl group. A calculation of migration barriers readily explains the observed product. Scheme 10 shows that migration of the *endo*-C6 hydrogen in **11** is an extremely facile process ($\Delta E^\ddagger$ = 1.9 kcal/

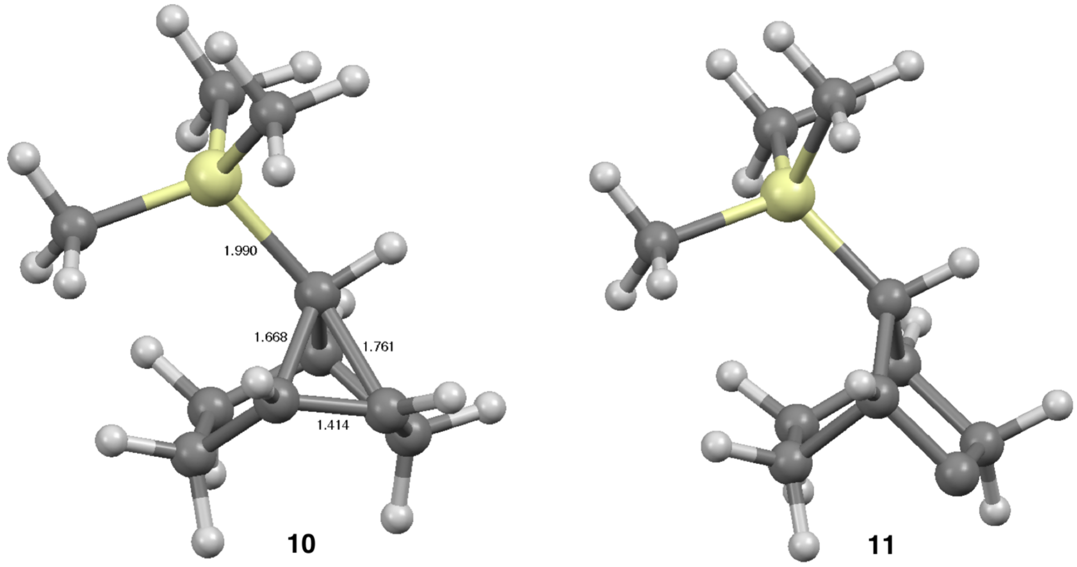
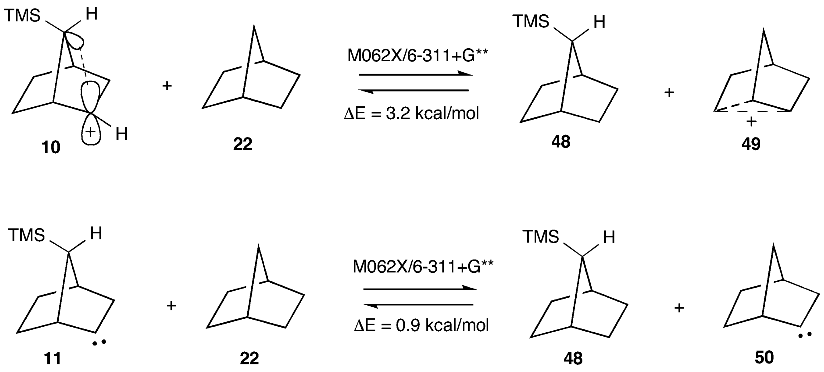
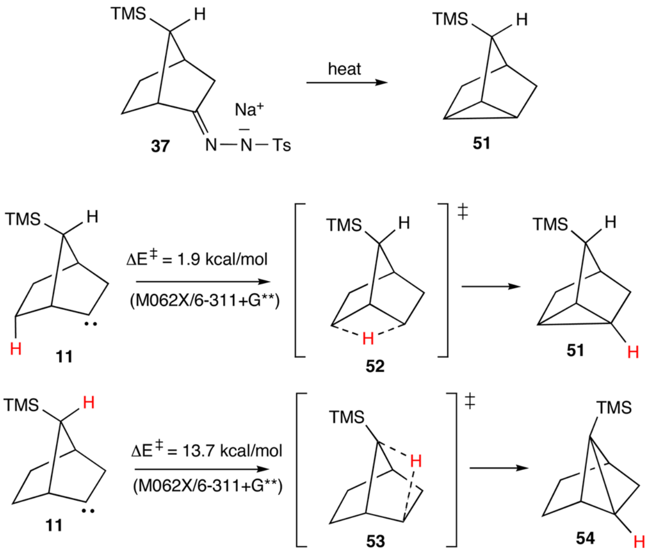


Figure 2. M062X/6-311+G** calculated structures of cation **10** and carbene **11**.

Scheme 9. Isodesmic Reactions of Cation 10 and Carbene 11



Scheme 10. Generation and Rearrangement Pathways of Carbene 11



mol). The trimethylsilyl-perturbed hydrogen on C7 shows little propensity to migrate, as revealed by the 13.7 kcal/mol migration barrier.

