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3-Trimethylsilylcyclobutylidene. The γ-Effect of Silicon on Carbenes

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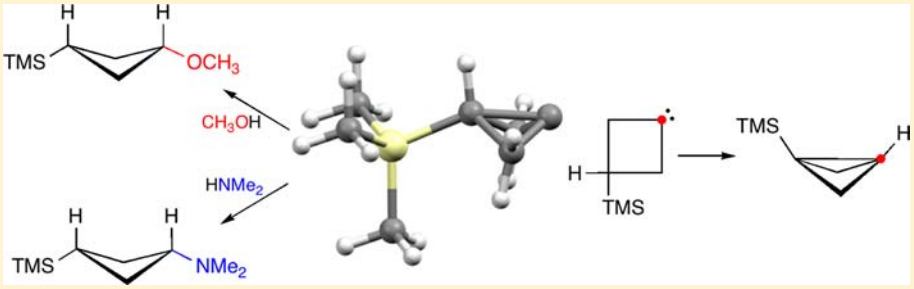
Supporting Information



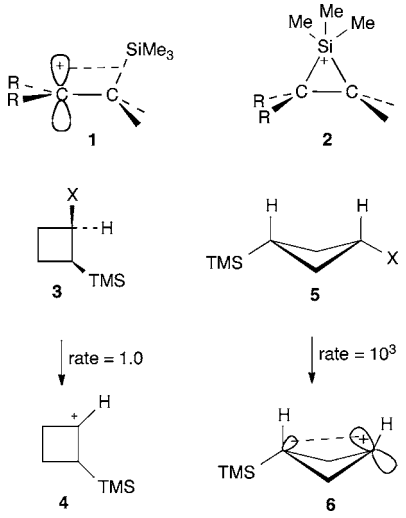
ABSTRACT: 3-Trimethylsilylcyclobutylidene was generated by pyrolysis of the sodium salt of the tosylhydrazone derivative of 3-trimethylsilylcyclobutanone. This carbene converts to 1-trimethylsilylbicyclobutane as the major product. A labeling study shows that this intramolecular rearrangement product comes from 1,3-hydrogen migration to the carbenic center and not 1,3-silyl migration. Computational studies show two carbene minimum energy conformations, with the lower energy conformation displaying a large stabilizing interaction of the carbene center with the rear lobe of the C3−Si bond. In this conformation, the trimethylsilyl group cannot migrate to the carbene center, and the most favorable process is 1,3-hydrogen migration. When the carbene is generated photochemically in methanol, it reacts by a protonation mechanism giving the highly stabilized 3-trimethylsilylcyclobutyl carbocation as an intermediate. When generated in dimethylamine as solvent, the carbene undergoes preferred attack of this nucleophilic solvent from the back of this C−Si rear lobe stabilized carbene.

INTRODUCTION

The effect of a β-silyl group on carbocation **1** has been extensively studied.[1] These cations are formed much more readily (up to 10^{11} times faster) than unsilylated analogues.[2] β-Silyl cations **1** are stabilized by a very favorable interaction between the cationic center and the adjacent carbon−silicon bond. Computational studies,[3] as well as an X-ray crystallographic study,[4] are consistent with this mode of stabilization, as opposed to a potential stabilization mode involving a silicon bridged intermediate such as **2**. We have been interested in subtle aspects of the β-silyl effect.[5] Recently,[6] we have also studied the effect of a silyl group one carbon further removed from a developing carbocationic center, that is, "the γ-silyl effect". Shiner[7] and Grob[8] had earlier examined this phenomenon and found modest rate enhancements in solvolytic reactions when the silyl group was in the γ-position relative to a developing cationic center. We have found a remarkable rate enhancing effect in the substrate **5**, where the solvolysis rate of **5** is even greater than that of the β-silyl substrate **3**.[5] This effect was attributed to a γ-silicon stabilized carbocation **6** formed by assistance involving the rear lobe of the carbon−silicon orbital in a "W" fashion (Scheme 1). Computational studies[5] also provided evidence for this type of γ-trimethylsilyl stabilization.

Our laboratory has also extensively studied the effect of both β- and γ-silyl groups on a variety of carbenes.[9] Early studies showed that β-trimethylsilyl groups are prone to migrate to carbene centers, as in carbenes **7**[9a] and **9**.[9c] By way of contrast, a labeling study of the β-silylcarbene **11** showed that both trimethylsilyl and hydrogen migration occurred to the carbene center.[9a] The bicyclo [2.2.2] systems **14** and **16** were also used as a probe for γ-trimethylsilyl interactions.[9b] The rearranged product **15** indicates that the γ-trimethylsilyl group interacts quite effectively

Scheme 1. Carbocation Stabilization by the Trimethylsilyl Group



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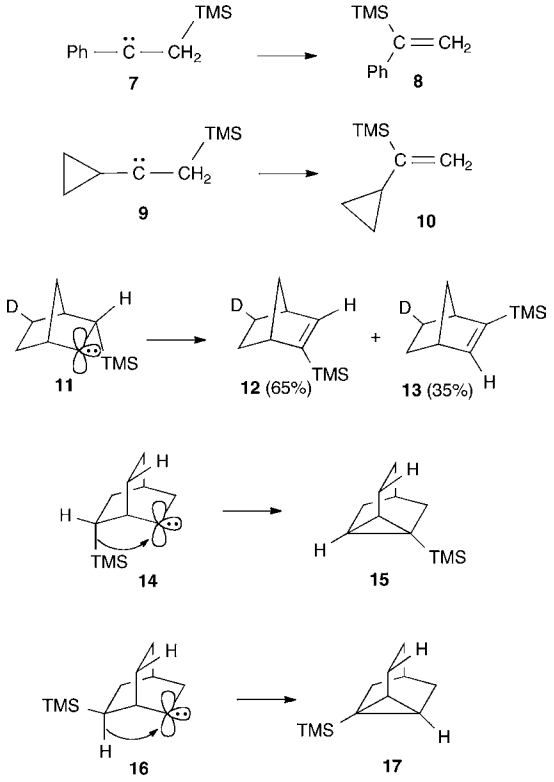
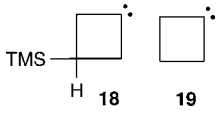
with a carbenic center and that this migration is more effective than that of an unactivated hydrogen. The product **17** derived from the carbene **16** suggests that the trimethylsilyl group also activates hydrogen toward migration to a carbenic center (Scheme 2).

