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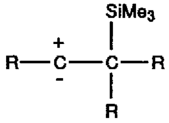
β-SILYL CARBENES

Xavier Creary * and You-Xiong Wang
Department of Chemistry
University of Notre Dame, Notre Dame, IN 46556

Summary: β-Trimethylsilyl carbenes rearrange to form alkenes by facile migration of the β-silyl group. In the norbornyl system, β-hydrogen migration can also compete with silyl migration.

The use of silicon based chemistry in Organic synthesis has proliferated during the past two decades.[1] The effect of silicon on reactive intermediates has therefore been of much interest. Silicon in the β-position is a very effective carbocation stabilizing group.[2] β-Silicon containing groups are also effective radical stabilizing groups.[3] However, in contrast to α-silyl carbenes,[4] not much is known about the effect of β-silicon containing groups on carbenic centers. In this report we describe the generation of β-trimethylsilyl carbenes of general type **1**, and the fate of these reactive intermediates in terms of intramolecular rearrangement processes.



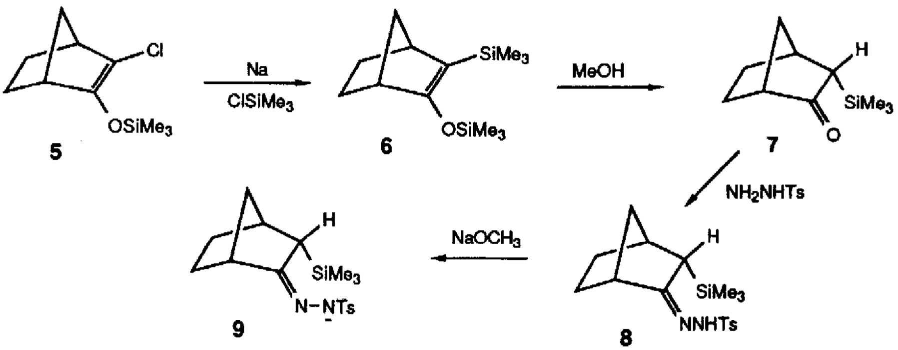
$R-\overset{+}{\underset{-}{C}}-\overset{SiMe_3}{\underset{R}{C}}-R$

1

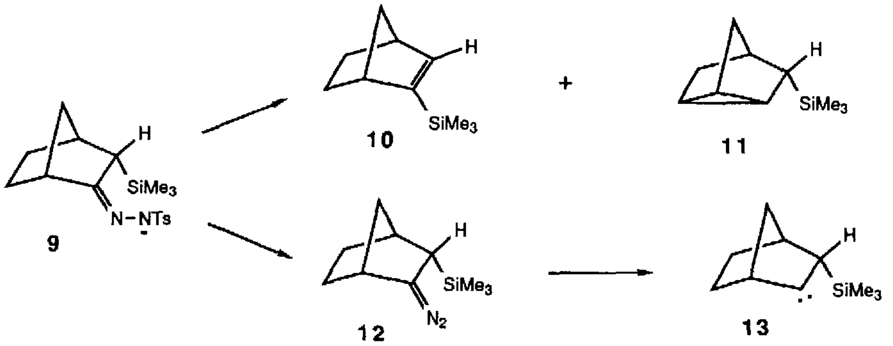
2 **3**

4

For initial studies, we chose to investigate the norbornyl system. The chemistry of the carbene **2** had been previously described.[5] The sole product derived from this carbene is nortricyclane, **3**, a product of 1,3-C-H insertion. The product of 1,2-hydrogen migration, which is usually observed from carbenes with hydrogen in the β-position,[6] was not observed. We therefore wanted to generate the carbene **4** in order to evaluate the propensity for silicon to migrate to the carbenic center as opposed to the tendency for this carbene to undergo 1,3-C-H insertion.



The precursor to **4** was prepared from the silyl enol ether **5**.[7a] Dehalogenation with sodium sand in the presence of chlorotrimethylsilane gave **6** which was O-desilylated (10^{-3} M CF_3CO_2H in MeOH) to give the β-trimethylsilyl ketone **7**. The stereochemistry of **7** was based on methanolyses of analogs of **6** which led to endo-3-substituted norcamphor derivatives.[7b] Reaction of **7** with tosylhydrazine in methanol (10^{-2} M in TsOH) gave the tosylhydrazone **8** along with norcamphor tosylhydrazone. This desilylated material could be separated from **8** by recrystallization. Conversion to the sodium salt **9** and pyrolysis under vacuum gave the alkene **10** and the tricyclic derivative **11** in a 2.6 to 1 ratio (74% yield). The diazocompound **12** was not isolated and presumably the carbene **13** is the source of **10** and **11**.