■ CONCLUSIONS

Experimental and computational studies reveal a significant γ-silyl stabilization of the *endo*-2-trimethylsilyl-7-norbornyl cation as well as the *endo*-2-trimethylsilyl-7-norbornyl carbene. By way of contrast, computational and experimental studies suggest only minimal γ-silyl stabilization of the *anti*-7-trimethylsilyl-2-norbornyl cation and no stabilization of the *anti*-7-trimethylsilyl-2-norbornyl carbene. Therefore γ-silyl stabilization can best be described as "enormous" in the 3-trimethylsilylcyclobutyl carbocation and carbene, "quite significant" in 2-trimethylsilyl-7-norbornyl carbocation and carbene, and "minimal to non-existent" in the 7-trimethylsilyl-2-norbornyl carbocation and carbene.

■ EXPERIMENTAL SECTION

General. NMR spectra were recorded on a 600 MHz spectrometer. HRMS measurements were carried out using either an electrospray ionization source with time-of-flight mass analyzer or a GC-mass spectrometer with an electron impact ionization source. NMR analyses were carried out on an instrument operating at 600 MHz for ^{1}H NMR.

*Preparation of anti-7-t-Butyldimethylsiloxybicyclo[2.2.1]hept-2-ene, **13**.* A solution of 345 mg of *anti*-bicyclo[2.2.1]hept-2-en-7-ol (3.14 mmol), **12**,[12] and 520 mg of *t*-butyldimethylsilyl chloride (3.46 mmol) in 5 mL of dry THF was stirred as 391 mg of imidazole (5.75 mmol) was added. The mixture was refluxed for 3 h and then taken up into 20 mL of pentane and 15 mL of water. The pentane extract was washed with 2 additional portions of water, saturated NaCl solution, and dried over a mixture of Na_2SO_4 and $MgSO_4$. After filtration, the solvent was removed using a rotary evaporator. The residue was distilled to give 669 mg of liquid **13** (95% yield), bp 88−91 °C (15 mm). ^{1}H NMR of **13** ($CDCl_3$) δ 5.94 (t, J = 2.2 Hz, 2 H), 3.43 (br s, 1 H), 2.42 (m, 2 H), 1.80 (m, 2 H), 0.91 (m, 2 H), 0.87 (s, 9 H), 0.02 (s, 6 H). ^{13}C NMR of **13** ($CDCl_3$) δ 134.2, 82.8, 46.3, 25.8, 21.8, 17.9, −4.8. Exact mass (EI) calcd for $C_{13}H_{24}OSi$: 224.1596. Found: 224.1592.

*Preparation of anti-7-t-Butyldimethylsilyloxy-2-bromobicyclo-[2.2.1]hept-2-ene, **14**.* A solution of 667 mg of the TBS ether **13** (2.98 mmol) in 9 mL of CH_2Cl_2 was stirred as 705 mg of PhSeBr (2.99 mmol) was added in small portions over 30 min. The color faded gradually after each addition. On completion of the addition, the mixture was stirred for 1.5 h at room temperature. The CH_2Cl_2 was then removed via rotary, the residue was immediately dissolved in 10 mL of dry THF, and the solution was cooled in an ice bath. The solution was stirred as 1.95 g of 30% H_2O_2 was added dropwise, followed by 30 mg of acetic acid. The mixture was then warmed to room temperature for 3 h and then transferred to a separatory funnel using pentane. The mixture was washed with two portions of water and then with Na_2CO_3 solution. The pentane extract was dried over Na_2SO_4 and filtered, and the solvent was then removed using a rotary evaporator. The residue was chromatographed on 12 g of silica gel, and the column was eluted with pentane. The product rapidly eluted, and the pentane was removed using a rotary evaporator. The residue was distilled to give 403 mg of liquid **14** (45% yield), bp 90−93 °C (1 mm). ^{1}H NMR ($CDCl_3$) δ 6.02 (d of d, J = 3.7, 1.2 Hz, 1 H), 3.60 (br s, 1 H), 2.55 (m, 1 H), 2.50 (m, 1 H), 1.83 (m, 2 H), 1.10 (m, 2 H), 0.86 (s, 9 H), 0.03 (br s, 6 H). ^{13}C NMR of **14** ($CDCl_3$) δ 133.5, 122.7, 81.5, 54.7, 48.7, 25.7, 23.1, 21.7, 17.9, −4.83, −4.87. Exact mass (EI) calcd for $C_{13}H_{23}BrOSi$: 302.0702. Found: 302.0743.

*Preparation of anti-7-t-Butyldimethylsiloxy-2-trimethylsilylbicyclo[2.2.1]hept-2-ene, **15**.* A solution of 374 mg of the vinyl bromide **14** (1.23 mmol) in 6 mL of THF was cooled to −78 °C, and 820 μL of 1.6 M *n*-BuLi in hexanes (1.31 mmol) was added. The mixture was stirred at −78 °C for 45 min, and then 225 mg of $ClSiMe_3$ (2.07 mmol) was added. The mixture was warmed and kept at room temperature for 1.5 h and then recooled in an ice bath. Triethylamine (75 mg) was then added followed by water, and the mixture was then transferred to a separatory funnel using pentane. The pentane phase was washed with 3 portions of water, saturated NaCl solution, and dried over Na_2SO_4. The solvent was removed using a rotary evaporator, and the residue was distilled to give 336 mg (92% yield) of liquid **15**, bp 72−75 °C (0.3 mm). ^{1}H NMR of **15** ($CDCl_3$) δ 6.22 (d of d, J = 3.3, 0.9 Hz, 1 H), 3.36, (br s, 1 H), 2.48 (m, 1 H), 2.42 (m, 1 H), 1.78 (m, 2 H), 0.88 (m, 1 H), 0.86 (s, 9 H), 0.77 (m, 1 H), 0.03 (s, 9 H), 0.011 (s, 3 H), 0.005 (s, 3 H). ^{13}C NMR of **15** ($CDCl_3$) δ 148.4, 143.4, 82.9, 48.9, 47.8, 25.8, 21.84, 21.82, 17.9, −1.8,