Scheme 2. Rearrangements of Trimethylsilyl-Substituted Carbenes



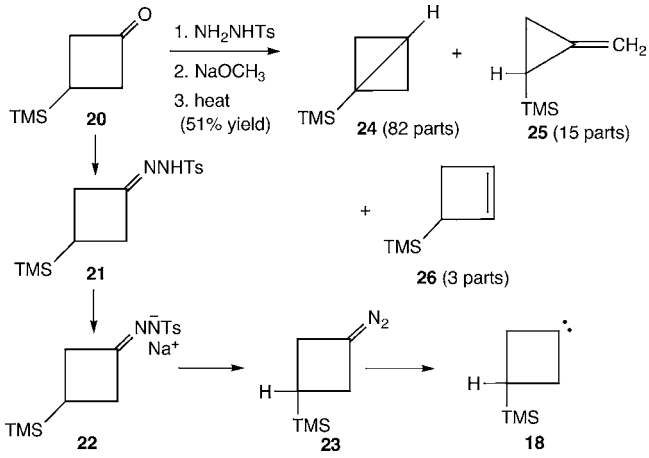
With these carbocation and carbene studies in mind, we therefore wanted to examine the carbene **18**. What role will the TMS group play in stabilization of this carbene? What rearrangement products will be formed from this carbene? How does the chemistry of carbene **18** compare to that of the desilylated analogue, cyclobutylidene, **19**? Reported here are the results of these studies.



RESULTS AND DISCUSSION

3-Trimethylsilylcyclobutanone, **20**, served as the starting material for generation of the carbene **18** (Scheme 3). The standard Bamford–Stevens reaction[10] was used to generate the diazocompound **23** from the tosylhydrazone **21**. Thus, reaction of **20** with tosylhydrazine followed by deprotonation of the tosylhydrazone **21** with sodium methoxide and pyrolysis of the salt **22** leads to the in situ generated diazocompound **23**. Loss of molecular nitrogen from **23** under the thermal conditions leads to the bicyclobutane **24** as the major product, as shown in Figure 1. Also produced is a smaller amount of the methylenecyclopropane **25**, as well as a trace amount of 3-trimethylsilylcyclobutene,

Scheme 3. Generation of Carbene 18 via the Bamford–Stevens Reaction



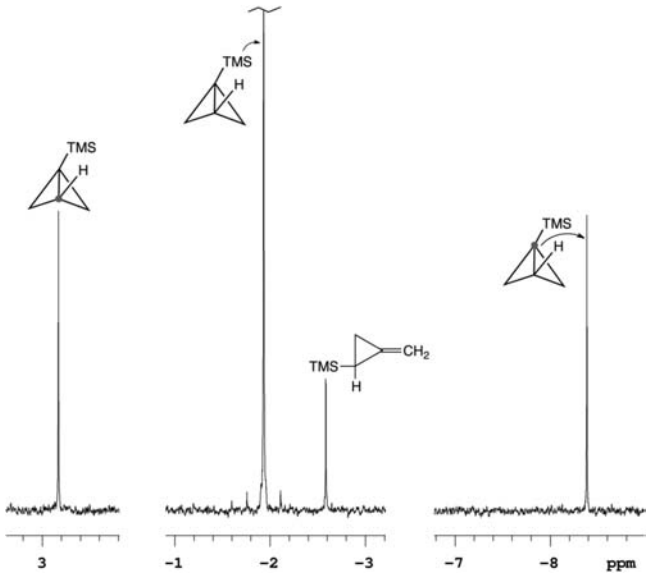


Figure 1. Partial ^{13}C NMR spectrum of the products of pyrolysis of the sodium salt **22**.

26. These products presumably arise by way of the intermediate carbene **18**.[11]

The formation of the minor products **25** and **26** is reminiscent of the behavior of the parent cyclobutylidene, **19**, where methylenecyclopropane and cyclobutene are formed in an 85:15 ratio.[11,12] Of more interest is the major bicyclobutane product **24**.[13] To determine the origin of this product, that is, which group (H or TMS) had migrated to the carbene center, a labeling study was necessary. Generation of a labeled carbene required a 3-trimethylsilylcyclobutanone with the label either in the C1 or in the C3 position. Because 3-trimethylsilylcyclobutanone can be prepared from trimethylsilylketene,[14] labeled 3-trimethylsilylcyclobutanone was needed. We chose to carry out such a synthesis using ^{13}C depleted CO as the starting material (Scheme 4).[15] Carbon monoxide (99.95% ^{12}C) is commercially available and is less expensive than ^{13}C enriched CO. The synthesis began with the knowledge the carbonyl groups of $Co_2(CO)_8$ rapidly exchange with ^{14}CO.[16] Hence ^{13}C depleted ^{12}CO was bubbled through a solution of $Co_2(CO)_8$, and then trimethylsilyldiazomethane was added. Subsequent purging of the mixture with ^{12}CO using a reaction developed by Ungváry[17]

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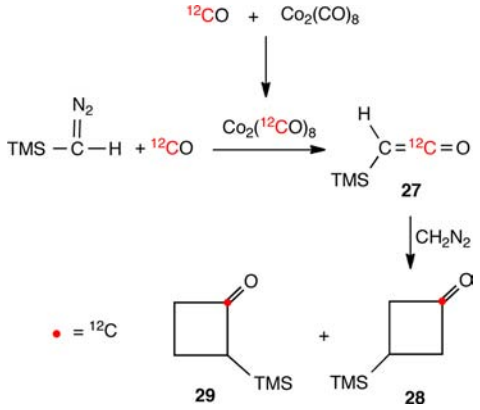
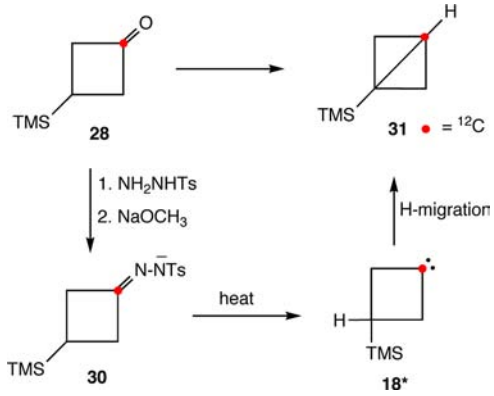
Scheme 4. Synthesis of Labeled 3-Trimethylsilylcyclobutanone



Scheme 5. Generation and Rearrangement of Labeled Carbene 18*



led to the formation of ^{13}C depleted product, that is, labeled trimethylsilylketene **27**. Addition of diazomethane to **27** gave a mixture of silylated cyclobutanones **28** and **29**, from which pure **28** could be isolated. The ^{13}C NMR spectrum of **28** was devoid of the carbonyl signal at δ 208.3, which appears in the spectrum of **20**.