The presence of the alkene **10** as the major product suggests that the trimethylsilyl group migrates very effectively to the carbenic center in **13**. Indeed, this result suggests that silyl migration occurs even more readily than the very facile 1,3-C-H insertion process. This discussion presumes that the trimethylsilyl group is indeed the migrating group in the formation of **10** and that migration of the exo-hydrogen in **13** remains slow relative to 1,3-C-H insertion as is the case in the norbornyl carbene **2**. In order to test these assumptions, we have converted the labeled norcamphor, **14**,[8] to the corresponding silylated tosylhydrazone salt **16**. Ketone **14** was also converted to the silylated derivative **19**. This served as an authentic sample of the product of trimethylsilyl migration in the carbene derived from **16**.

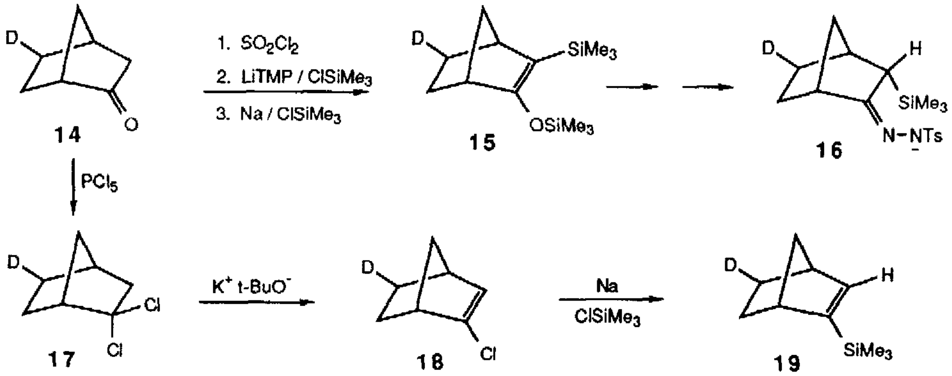


Figure 1 shows the ^{13}C NMR spectrum of the alkene pyrolysis product derived from **16** (after separation of the tricyclic C-H insertion product **22**). The spectrum of an authentic sample of **19** is shown in Figure 2. Figure 1 shows that both **19** and **21** are produced in comparable amounts in pyrolysis of **16**. Therefore our original presumption was not correct. Both the endo trimethylsilyl group *and the exo hydrogen atom* migrate to the carbenic center in **20**. The exo hydrogen in **20** therefore behaves quite differently from the analogous hydrogen in **2**. To account for this differing behavior we suggest that the trimethylsilyl group in **20** (or in **13**) makes the exo-hydrogen somewhat hydridic and hence more prone to migrate than the exo-hydrogen in the unsubstituted carbene **2**. Since the migration process begins with overlap of the migrating group with the vacant carbene 2p orbital,[9] a hydridic hydrogen should migrate readily to a carbenic center.

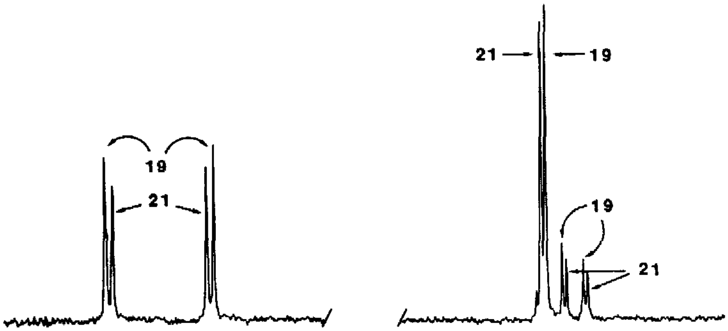


Figure 1. ^{13}C NMR spectrum of alkenes formed on pyrolysis of **16**.