−4.78, −4.85. Exact mass (EI) calcd for $C_{16}H_{32}OSi_2$: 296.1992. Found: 296.1995.

*Preparation of anti-7-Hydroxy-endo-2-trimethylsilylbicyclo-[2.2.1]heptane, **16**.* The vinyl silane **15** (375 mg; 1.27 mmol) was dissolved in 15 mL of dry ether, and 57 mg of 10% Pd/C was added. The flask was flushed with H_2, and the mixture was stirred under H_2 at 1 atm pressure for 8 h. The mixture was then filtered through a small amount of $MgSO_4$ to remove the Pd/C, and the solvent was removed using a rotary evaporator. The ^1H NMR spectrum of the crude residue showed 84% of *endo*-2-trimethylsilyl-*anti*-7-(*t*-butyldimethylsiloxy)-bicyclo[2.2.1]heptane and 16% of *exo*-2-trimethylsilyl-*anti*-7-(*t*-butyldimethylsiloxy)bicyclo[2.2.1]heptane. This crude residue was used directly in the hydrolysis step.

The mixture obtained above was dissolved in 12 mL of THF, and 12 mL of 1.0 M HCl in water was added with stirring. After 22 h at room temperature NMR analysis of a small portion of the reaction mixture showed about 50% reaction. The mixture was then heated with stirring at 50 °C for 24 h to complete the hydrolysis. The mixture was then transferred to a separatory funnel with pentane, and the aqueous phase was separated. The pentane extract was washed with two portions of water and dried over $MgSO_4$. After filtration, the solvent was removed using a rotary evaporator. The NMR spectrum showed a mixture containing 84% *endo*-2-trimethylsilylbicyclo[2.2.1]-heptan-*anti*-7-ol, **16**, and 16% *exo*-2-trimethylsilylbicyclo[2.2.1]heptan-*anti*-7-ol, **17**. The crude products were chromatographed on 15 g of silica gel and eluted with increasing amounts of ether in pentane. Mixtures of the alcohols **16** and **17** (205 mg, 88% yield) eluted with 13−16% ether in pentane. The early fractions were enriched in alcohol **17**, while the latter fractions were enriched in alcohol **16**, mp 66−68 °C. NMR of **16** ($CDCl_3$) δ 4.03 (br, 1 H), 2.00 (m, 2 H), 1.88−1.72 (m, 3 H), 1.49 (m, 1 H), 1.41 (d, J = 3.5 Hz, 1 H), 1.18 (m, 1 H), 1.07 (d of d, J = 12, 7 Hz, 1 H), 1.00 (m, 1 H), 0.00 (s, 9 H). ^{13}C NMR of **16** ($CDCl_3$) δ 82.1, 43.0, 40.8, 28.6, 27.1, 25.3, 24.1, −1.6. Exact mass (EI) calcd for $C_{10}H_{20}OSi$: 184.1283. Found: 184.1304.

*Preparation of endo-2-Trimethylsilyl-anti-bicyclo[2.2.1]hept-7-yl Triflate, **18**.* The alcohol **16** (23.3 mg; 0.127 mmol) was dissolved in 0.5 mL of CH_2Cl_2, and 23 mg of 2,6-lutidine (0.215 mmol) was added. The mixture was cooled to −10 °C, and 49 mg of triflic anhydride (0.174 mmol) in a small amount of CH_2Cl_2 was added in one portion. The mixture was warmed to room temperature and then transferred to a separatory funnel using a small amount of CH_2Cl_2. Five mL of pentane was then added and a rapid aqueous workup followed. The organic phase was washed successively with cold water, cold dilute HCl solution, cold water, $NaHCO_3$ solution, and saturated NaCl solution. The solution was dried over $MgSO_4$ and filtered, and the solvent was removed using a rotary evaporator to give 38.8 mg of liquid triflate **18** (97% yield). The unstable **18** was stored in pentane solution at −20 °C. ^1H NMR of **19** ($CDCl_3$) δ 4.99 (br s, 1 H), 2.42, (m, 2 H), 1.89 (m, 1 H), 1.82 (m, 2 H), 1.62 (m, 1 H), 1.32 (m, 1 H), 1.18 (d of d, J = 12.5, 7.2 Hz, 1 H), 1.04 (m, 1 H), 0.035 (s, 9 H). ^{13}C NMR of **18** ($CDCl_3$) δ 118.7 (q, J = 319 Hz), 96.2, 42.1, 39.9, 27.03, 26.96, 23.9, 23.5, −1.8.