Conversion of labeled **28** to the tosylhydrazone salt **30** was straightforward. The vacuum pyrolysis products from **30** were analyzed by ^{13}C NMR spectroscopy (decoupled spectrum with no NOE) to determine the position of the ^{12}C label, and the result is shown in Figure 2. The signal at δ = 2.8 ppm has

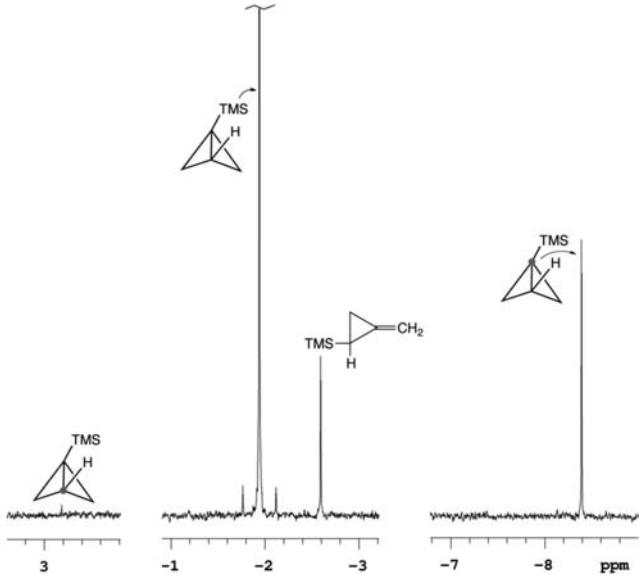


Figure 2. Partial ^{13}C NMR spectrum of the products of pyrolysis of the sodium salt **30**.

essentially disappeared, while the signal at δ = −8.4 ppm remains strong. The signal at δ = 2.8 ppm is due to the carbon attached to the bridgehead hydrogen, and hence this is the labeled (^{12}C) carbon atom. The product is therefore bicyclobutane **31**; that is, hydrogen has migrated to the carbenic center of **18*** (Scheme 5).

Computational Studies. Calculations have been used to gain insight into modes of stabilization of carbene **18**, as well as the reasons for the observed hydrogen migration to the carbene center. Two conformational energy minima for **18** have been located at the M062X/6-311+G** level.[18] The lower energy conformation **18a** (Figure 3) is highly puckered with a very short distance (1.709 Å) between the carbene center and C3. The C3−Si bond is also somewhat elongated (1.901 Å) relative to the C−Si bond in bicyclobutane **24** (1.853 Å), but not as long as in cation **6** (2.000 Å). Also of interest are the ring bonds of **18a**, where the C1−C2 bond (1.460 Å) is significantly shorter than the C2−C3 bond (1.592 Å). It is of interest to compare the structure of **18a** to that of the unsubstituted cyclobutenylidene, **19**. A previous computational study on **19** has been carried out using various levels of theory.[19] These calculations show that **19** is a puckered species with a significant interaction between the carbene center and C3. NBO analysis confirms a bonding transannular interaction. At the M062X/6-311+G** computational level in this Article (Figure 3), **19** is more puckered and the C1−C3 bond (1.704 Å) is even shorter than previously calculated. The similar C1−C2 and C2−C3 bond lengths in **19** and **18a**, as well as the similar C1−C3 distance, suggest similar carbene stabilizing interactions occur in **19** and in **18a**.

It is proposed that stabilization of carbene **18a** involves an interaction of the carbene vacant 2p orbital with the C2−C3 σ-orbitals. This leads to a shortening of the C1−C2 bond (1.460 Å) as well as a lengthening of the C2−C3 bonds (1.592 Å). An additional interaction with the rear lobe of the C3−Si bond is also suggested. This leads to a lengthening of the Si−C3 bond. A representation of these interactions is given in Figure 4. The shortening of C1−C2 and lengthening of C2−C3 in **19**, relative to **18a**, reflect the loss of the additional stabilization from the rear lobe of the C3−Si bond in **18a**.

A more quantitative measure of the stabilization of **18a** by the trimethylsilyl group comes from the isodesmic calculations shown in Scheme 6. A comparison with the simple carbene cyclohexylidene, **32**, suggests that net stabilization of **18a** is quite large. Relative to the parent cyclobutylidene **19**, **18a** is stabilized by an additional 7.5 kcal/mol. While this additional trimethylsilyl group stabilization is substantial, it is not as large as that calculated for the carbocation **6**, where additional TMS stabilization of **6** relative to the cyclobutyl cation amounts to 22.6 kcal/mol.

A second energy minimum, **18b**, has been located at various levels of theory. At the M062X/6-311+G** level, this carbene is also highly puckered, with a short C1−C3 bond distance (1.678 Å). As in **18a**, the C1−C2 bond in **18b** is quite short, while the C2−C3 bond is quite long. It therefore appears that some of the same stabilizing interactions occur in **18b** as in **18a** and **19**, but conformation **18b** is somewhat higher energy than **18a**. It is suggested that the higher energy of **18b** is due to the lack of the

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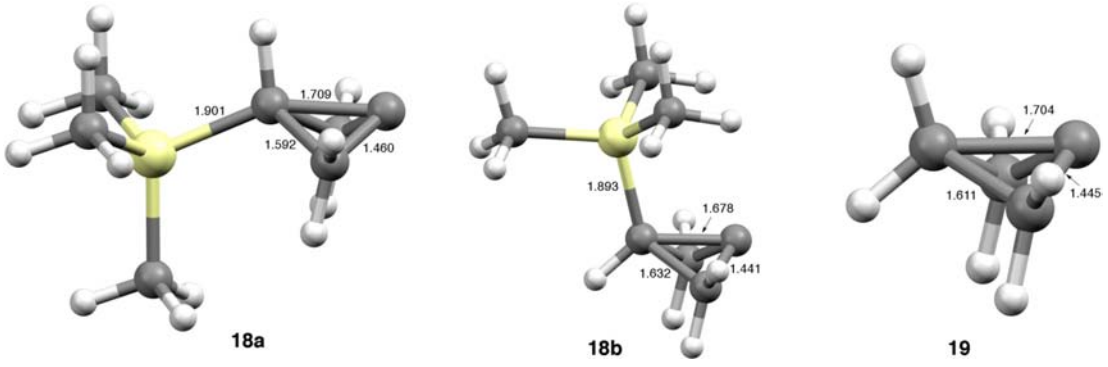


Figure 3. M062X/6-311+G** calculated structures of carbenes **18a**, **18b**, and **19**.

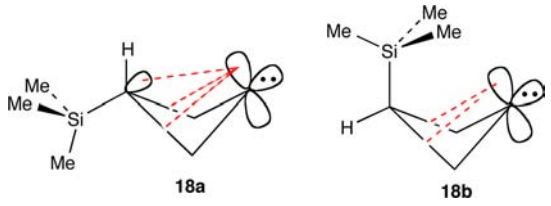


Figure 4. Stabilizing interactions in carbenes **18a** and **18b**.

additional rear lobe stabilization that is present in conformation **18a**.