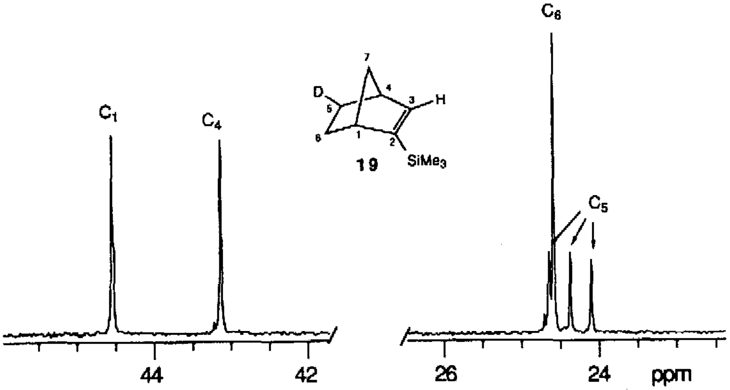
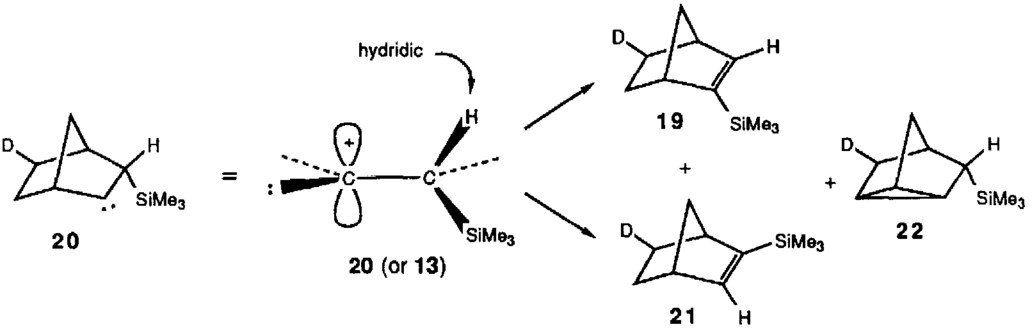
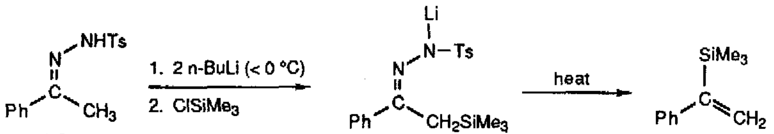


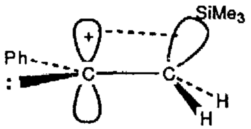
Figure 2. ^{13}C NMR spectrum of **19**.



Attention was next focused on a β-silyl containing system that was less constrained than the rigid norbornyl system. The tosylhydrazone salt **24** could not be produced in a straightforward fashion. All attempts to prepare the tosylhydrazone derivative of α-trimethylsilyl acetophenone led to desilylation and subsequent formation of **23**. However, treatment of **23** with 2 equivalents of n-butyllithium (-40 to 0 °C) followed by addition of 1 equivalent of chlorotrimethylsilane led to formation of the lithium salt **24**. When the solvent was removed and the dry salt was pyrolyzed under vacuum, the silylated alkene **25** was the only product formed. *The product **25** is produced only on pyrolysis.* *When the dry salt was quenched with water before pyrolysis, no trace of styrene or the alkene **25** was* detected in an ether extract. This rules out α-lithiostyrene, a product of the Shapiro reaction,[10] as the source of **25**. Apparently loss of Ts^- and N_2 from the dianion derived from **23** are slow enough to permit silylation to occur.



23 **24** **25**



26

This study indicates that trimethylsilyl migration to the carbenic center in **26** predominates over hydrogen migration. This finding contrasts with the behavior of **13** (or **20**) where both groups migrate at comparable rates. We suggest that in the unconstrained carbene **26**, overlap of the vacant carbene orbital with the C-Si σ bond is very effective (as in the case of β-silyl carbocations). The trimethylsilyl group therefore migrates in preference to the hydridic hydrogen atoms since the alkene double bond is already partially established by the effective carbon 2p-silicon overlap.

In conclusion, the β-trimethylsilyl group appears to be a very efficient migrating group to carbenic centers. The β-trimethylsilyl group also appears to enhance the migratory aptitude of the exo-hydrogen atom in norbornyl carbenes so that this hydrogen migration can compete with the very facile 1,3-insertion reaction. This is presumably due to an increase in hydridic character of the migrating hydrogen due to β-trimethylsilyl substitution.

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