Solvolysis of Triflate 18 in CD_3CO_2D. A solution of 4.0 mg of triflate **18** and 3.1 mg of 2,6-lutidine in 350 mg of CD_3CO_2D was placed in a sealed 3 mm NMR tube at 25 °C for 72 h. The tube was then analyzed by ^1H NMR spectroscopy that showed acetate **21** as the sole product. Acetate **21** was identified by ^1H NMR spectral comparison with an authentic sample of **21**-H_3 in CD_3CO_2D prepared as described below.

*Preparation of anti-7-Acetoxy-endo-2-trimethylsilylbicyclo-[2.2.1]heptane, **21**-H_3.* A solution of 5.9 mg of alcohol **16** (0.0321 mmol) and 8 mg of acetic anhydride (0.0784 mmol) in 0.7 mL of CH_2Cl_2 was stirred as 1.5 mg of dimethylaminopyridine was added. After 3 h at room temperature, about 10 mg of CH_3OH was added followed by 3 mL of pentane. The mixture was extracted with water, dilute HCl solution, water, saturated NaCl solution, and then dried over $MgSO_4$. After filtration, the solvent was removed using a rotary evaporator to give 7.0 mg (96% yield) of liquid acetate product **21**-H_3. ^1H NMR ($CDCl_3$) δ 4.71 (br s, 1 H), 2.25, (m, 1 H), 2.19, (m, 1 H), 2.03 (s, 3 H), 1.84−1.73 (m, 2 H), 1.67 (m, 1 H), 1.48 (m, 1 H), 1.19 (m, 1 H), 1.12−1.04 (m, 2 H), 0.004 (s, 9 H). ^{13}C NMR ($CDCl_3$) δ 171.3, 83.5, 40.8, 38.7, 28.0, 27.7, 24.6, 24.5, 21.3, −1.7. Exact mass (EI) calcd for $C_{12}H_{22}O_2Si$: 226.1389. Found: 226.1373. Except for the singlet at δ 2.03, the ^1H NMR spectrum of **21**-H_3 in CD_3CO_2D was identical to that of the product formed on solvolysis of **18** in CD_3CO_2D.

*Preparation of endo-2-Trimethylsilylbicyclo[2.2.1]heptan-7-one, **19**.* A solution of 88 mg of alcohol **16** (0.478 mmol) in 4 mL of CH_2Cl_2 was stirred as 128 mg of pyridinium chlorochromate (0.594 mmol) was added in one portion. The mixture was stirred at room temperature for 17 h, and then 8 mL of pentane was added. The mixture was filtered through a small amount of silica gel, and the solvent was removed using a rotary evaporator. The residue was chromatographed on 4.5 g of silica gel, and the column was eluted with increasing amounts of ether in pentane. The liquid ketone **19** (27.8 mg; 32% yield) eluted with 5% ether in pentane. ^1H NMR of **19** ($CDCl_3$) δ 2.06 (m, 1 H), 1.95−1.87 (m, 3 H), 1.83 (m, 1 H), 1.76 (m, 1 H), 1.47 (m, 1 H), 1.39 (d of d, J = 12, 8 Hz), 1.26 (m, 1 H), 0.09 (s, 9 H). ^{13}C NMR of **19** ($CDCl_3$) δ 217.2, 40.2, 38.4, 25.4, 24.9, 22.1, 21.2, −1.6. Exact mass (EI) calcd for $C_{10}H_{18}OSi$: 182.1127. Found: 182.1133.

Preparation and Pyrolysis of Tosylhydrazone Salt 26. A solution of 26.8 mg of ketone **19** (0.147 mmol) in 150 μL of CH_3OH was added to a suspension of 30.3 mg of tosylhydrazine (0.163 mmol) in 350 μL of methanol. The mixture was stirred for 3 h at room temperature, and then 380 μL of freshly prepared 0.478 M $NaOCH_3$ in methanol (0.182 mmol) was added to the tosylhydrazone solution. The solvent was then removed using a rotary evaporator, and the residue was evacuated at 15 mm for 5 h, during which time the salt **26** gradually solidified.

The solid tosylhydrazone salt **26** was broken up with a spatula, and a short path distillation head with a 5 mL receiver flask was attached. The pressure was lowered to <0.1 mm, and the flask was gradually heated (oil bath) to 90 °C. The receiver flask was cooled in a dry ice/acetone bath, and the temperature of the oil bath was slowly raised to 135 °C. At around 120 °C the pressure rose slightly and remained slightly elevated until about 130 °C. On completion of the pyrolysis, the products **28** and **23** (96.5:3.5 ratio) were identified by ^1H and ^{13}C NMR spectroscopy. The structure of **23** was based on NMR spectral comparison with an authentic sample.[20] ^1H NMR of **28** ($CDCl_3$) δ 2.39 (m, 1 H), 2.10 (d of t, J = 4.7, 2.7 Hz, 1 H), 2.02−1.95 (m, 2 H), 1.91 (m, 1 H), 1.63 (m, 1 H), 1.45 (d of d of t, J = 12, 7, 1.3 Hz, 1 H), 1.39 (t, J = 4.8 Hz, 1 H), 0.88 (d of d of d, J = 10, 2.7, 1.1 Hz, 1 H), −0.10 (s, 9 H). ^{13}C NMR of **28** ($CDCl_3$) δ 37.8 (d, J = 145 Hz), 35.6 (t, J = 128 Hz), 29.3 (d, J = 181 Hz), 26.5 (d, J = 161 Hz), 24.9 (t, J = 134 Hz), 22.8 (t, J = 130 Hz), 14.1 (s), −2.9 (q, J = 118 Hz). Exact mass (EI) calcd for $C_{10}H_{18}Si$: 166.1178. Found: 166.1164.