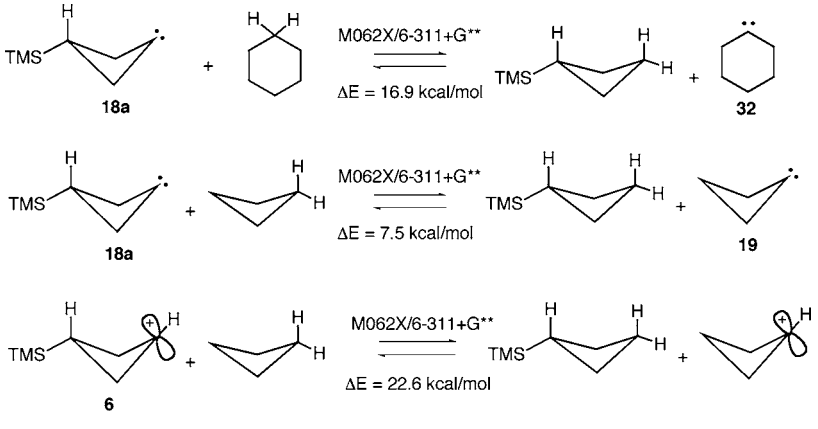
The energy diagram shown in Figure 5 implies that conformations **18a** and **18b** do not readily interconvert. The transition state **33** (Figure 6) for interconversion of these confomations lies 16.5 kcal/mol above **18a**. In this flattened structure, there is little or no interaction of the carbene vacant orbital with the σ-bonds of the cyclobutane or with the rear lobe of the Si−C σ-bond. This transition state gives an approximation of the net stabilization of **18a** by interaction of the carbene center with the cyclobutane σ bonds and the rear lobe of the Si−C orbital.

The transition state for hydrogen migration in **18a** to give the bicyclobutane **24** has also been located. This transition state **34** lies 10.4 kcal/mol above **18a**. This is a rather large barrier for hydrogen migration,[20] but it is still below the transition state for inversion of the carbene **18a** to **18b**. There is also a rather significant barrier for trimethylsilyl migration in **18b**, and the transition state **35** for such a migration lies 7.0 kcal/mol above **18b**. Finally, the transition state **36** for formation of the minor methylenecyclopropane **25** has been located, along with the two possible transition states, **37** and **38**, for formation of the trace amount of trimethylsilylcyclobutene **26**. These latter three transition states are all of significantly higher energy than that of **34**, which leads to the major product. Hence, these computational studies are qualitatively consistent with the experimental observation of bicyclobutane **24** as the major product from **18** via 1,3-hydrogen migration to the carbene center. The computational studies also suggest that **18a** is a highly stabilized carbene with relatively large barriers to intramolecular rearrangement. As such, it should have a relatively long lifetime prior to intramolecular rearrangement. Finally, it should be noted that these M062X/6-311+G** transition state energies of **36**−**38** (Figure 7) are quite high relative to carbene **18a** and may be overestimated by this computational method. B3LYP/6-311+G** relative energies are lower, but trends are analogous.[21]

Photolysis of Tosylhydrazone Salts in Methanol and Dimethylamine. To gain further insights into the behavior of carbene **18**, the tosylhydrazone salt **22** was irradiated in methanol solvent (Scheme 7). The major product of this photolysis was the *cis*-methyl ether **39**.[22] Careful examination of the product revealed that a trace (2%) of the bicyclobutane **24** was also formed. These products undoubtedly arise from photoextrusion of *p*-toluenesulfinate anion to generate diazocompound **23** as a transient intermediate. There are a number of mechanisms by which **23** could be converted to the product **39**. These mechanistic suggestions should address this stereospecificity of the reaction.

Photoinitiated loss of nitrogen from **23** could generate the carbene **18**, and the ether **39** would be the product of formal insertion into the OH bond of methanol. The reaction of

Scheme 6. Isodesmic Reactions of Carbene 18a and Cation 6



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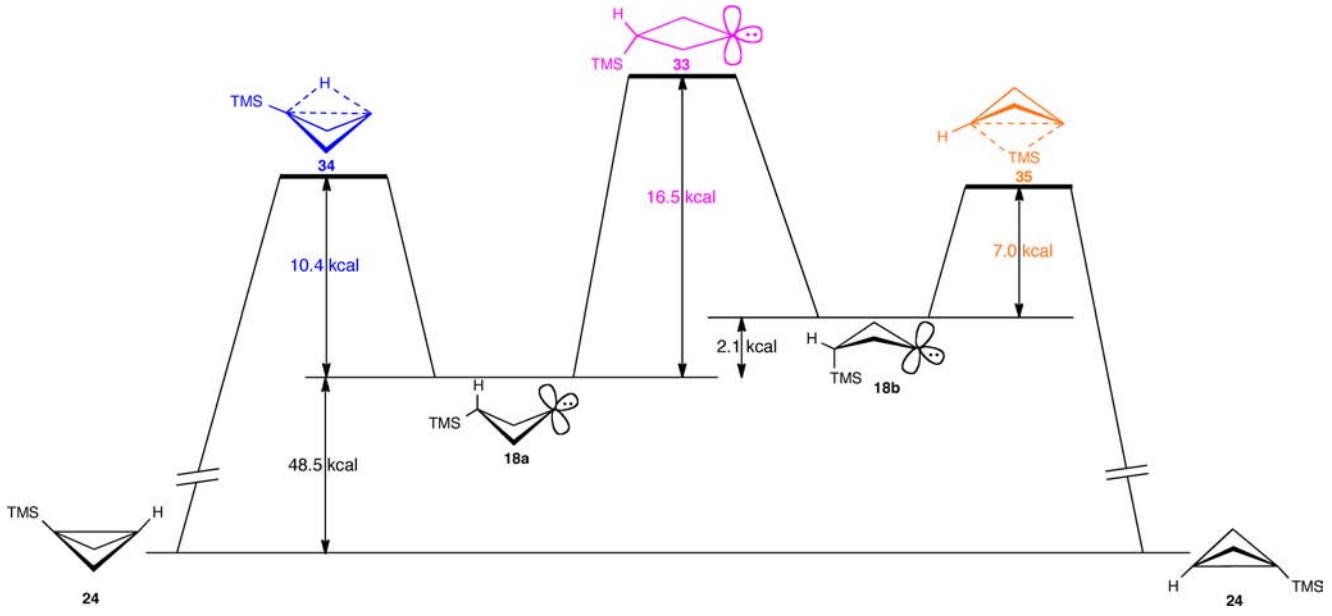

Figure 5. M062X/6-311+G** calculated energy diagram for conversion of carbenes **18a** and **18b** to trimethylsilylbicyclobutane **24**.

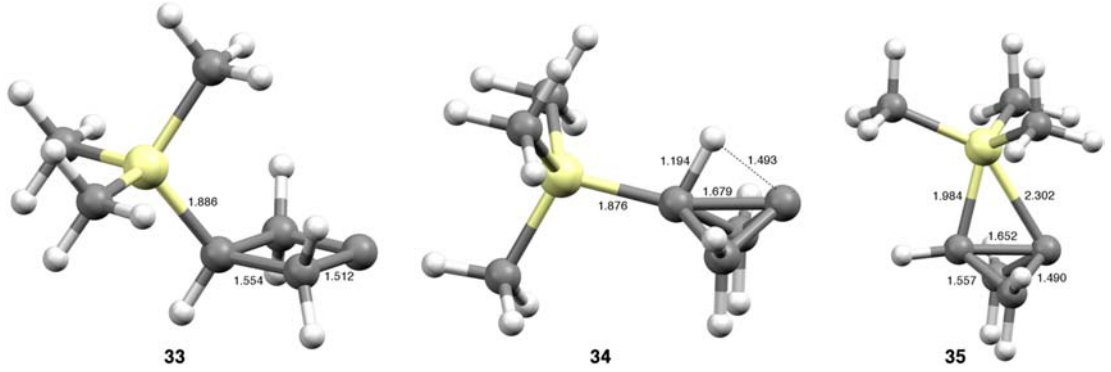

Figure 6. M062X/6-311+G** calculated structures of transition states **33**, **34**, and **35**.

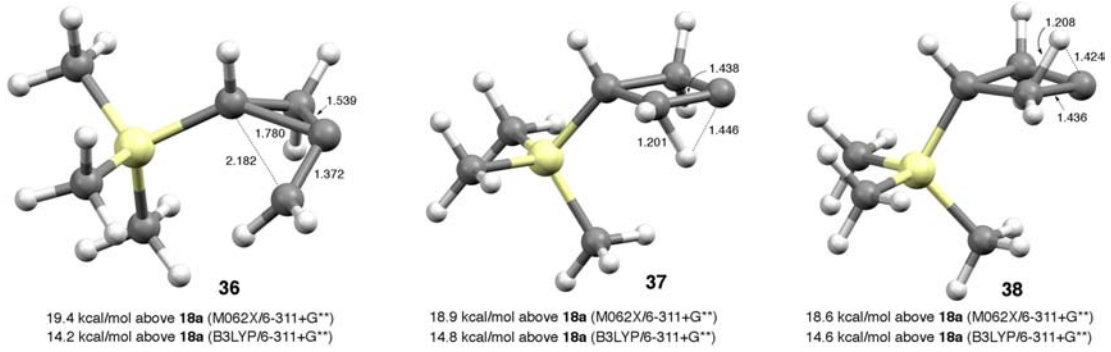

Figure 7. M062X/6-311+G** calculated structures of transition states **36**, **37**, and **38**.

carbenes with alcohols has been previously reviewed.[23] This formal insertion can occur by two stepwise processes or, theoretically, by a concerted process. Alternatively, studies have shown that diazocompounds can be protonated by alcohol solvent to give diazonium ions (path A), which can serve as precursors to ether products by way of carbocation intermediates.[23] This mechanism bypasses carbene intermediates. These potential mechanistic pathways are summarized for diazocompound **23** in Scheme 8.

To shed light on these mechanistic possibilities, the photolysis of **22** was carried out in an equimolar CH_3OH/CH_3OD mixture, and the extent of deuterium incorporation in the product was measured. The ratio of **39** to the mono deuterated analogue was 3.1 ± 0.1. This substantial isotope effect argues in favor of either protonation of diazocompound **23** (path A) or protonation of carbene **18** (path B). A precedent is the directly measured isotope effect for reaction of dimethoxycarbene, MeO−C−OMe, with CH_3OH and CH_3OD, where the isotope effect is 3.3.[24] Our isotope effect of 3.1 also argues against path D as the source of **39**

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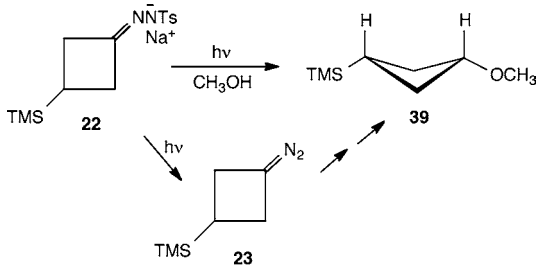
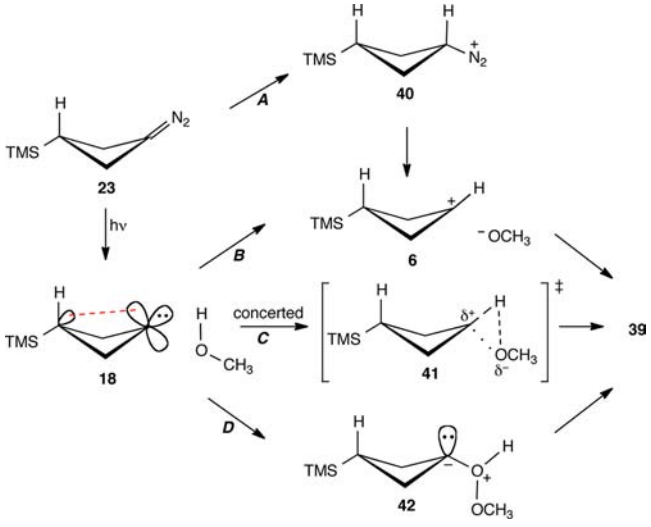
Scheme 7. Photochemical Reaction of Tosylhydrazone Salt 22 in Methanol



Scheme 8. Potential Mechanisms for Formation of Ether 39 from Diazocompound 23

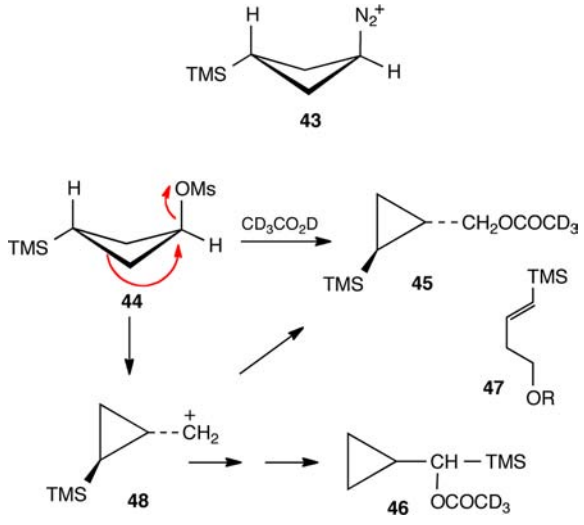


because this mechanism, which involves no OH/OD bond breaking in the product determining step, predicts essentially no isotope effect. Along these lines, the OH insertion reaction of phenylcarbene, Ph−C−H, with CH_3OH/CH_3OD, which probably proceeds by path D, gives a very small isotope effect.[25] The nonlinear transition state involved in path C should also result in a relatively small isotope effect.[26]

The stereochemistry of ether **39** is consistent with the intermediacy of carbocation **6**. Our previous studies[5] under solvolytic conditions have shown that the 3-trimethylsilylcyclobutyl cation **6** captures nucleophile from the rear of this delocalized cation to give exclusive *cis*-product. The ion-pair **6** is therefore an attractive possibility in the photolysis of **22**. A choice between path A (diazonium ion) and path B (carbene protonation) is more problematic. Here, we rely on some of our previous data to argue in favor of mechanism B. If the diazocompound **23** were to undergo protonation, there is no apparent reason why only diazonium ion **40** would be formed. Some of the isomeric diazonium ion **43** should also be formed. We have previously studied solvolytic ionization of the analogous mesylate **44** (Scheme 9), and this leads to exclusively rearranged products **45**−**47** in the cyclopropylcarbinyl-homoallylic carbocation manifold.[6] If diazonium ion **43** were formed, then loss of nitrogen should result in analogous rearranged products. Because no rearranged methyl ethers are formed when **22** is irradiated in methanol, diazonium ion **43** is not involved. Hence, it is unlikely that the isomeric diazonium ion **40** is involved.