*Preparation of anti-7-Trimethylsilyl-endo-bicyclo[2.2.1]heptan-2-ol, **34**.* A solution of 29.0 mg of ketone **33**[16] (0.159 mmol) in 2 mL of dry THF was cooled to −78 °C, and 250 μL of 1.0 M L-selectride in THF (0.250 mmol) was added via syringe to the stirred solution. The mixture was allowed to warm to room temperature and then recooled to 0 °C, and a solution of 100 mg of NaOH in 1 mL of water was added dropwise. After a few minutes, 300 μL of 30% hydrogen peroxide was added, and the mixture was warmed to room temperature. After 30 min the mixture was taken up into ether and water. The ether extract was washed with water and dried over $MgSO_4$. After filtration, the solvent was removed using a rotary evaporator. The residue was taken up into pentane and redried with Na_2SO_4, and the pentane was removed using a rotary evaporator to give 26.8 mg (91% yield) of alcohol **34**. ^1H NMR of **34** ($CDCl_3$) δ 4.17 (m, 1 H), 2.28 (t, J = 4.2 Hz, 1 H), 2.25 (t, J = 4.2 Hz, 1 H), 1.98 (m, 1 H), 1.88 (m, 1 H), 1.58 (m, 1 H), 1.42 (br, 1 H), 1.39 (m, 1 H), 1.29 (m, 1 H), 0.85 (d of d, J = 12.6, 3 Hz, 1 H), 0.76 (m, 1 H), 0.01 (s, 9 H). ^{13}C NMR of **34** ($CDCl_3$) δ 74.6, 44.8, 42.3, 39.8, 39.3, 29.7, 19.6, −0.8. Exact mass (ESI) (M + Na^+) calcd for $C_{10}H_{20}NaOSi$ 207.1176. Found 207.1163.

*Preparation of anti-7-Trimethylsilyl-endo-bicyclo[2.2.1]hept-2-yl Mesylate, **35**.* A solution of 13.5 mg of alcohol **34** (0.0734 mmol) in 0.7 mL of CH_2Cl_2 was cooled to −60 °C, and 13.5 mg of CH_3SO_2Cl (0.118 mmol) in a small amount of CH_2Cl_2 was added. A solution of

15 mg of Et_3N (0.149 mmol) in a small amount of CH_2Cl_2 was then added dropwise. The mixture was allowed to warm to room temperature and then taken up into ether, washed with cold water, dilute HCl solution, water, $NaHCO_3$ solution, saturated NaCl solution, and then dried over a mixture of Na_2SO_4 and $MgSO_4$. After filtration, the solvent was removed using a rotary evaporator to give 18.1 mg of mesylate **35** (94% yield). The crude product was slurried with pentane, and the mixture was cooled to about −40 °C. The pentane was decanted, and the residual solvent was removed using a rotary evaporator to give mesylate **35**, mp 57−58 °C. ^{1}H NMR of **35** ($CDCl_3$) δ 4.92 (m, 1 H), 2.99 (s, 3 H), 2.61 (t, J = 4.2 Hz, 1 H), 2.33 (t, J = 4.2 Hz, 1 H), 2.07 (m, 1 H), 1.87 (m, 1 H), 1.62 (m, 1 H), 1.49 (m, 1 H), 1.33 (m, 1 H), 1.24 (d of d, J = 13.2, 3.6 Hz, 1 H), 0.76 (m, 1 H), 0.03 (s, 9 H). ^{13}C NMR of **35** ($CDCl_3$) δ 83.6, 43.7, 39.4, 38.9, 38.7, 38.3, 29.2, 20.4, −0.9.

Solvolysis of Mesylate 35 in CD_3CO_2D. A solution of 3.5 mg of mesylate **35** and 2.5 mg of 2,6-lutidine in 460 mg of CD_3CO_2D was sealed in a 3 mm NMR tube, and the tube was placed in a water bath at 60.0 °C for 52.5 h. The tube was then analyzed by ^{1}H NMR spectroscopy that showed **38**, **39**, **40**, **41**, and **42** in a 6:22:17:37:18 ratio (see Supporting Information). These products were all identified by ^{1}H NMR spectral comparison with authentic samples in CD_3CO_2D. Authentic samples of acetates **41**-H_3 and **42**-H_3 were prepared as described below.