It is now suggested that carbene **18** has some nucleophilic character due to the rear lobe interaction of the carbene vacant

Scheme 9. Solvolytic Reaction of *trans*-Mesylate 44 in CD_3CO_2D



orbital with the C−Si bond as well as the C2−C3 sigma bonds. Hence, an interaction of **18** with methanol results in initial proton transfer to the filled carbene orbital. Subsequent ion-pair capture of methoxide from the rear of delocalized cation **6** gives the observed stereochemistry as shown in Scheme 8.

To carry out the reaction under conditions where protonation of diazocompound **23** was improbable, dimethylamine was used as solvent. Because of the low solubility of the sodium salt **22** in this solvent, the more soluble lithium salt **49** was irradiated in neat dimethylamine. The major product of this reaction was the amine **50**, which was also formed in a stereospecific fashion. Also formed was about 20% of a formal carbene dimer **51**. It is highly unlikely that the insertion product **50** arises from protonation of the diazocompound **23** by the dimethylamine. Stepwise protonation of carbene **18** by dimethylamine to give an ion pair is also unlikely.

The product **50** speaks to the stereochemistry of reaction of carbenes with nucleophiles.[27] The stereospecificity of the reaction suggests that dimethylamine approaches carbene **18** from the back of a delocalized carbene, as shown in Scheme 10, and further supports the proposed delocalized bonding in the carbene **18**. The overall reaction could be a concerted insertion process proceeding through transition state **52**. A stepwise process analogous to path D of Scheme 8, involving an intermediate **53** analogous to Platz's pyridinium ylids,[28] cannot be eliminated. In other words, the nucleophilic carbene **18** in methanol has become an electrophilic carbene in dimethylamine; that is, **18** is ambiphilic. To support the suggestion that carbene **18** can become electrophilic, the salt **49** was irradiated in a pyrrolidine/diethylamine mixture. This led to a mixture of amine products **54** and **55** where carbene **18** reacted preferentially with the more nucleophilic pyrrolidine[29] over diethylamine by a factor of 3.0.

■ CONCLUSIONS

The carbene **18** rearranges to give the bicyclobutane **24** as well as smaller amounts of the methylenecyclopropane **25** and cyclobutene **26**. A labeling study shows that the bicyclobutane product is exclusively derived from trans-annular 1,3-hydrogen migration to the carbene center. Computationally, there are two isomeric carbenes, **18a** and **18b**, with the more stable form **18a** lying in an

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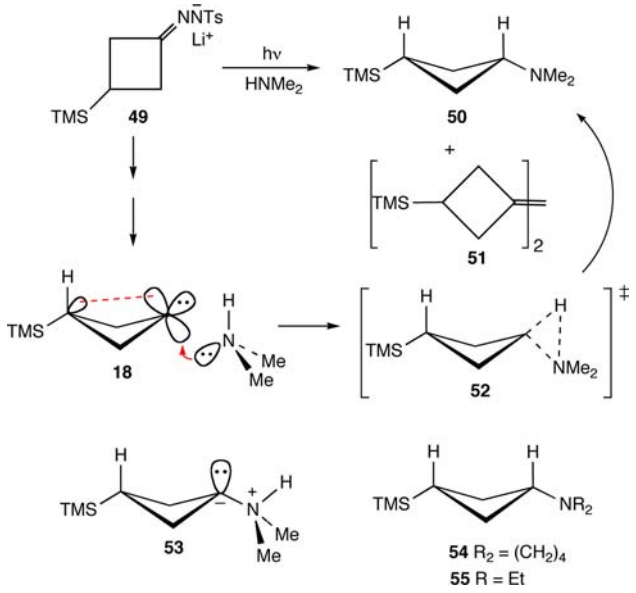
Scheme 10. Photochemical Reaction of Tosylhydrazone Salt 49 in Dimethylamine



energy well such that there is a relatively large barrier to interconversion of these isomeric carbenes. The carbene **18a** is highly stabilized by the σ-bent bonds of the cyclobutane as well as a significant rear lobe interaction with the trimethylsilyl group. There are also relatively large barriers to intramolecular rearrangement. Carbene **18** is effectively trapped by methanol to give *cis*-3-trimethylsilyl-1-methoxycyclobutane, via the highly stabilized 3-trimethylsilylcyclobutyl cation. Dimethylamine also effectively traps carbene **18** to give *cis*-trimethylsilyl-1-dimethylaminocyclobutane. The stereochemistry of this product suggests preferential approach of dimethylamine from the back of the rear lobe stabilized carbene **18**.

EXPERIMENTAL SECTION

General. NMR spectra were recorded on a Varian DirectDrive 600 MHz spectrometer. HRMS measurements were carried out using a Bruker MicroTOF-II spectrometer (electrospray ionization source with time-of-flight mass analyzer).

Preparation of Tosylhydrazone 21. Tosylhydrazine (340 mg; 1.826 mmol) was placed in a flask and stirred as 255 mg (1.792 mmol) of 3-trimethylsilylcyclobutanone in about 2 mL of methanol was rapidly added. The mixture was stirred, and the tosylhydrazine dissolved in a few minutes. The tosylhydrazone **21** crystallized after about 40 min. After 9 h at room temperature, most of the methanol was removed using a rotary evaporator, and the solid residue was slurried with about 3 mL of cold 50% ether in pentane. The solvent was then decanted, and the residue was dried under aspirator vacuum to give 540 mg (97% yield) of **21**, mp 121−122 °C (dec). ^{1}H NMR of **21** ($CDCl_3$): δ 7.82 (d, J = 8.3 Hz, 2H), 7.44 (br s, 1H), 7.31 (d, J = 8.3 Hz, 2H), 2.99 (m, 1H), 2.86 (m, 1H), 2.65 (m, 1H), 2.50 (m, 1H), 2.42 (s, 3H), 1.56 (t of t, J = 10.8, 7.4 Hz, 1H), −0.08 (s, 9H). ^{13}C NMR of **21** ($CDCl_3$): δ 1.60.4, 144.1, 135.4, 129.7, 127.9, 35.0, 32.6, 21.6, 13.2, −4.0. HRMS (ESI) (MH^+) calculated for $C_{14}H_{23}N_2O_2SSi$ 311.1244, found 311.1271.

Preparation and Pyrolysis of Tosylhydrazone Salt 22. Tosylhydrazone **21** (557 mg, 1.797 mmol) was placed in a 25 mL flask, and 3.5 mL of 0.579 M $NaOCH_3$ in methanol (2.026 mmol) was added. After 20 min, the methanol solvent was removed using a rotary evaporator, and the pressure was maintained at 15 mm for 4 h. The last traces of methanol were removed using a vacuum pump at 0.2 mm for 3 h. The solid tosylhydrazone salt **22** was broken with a spatula, and the flask containing the dry salt was then fitted with a short path distillation head and a receiver flask. The pressure was maintained at 0.2 mm as the flask containing the salt was placed in an oil bath, and the temperature of the oil bath was gradually raised to 80 °C. The receiver flask was then cooled in a dry ice−acetone bath as the temperature of the oil was then raised gradually to 160 °C. At about 140 °C, decomposition occurred as evidenced by a pressure increase. The products of the pyrolysis collected in the cold receiver flask. The yield of distillate was 116 mg (51% yield). The products **24**,[30] **25**,[31] and **26**[32] were identified by NMR spectral comparisons with authentic samples.

Preparation of Labeled 3-Trimethylsilylcyclobutanone 28. A solution of 220 mg of $Co_2(CO)_8$ in 75 mL of pentane in a three-neck flask was cooled in a water bath to about 10 °C under an argon atmosphere. ^{13}C depleted CO (99.95% ^{12}C; Cambridge Isotope Laboratories) from a lecture bottle was slowly bubbled into the stirred mixture over a 2 h period. The volume of ^{12}CO used was about 2 L. At the end of this period, 1.0 g of distilled $TMSCHN_2$ (Caution: safety hazard)[33] was added to the solution. ^{12}CO was again periodically bubbled through the mixture over a 3 h period at 10 °C. A total of about 3.5 g of ^{12}CO was used for the entire procedure.

A Vigreux column was attached to the reaction flask, along with a receiver flask that was cooled in a dry ice/acetone bath. The pressure was gradually lowered to 320 mm, and the volatile material was condensed in the receiver flask. The pot was heated using an oil bath to 40−50 °C as the pentane and trimethylsilylketene distilled. The pressure was gradually reduced to 15 mm, and the reaction flask was distilled to dryness as the receiver flask was thoroughly cooled in the dry ice bath.

A solution of diazomethane in ether was prepared from Diazald (6.0 g) in 60 mL of ether by dropwise addition to 3.0 g of KOH in 4.8 mL of water and 17 mL of carbitol and 10 mL of ether. The diazomethane/ether solution was cooled in a dry ice/acetone bath, and the solution of trimethylsilylketene prepared above in pentane was added in a single portion to the cold diazomethane solution. The solution was allowed to gradually warm to room temperature. After about 30 min at room temperature, most of the solvents were removed using a rotary evaporator. The residue was transferred to a 10 mL flask fitted with a short path distillation head. The products were distilled at 15 mm pressure. The yield of the distilled mixture of **28** and **29** was 756 mg (42% yield).

The mixture of ketones **28** and **29** was placed in a flask with about 0.5 mL of ether. Water (20 mL) was then added followed by 41 mg of K_2CO_3. The mixture was then stirred vigorously for 2.5 h and then transferred to a separatory funnel using 25 mL of pentane. The pentane phase was separated, dried over Na_2SO_4, decanted from the drying agent, and the pentane was removed using a rotary evaporator. The residue was distilled to give 335 mg of pure **28**, bp 70 °C (15 mm). The ^{1}H NMR spectrum of **28** was identical to that of **20**. The ^{13}C NMR spectrum (Supporting Information) showed no carbonyl signal at 208.3 ppm.

Preparation and Pyrolysis of Labeled Tosylhydrazone Salt 30. The procedure for preparation of the tosylhydrazone salt **30** from ketone **28** was identical to that described above to prepare the unlabeled salt **22**. The pyrolysis procedure was also identical. The ^{13}C NMR spectrum of the pyrolysis product is shown in Figure 2. The spectrum was recorded without a NOE by turning the decoupler off except during signal acquisition (dm = "nny" using the Varian simple 2-pulse sequence). A relaxation delay (d1) of 90 s between pulses was also included to ensure complete relaxation of all ^{13}C signals.

Photolysis of Tosylhydrazone Salt 22 in Methanol. Tosylhydrazone **21** (42.3 mg; 0.136 mmol) was placed in a vial, and 250 μL of 0.579 M $NaOCH_3$ (0.145 mmol) in CH_3OH was added via syringe. The mixture was stirred with a micro stir bar to dissolve the tosylhydrazone **21**, and an additional 1.75 mL of methanol was added. The methanol solution was placed in a 5 mm NMR tube, and the air-cooled tube was irradiated with a Hanovia 450 W source for 15 min. The solution was then transferred to a vial, and 5 mL of water was added followed by 1.6 mL of C_6D_6. The mixture was stirred to extract the product into the C_6D_6. The aqueous phase was separated, and the C_6D_6 phase was then washed with two additional portions of water and then dried over Na_2SO_4. NMR spectra of the products were determined in the C_6D_6 extract. The 1-trimethylsilylbicyclobutane **24** (2%) was identified by spectral comparison with an authentic sample. ^{1}H NMR of **39** (C_6D_6): δ

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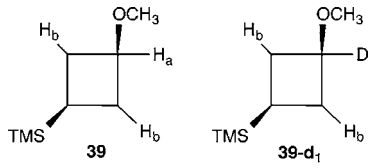
3.73 (t of t, J = 8.0, 6.9 Hz, 1H), 3.04 (s, 3H), 2.90 (m, 2H), 1.77 (m, 2H), 0.90 (t of t, J = 11.7, 8.1 Hz, 1H), −0.06 (s, 9 H). ^{13}C NMR of **39** (C_6D_6): δ 74.8, 54.5, 31.7, 12.4, −3.3. HRMS (EI) (M^+) calculated for $C_8H_{18}OSi$ 158.1121, found 158.1149.

Photolysis of Tosylhydrazone Salt 22 in CH_3OH/CH_3OD. A mixture of 4.003 g of CH_3OH and 4.132 g of 99.5% CH_3OD was prepared. The dry tosylhydrazone salt **22** was prepared as described above from 42.5 mg of **21** and 250 μL of 0.574 M $NaOCH_3$ in methanol. The salt **22** (20 mg) was placed in a vial, and 1.1 mL of the CH_3OH/CH_3OD mixture was added. The mixture was transferred to an NMR tube under argon, and the air-cooled tube was irradiated with a Hanovia 450 W source for 22 min. The contents of the tube were poured into a vial containing 3 mL of water, and 1 mL of C_6D_6 was then added. The mixture was stirred, and the aqueous phase was separated. The C_6D_6 extract was washed with an additional three portions of water and then dried over Na_2SO_4. The ratio of the two ether products **39** and **39-d_1** was determined by ^{1}H NMR from the relative areas of H_a (3.73 ppm) and H_b (1.77 ppm). The ratio of **39**:**39-d_1** was 3.1 ± 0.1 in duplicate runs. Details are given as Supporting Information.