*Preparation of exo-2-Acetoxy-endo-3-trimethylsilylbicyclo[2.2.1]-heptane, **41**-H_3.* A solution of 150 mg of *endo*-2-hydroxy-*endo*-3-trimethylsilylbicyclo[2.2.1]heptane[4b] (0.815 mmol) and 131 mg of 2,6-lutidine (1.223 mmol) in 5 mL of ether was cooled to −10 °C, and 255 mg of trifluoroacetic anhydride (1.214 mmol) in 0.5 mL of ether was added dropwise. The mixture was warmed to room temperature, and after 10 min the mixture was taken up into pentane. The solution was consecutively washed with cold water, cold dilute HCl solution, water, $NaHCO_3$ solution, and then dried over $MgSO_4$. After filtration, the solvent was removed using a rotary evaporator to give 226 mg (99% yield) of *endo*-2-trifluoroacetoxy-*endo*-3-trimethylsilylbicyclo-[2.2.1]heptane.

A solution of 220 mg of the trifuoroacetate (0.786 mmol) prepared above, and 110 mg of 2,6-lutidine (1.027 mmol) in 8 mL of CH_3CO_2H was heated in a sealed tube at 100 °C for 18 h. The mixture was taken up into 15 mL of ether and 15 mL of pentane, and the solution was washed with two portions of water, followed by dilute Na_2CO_3 solution. The organic extract was dried over $MgSO_4$ and filtered, and the solvents were then removed using a rotary evaporator. The residue was chromatographed on 3 g of silica gel, and the column was eluted with increasing amounts of ether in pentane. The liquid acetate **41**-H_3 (69 mg; 39% yield) eluted with 3% ether in pentane. NMR spectra of **41**-H_3 showed 6% of an unidentified isomeric acetate. ^{1}H NMR of **41**-H_3 ($CDCl_3$) δ 4.61 (d, J = 4 Hz, 1 H), 2.35 (m, 1 H), 2.30 (d, J = 5 Hz, 1 H), 1.98 (s, 3 H), 1.55−1.46 (m, 2 H), 1.33 (m, 1 H), 1.27−1.19 (m, 2 H), 1.06 (m, 1 H), 0.90 (m, 1 H), 0.04 (s, 9 H). ^{13}C NMR of **41**-H_3 ($CDCl_3$) δ 170.7, 79.2, 42.8, 38.7, 38.20, 38.17, 26.0, 24.4, 21.5, −1.4. Exact mass (ESI)(M + Na^+) calcd for $C_{12}H_{22}O_2SiNa$: 249.1281. Found: 249.1284.

*Preparation of anti-7-Trimethylsilyl-endo-2-acetoxybicyclo-[2.2.1]heptane, **42**-H_3.* A solution of 9.8 mg of alcohol **34** (0.0533 mmol) and 12 mg of acetic anhydride (0.118 mmol) in 1.0 mL of CH_2Cl_2 was stirred as 3.3 mg of dimethylaminopyridine was added. After 8 h at room temperature 15 mg of CH_3OH was added followed by 5 mL of pentane. The mixture was extracted with water, dilute HCl solution, water, saturated NaCl solution, and then dried over $MgSO_4$. After filtration, the solvent was removed using a rotary evaporator to give 11.5 mg (96% yield) of liquid acetate **42**-H_3. ^{1}H NMR ($CDCl_3$) δ 4.87 (m, 1 H), 2.54 (t, J = 4.2 Hz, 1 H), 2.29 (t, J = 4.4 Hz, 1 H), 2.04 (s, 3 H), 2.00 (m, 1 H), 1.72 (m, 1 H), 1.58 (m, 1 H), 1.38 (m, 1 H), 1.27 (m, 1 H), 1.02 (d of d, J = 13, 3.6 Hz, 1 H), 0.78 (br, 1 H), 0.015 (s, 9 H). ^{13}C NMR ($CDCl_3$) δ 171.4, 77.0, 42.5, 39.4, 39.1, 38.8, 29.3, 21.3, 20.7, −0.8. Exact mass (ESI)(M + Na^+) calcd for $C_{12}H_{22}O_2SiNa$: 249.1281. Found: 249.1281.

Preparation and Pyrolysis of Tosylhydrazone Salt 37. A solution of 88 mg of ketone **33** (0.484 mmol) in 500 μL of CH_3OH was added to a suspension of 92 mg of tosylhydrazine (0.494 mmol) in 500 μL of methanol. The stirred mixture was allowed to stand at room temperature for 4 h, and then 1.15 mL of 0.478 M $NaOCH_3$ in methanol (0.550 mmol) was added. After 10 min, the methanol was removed using a rotary evaporator, and the residue was evacuated at 15 mm for 5 h. The tosylhydrazone salt **37** gradually solidified. The solid salt **37** was then broken up with a spatula.

A short path distillation head with a 5 mL receiver flask was attached, and the pressure was lowered to <0.1 mm. The flask was gradually heated (oil bath) under vacuum and at 100 °C, and the receiver flask was cooled in a dry ice/acetone bath. The temperature was slowly raised to 155 °C. At around 130 °C the pressure rose slightly and remained slightly elevated until about 150 °C. On completion of the pyrolysis, the yield of the liquid product **51** in the receiver flask was 69 mg (86% yield). ^{1}H NMR of **51** ($CDCl_3$) δ 1.95 (m, 1 H), 1.26 (m, 1 H), 1.19 (m, 1 H), 1.12 (m, 1 H), 1.10−1.05 (m, 2 H), 1.03−0.99 (m, 2 H), 0.62 (m, 1 H), −0.01 (s, 9 H). ^{13}C NMR of **51** ($CDCl_3$) δ 36.4 (t, J = 132 Hz), 33.1 (d, J = 118 Hz), 32.2 (d, J = 146 Hz), 31.5 (t, J = 132 Hz), 12.8 (d, J = 173 Hz), 10.5 (d, J = 174 Hz), 10.0 (d, J = 174 Hz), −1.4 (q, J = 119 Hz). Exact mass (EI) calcd for $C_{10}H_{18}Si$: 166.1178. Found: 166.1182.

Solvolyses of Triflates and Mesylates. Kinetics Procedures. Rate constants reported in Table 1 were all determined using 600 MHz ^{1}H NMR spectroscopy. Kinetic studies in CD_3CO_2D were carried out by dissolving ∼4 mg of the appropriate substrate in 350 mg of CD_3CO_2D containing ∼1.5 equiv of 2,6-lutidine. The sample was then sealed in a 3 mm NMR tube, and the tube was placed in a constant temperature bath at the appropriate temperature. At appropriate time intervals, the tube was quenched in a water bath at 15 °C and rapidly analyzed by ^{1}H NMR at ambient temperature to determine relative amounts of starting triflate or mesylate. For triflate **18**, readings were carried out with the NMR probe temperature at 25.0 °C, and the sample was placed in a constant temperature bath at 25.0 °C between readings. All kinetic studies in trifluoroethanol (0.05 M in 2,6-lutidine) were carried out using our previously described method[21] where the chemical shift of the added 2,6-lutidine was monitored as a function of time.

For triflate **18** in CD_3CO_2D, the rate of disappearance of the TMS singlet at δ 0.054 was monitored relative to the product signal at δ 0.024. For 7-norbornyl triflate, **20**,[22] the peak at δ 5.06 was monitored using the 2,6-lutidine signal at δ 7.60 as an internal standard. For mesylate **35**, the area of the mesylate signal at δ 3.025 was monitored using the 2,6-lutidine signal at δ 2.74 as an internal standard. For 2-norbornyl mesylate, **45**,[23] the rate of disappearance of the signal at δ 3.026 was monitored relative to the product mesylate anion developing at δ 2.857. First-order rate constants for disappearance of substrates were calculated by standard least-squares procedures. Correlation coefficients were all greater than 0.9998. Typical data are given as Supporting Information.

Computational Studies. Ab initio molecular orbital calculations were performed using the Gaussian 09 series of programs.[13] Structures were characterized as energy minima via frequency calculations that showed no negative frequencies or as transition states that showed one negative frequency.

■ ASSOCIATED CONTENT

Supporting Information

Complete ref 13, the M062X/6-311+G* calculated structures, energies, and Cartesian coordinates of **8**−**11**, **22**−**25**, **30**, **31**, **47**−**50**, **52**, and **53**, ^{1}H and ^{13}C NMR spectra of **13**−**16**, **18**, **19**, **21**-H_3, **23**, **28**, **34**, **35**, **41**-H_3, **42**-H_3, **43**, **44**, and **51**, the ^{1}H NMR spectrum of the acetolysis products from mesylate **35** as well as kinetics studies on **18** and **35**. This material is available free of charge *via* the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: creary.1@nd.edu

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) (a) Creary, X.; O'Donnell, B. D.; Vervaeke, M. *J. Org. Chem.* **2007**, *72*, 3360. (b) Creary, X.; Kochly, E. D. *J. Org. Chem.* **2009**, *74*, 2134.

(2) (a) Creary, X.; Wang, Y.-X. *Tetrahedron Lett.* **1989**, *19*, 2493. (b) Creary, X.; Butchko, M. A. *J. Org. Chem.* **2001**, *66*, 1115. (c) Creary, X.; Butchko, M. A. *J. Org. Chem.* **2002**, *67*, 112.

(3) For reviews and early studies, see (a) Ushakav, S. N.; Itenberg, A. M. *Zh. Obshch. Khim.* **1937**, *7*, 2495. (b) Sommer, L. H.; Dorfman, E.; Goldberg, G. M.; Whitmore, F. C. *J. Am. Chem. Soc.* **1946**, *68*, 488. (c) Sommer, L. H.; Bailey, D. L.; Whitmore, F. C. *J. Am. Chem. Soc.* **1948**, *70*, 2869. (d) Sommer, L. H.; Baughman, G. A. *J. Am. Chem. Soc.* **1961**, *83*, 3346. (e) Davis, D. D.; Jacocks, H. M., III *J. Organomet. Chem.* **1981**, *206*, 33. (f) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981. (g) White, J. M. *Aust. J. Chem.* **1995**, *48*, 1227.

(4) (a) Lambert, J. B.; Wang, G. T.; Finzel, R. B.; Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838. (b) Lambert, J. B.; Chelius, E. C. *J. Am. Chem. Soc.* **1990**, *112*, 8120. (c) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677. (d) Lambert, J. B.; Liu, X. *J. Organomet. Chem.* **1996**, *521*, 203. (e) Lambert, J. B.; Zhao, Y.; Emblidge, R. W.; Salvador, L. A.; Liu, X.; So, J. H.; Chelius, E. C. *Acc. Chem. Res.* **1999**, *32*, 183.