Photolysis of Tosylhydrazone Salt 49 in Dimethylamine. Tosylhydrazone **21** (49.4 mg; 0.159 mmol) was placed in a small vial, and 324 μL of 0.516 M $LiOCH_3$ in methanol (0.167 mmol) was added. After the mixture was stirred for a few minutes at room temperature, the methanol solvent was removed using a rotary evaporator. Evacuation at 15 mm pressure was continued for 10 h, and, during this time, the salt **49** solidified. The dry salt **49** was crushed with a spatula, and 7.0 mg was placed in an NMR tube under argon. The tube was cooled in an ice/acetone bath, and 1.25 mL of gaseous dimethylamine was condensed into the cold tube. The tube was sealed under argon and shaken to dissolve the salt **49**. The air-cooled tube was then irradiated with a Hanovia 450 W source for 5 min. The tube was cooled in ice, opened, and the contents were poured into 4 mL of ice water. The mixture was extracted with 1.2 mL of C_6D_6, and the aqueous phase was discarded. The C_6D_6 phase was then washed with two additional portions of water and then extracted with 2 mL of 1% aqueous HCl. The acidic extract was separated, neutralized with solid Na_2CO_3, and re-extracted with C_6D_6. The C_6D_6 phase was dried over Na_2SO_4 and analyzed by NMR. ^{1}H NMR of **50** (C_6D_6): δ 2.60 (t of t, J = 8.6, 7.0 Hz, 1H), 2.00 (s, 6H), 1.93 (m, 2H), 1.72 (m, 2H), 1.15 (t of t, J = 11.5, 8.2 Hz, 1H), −0.02 (s, 9H). ^{13}C NMR of **50** (C_6D_6): δ 62.8, 41.6, 29.3, 14.2, −3.3. HRMS (ESI) (MH^+) calculated for $C_9H_{22}NSi$ 172.1516, found 172.1505.

Preparation of Amines 54 and 55. Authentic samples of amines **54** and **55** were prepared in the same fashion as amine **50** by photolysis of tosylhydrazone salt **49** in pyrrolidine and diethylamine as solvent, respectively, as previously described.

^{1}H NMR of **54** (C_6D_6): δ (2.91, t of t, J = 8.6, 7.0 Hz, 1H), 2.34 (m, 4H), 1.98 (m, 2H), 1.85 (m, 2H), 1.61 (m, 4H), 1.27 (t of t, J = 11.5, 8.4 Hz, 1H), 0.00 (s, 9H). ^{13}C NMR of **54** (C_6D_6): δ 60.4, 50.7, 29.4, 24.0, 15.9, −3.2. HRMS (ESI) (MH^+) calculated for $C_{11}H_{24}NSi$ 198.1673, found 198.1695.

^{1}H NMR of **55** (C_6D_6): δ 3.07 (t of t, J = 9.0, 6.9 Hz, 1H), 2.43 (q, J = 7.1 Hz, 4H), 1.96 (m, 2H), 1.74 (m, 2H), 1.14 (t of t, J = 11.6, 8.1 Hz, 1H), 0.93 (t, J = 7.1 Hz, 6H), −0.01 (s, 9H). ^{13}C NMR of **55** (C_6D_6): δ 58.8, 42.7, 30.3, 15.3, 11.7, −3.1. HRMS (ESI) (MH^+) calculated for $C_{11}H_{26}NSi$ 200.1829, found 200.1855.

Photolysis of Tosylhydrazone Salt 48 in Pyrrolidine/Diethylamine. A mixture of pyrrolidine (930 mg) and Et_2NH (953 mg) was prepared, and 6.7 mg of the dry salt **49** was dissolved in 954 mg of this mixture. The solution was placed in a 5 mm NMR tube under argon, and the air-cooled tube was irradiated with a Hanovia 450 W source for 10 min. The tube was opened, and the contents were poured into 4 mL of water. The mixture was extracted with 1.2 mL of C_6D_6, and the aqueous phase was discarded. The C_6D_6 phase was then extracted with three additional portions of water. The C_6D_6 phase was then extracted with 1.2 mL of 0.5 M HCl, and the aqueous extract was then separated. Solid K_2CO_3 was then carefully added to the aqueous extract until the mixture became basic. The mixture was then re-extracted with C_6D_6, and the C_6D_6 phase was dried over Na_2SO_4 and analyzed by ^{1}H NMR. The ratio of the two products **54** and **55** was determined by ^{1}H NMR from the relative areas of the multiplets at 3.07 ppm (**55**) and 3.91 ppm (**54**). The ratio of **54**:**55** was 3.0. Details are given as Supporting Information.

Computational Studies. Ab initio molecular orbital calculations were performed using the Gaussian 09 series of programs.[18] 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 18, the M062X/6-311+G* calculated structures, energies, and Cartesian coordinates of **6**, **18a**, **18b**, **19**, **32**, **32**, **33**, **34**, **35**, **36**, **37**, and **38**, ^{1}H and ^{13}C NMR spectra of **21**, **28**, **39**, **50**, **54**, and **55** as well as the ^{1}H and ^{13}C NMR spectra of the products of vacuum pyrolysis of **22**, the products of photolysis of **22** in CH_3OH/CH_3OD, and the products of photolysis of **48** in pyrrolidine/diethylamine. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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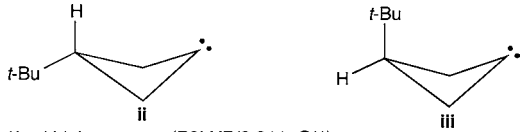
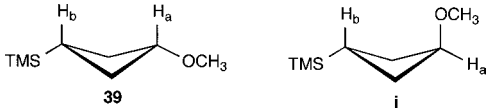
(21) A reviewer has suggested that steric effects could account for the energy difference between **18a** and **18b** as well as the observed hydrogen migration because a sterically locked **18a** cannot migrate the TMS group. We have now carried out computational studies on the *t*-butyl analogues of **18a** and **18b** (**ii** and **iii**). These computational studies indicate that steric effects are not very important because **iii** is actually of lower energy than **ii**. The lower energy of **18a** is therefore an electronic effect and not a steric effect.



1.2 kcal/mol higher energy (B3LYP/6-311+G**)
3.3 kcal/mol higher energy (M062X/6-311+G**)
Lower energy

(22) The stereochemistry of **39** is based on coupling information. J_{ab} = 0 Hz in the *cis*-isomer **39**, while *trans*-isomer **i** shows J_{ab} = 1.3 Hz.



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