(5) (a) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496. (b) Ibrahim, M. R.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 819.

(6) Klaer, A.; Saak, W.; Haase, D.; Müller, T. *J. Am. Chem. Soc.* **2008**, *130*, 14956.

(7) (a) Shiner, V. J., Jr.; Ensinger, M. W. *J. Am. Chem. Soc.* **1986**, *108*, 842. (b) Davidson, E. R.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 3135. (c) Shiner, V. J., Jr.; Ensinger, M. W.; Rutkowske, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 804. (d) Shiner, V. J., Jr.; Ensinger, M. W.; Huffman, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 7199. (e) Shiner, V. J., Jr.; Ensinger, M. W. *J. Org. Chem.* **1990**, *55*, 653. (f) Tilley, L. J.; Shiner, V. J., Jr. *J. Phys. Org. Chem.* **1999**, *12*, 564.

(8) Grob, C. A.; Sawlewicz, P. *Tetrahedron Lett.* **1987**, *28*, 951. (b) Grob, C. A.; Martin Gründel, M.; Sawlewicz, P. *Helv. Chim. Acta* **1988**, *71*, 1502.

(9) Adcock, W.; Clark, C. I.; Schiesser, C. H. *J. Am. Chem. Soc.* **1996**, *118*, 11541.

(10) Creary, X.; Kochly, E. D. *J. Org. Chem.* **2009**, *74*, 9044.

(11) Creary, X. *J. Am. Chem. Soc.* **2013**, *135*, 6570.

(12) Story, P. R. *J. Org. Chem.* **1961**, *26*, 287.

(13) Frisch, M. J. et al. *Gaussian 09*, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.

(14) For a discussion of the tosylhydrazone salt pyrolysis method of diazocompound and carbene generation, see (a) Bamford, W. R.; Stevens, T. S. *J. Chem. Soc.* **1952**, 4735. (b) Kaufman, G. M.; Smith, J. A.; Vander Stouw, G. G.; Shechter, H. *J. Am. Chem. Soc.* **1965**, *87*, 935. (c) Creary, X. *Org. Synth.* **1986**, *64*, 207.

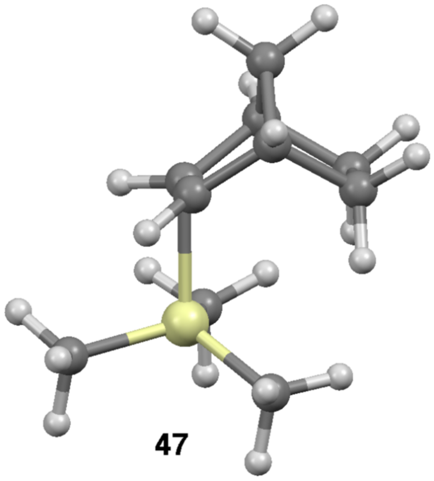
(15) Moss, R. A.; Whittle, J. R. *J. Chem. Soc. Chem. Commun.* **1969**, 341.

(16) Hwu, J. R.; Gilbert, B. A. *J. Am. Chem. Soc.* **1991**, *113*, 5917.

(17) (a) Winstein, S.; Clippinger, E.; Howe, R.; Vogelfanger, E. *J. Am. Chem. Soc.* **1965**, *87*, 376. (b) Winstein, S.; Trifan, D. *J. Am. Chem. Soc.* **1952**, *74*, 1147.

(18) Cation **47** is a β-silyl cation previously generated under solvolytic conditions.[4b] Our present calculation suggests that **47** is not as stable as one might expect due to angular constraints. The calculated structure of cation **47** shows a H−C2−C3−Si dihedral angle of 57.4°. The ideal angle for maximal overlap of the vacant cation orbital with the C−Si σ-orbital is 90°. Hence cation **47** gives some solvent capture and proton elimination to go along with the usual TMS elimination.

(19) (a) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1961**, *83*, 3159. (b) Freeman, P. K.; George, D. E.; Rao, V. N. M. *J. Org. Chem.* **1964**, *29*, 1682.



47

(20) Kuivila, H. G.; Warner, C. R. *J. Org. Chem.* **1964**, *29*, 2845.

(21) Creary, X.; Jiang, Z. *J. Org. Chem.* **1994**, *59*, 5106.

(22) For previous studies on 7-norbomyl triflate, see (a) Su, T. A.; Sliwinski, W. F.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1969**, *91*, 5386. (b) Creary, X.; McDonald, S. R. *J. Org. Chem.* **1985**, *50*, 474.

(23) (a) Masamune, S.; Rossy, P. A.; Bates, G. S. *J. Am. Chem. Soc.* **1973**, *95*, 6452. (b) Brown, H. C.; Ravindranathan, M.; Chloupek, F. J.; Rothberg, I. *J. Am. Chem. Soc.* **1978**, *100*, 3143. (c) Bentley, T. W.; Bowen, C. T.; Brown, H. C.; Chloupek, F. J. *J. Org. Chem.* **1981**, *46*, 38. (d) Creary, X.; Geiger, C. C. *J. Am. Chem. Soc.* **1982**, *104*, 4151. (e) Chang, S.; Le Noble, W. J. *J. Am. Chem. Soc.* **1984**, *106*, 810.