

Silyl-Substituted Carbenes

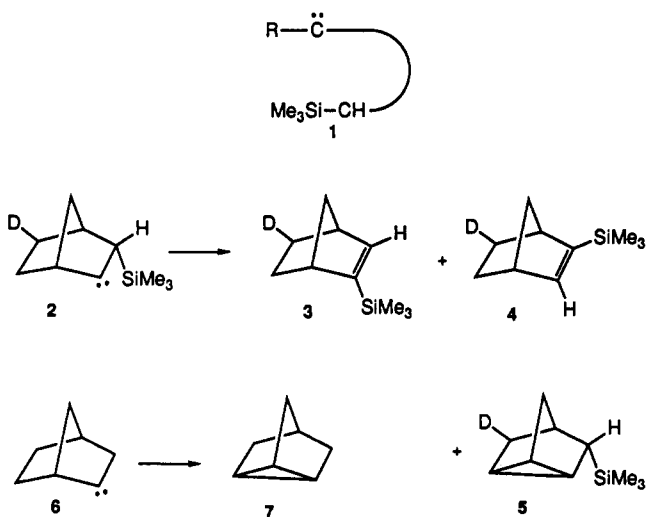
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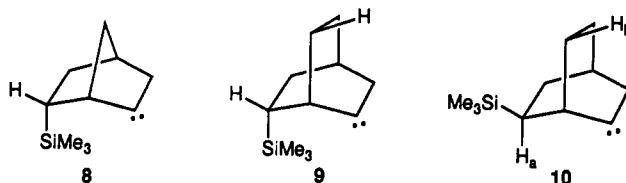
Summary: Generation of *endo*-6-(trimethylsilyl)bicyclo[2.2.1]hept-2-yl carbene and *syn*-6-(trimethylsilyl)bicyclo[2.2.2]oct-2-yl carbene leads to preferential 1,3-migration of the trimethylsilyl group to the carbenic center, while *anti*-6-(trimethylsilyl)bicyclo[2.2.2]oct-2-yl carbene gives preferential migration of the trimethylsilyl-activated hydrogen atom.

The effects of adjacent silicon on carbocation¹ and free-radical² intermediates have been a topic of considerable attention. However, in contrast to α -silyl carbenes,³ not much is known about the effects of silicon further removed from carbenic centers as in 1. We have recently observed that the β -SiMe₃-substituted carbene 2 gives mainly the alkenes 3 and 4, along with a smaller amount of the tricyclic



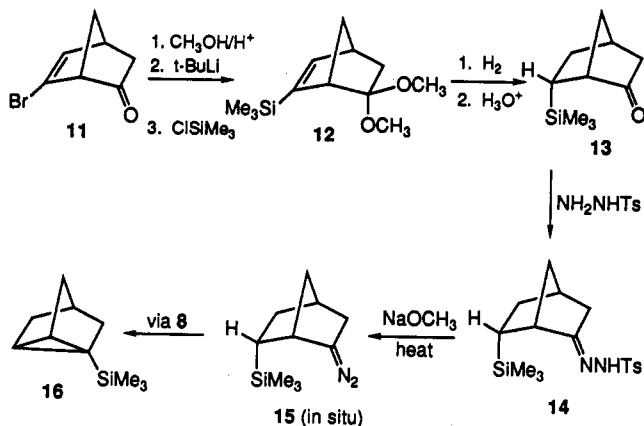
product 5.⁴ Labeling studies were used to determine that the alkene product is derived from 1,2-SiMe₃ migration as well as 1,2-H migration. This study suggests that the SiMe₃ group of 2 increases the migratory aptitude of the exo-hydrogen relative to the exo-hydrogen in the unsubstituted carbene 6. The behavior of 2 thus contrasts with that of the unsubstituted 2-norbornyl carbene 6, which gives exclusively nortricyclane, 7, a product of 1,3-insertion into the neighboring endo-CH bond.⁵ In order to develop a better understanding of long-range and short-range

interactions of silicon with carbenic centers we have carried out further studies on bicyclic carbenes of type 8-10. In



carbenes 8 and 9, SiMe₃ migration is pitted vs potential hydrogen migration pathways, while in 10, the migratory aptitudes of H_a (silicon perturbed) and H_b can be determined.

The precursors to carbene 8 were prepared starting with the known bromo ketone 11.⁶ Ketalization, lithium-halogen exchange, and silylation gave the unsaturated bicyclic ketal 12. Hydrogenation and hydrolysis gave the ketone 13, which was converted to the tosylhydrazone 14.



The tosylhydrazone 14 was converted to the sodium salt, and the dry sodium salt was pyrolyzed under vacuum. The sole product formed was (trimethylsilyl)nortricyclane, 16. Presumably, the carbene 8 is an intermediate in the pyrolysis leading to 16. The *endo*-6-(trimethylsilyl) group of 8 therefore appears to be a very effective migrating group in a 1,3 sense. By way of contrast, a methyl group in the endo-6-position position of a 2-norbornyl carbene shows no propensity to migrate to the carbenic center.⁷

Attention was next turned to the bicyclo[2.2.2]octyl carbene 9 where 1,3-silicon migration could be more directly compared with 1,3-hydrogen migration. The ketone precursor to this carbene was prepared using methodology similar to that described by Vogel and Salomon.⁶ Addition of PhSeBr to bicyclo[2.2.2]oct-6-en-

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(1) See: Lambert, J. B.; Wang, G.-T.; Finzel, R. B.; Teramura, D. H. *J. Am. Chem. Soc.* 1987, 109, 7838 and references cited therein.

(2) (a) Kochi, J. K.; Kawamura, J. *J. Am. Chem. Soc.* 1972, 94, 648. (b) Sakurai, H.; Hosomi, A.; Kumada, J. *J. Org. Chem.* 1969, 34, 1764. (c) Creary, X.; Mehrsheikh-Mohammadi, M. E.; McDonald, S. *J. Org. Chem.* 1987, 52, 3254.

(3) (a) Chapman, O. L.; Chang, C.-C.; Kolc, J.; Jung, M. E.; Lowe, J. A.; Barton, J.; Tumey, M. L. *J. Am. Chem. Soc.* 1978, 98, 7844. (b) Chedekel, M. R.; Skoglund, M.; Kreeger, R. L.; Shechter, H. *J. Am. Chem. Soc.* 1978, 98, 7844.

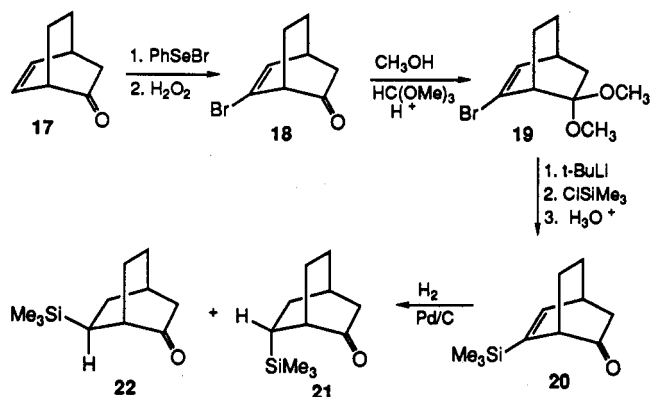
(4) Creary, X.; Wang, Y.-X. *Tetrahedron Lett.* 1989, 30, 2496.

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

(6) (a) Lal, K.; Salomon, R. G. *J. Org. Chem.* 1989, 54, 2628. See also: (b) Carrupt, P.-A.; Vogel, P. *Tetrahedron Lett.* 1982, 23, 2563.

(7) Freeman, P. K.; Hardy, T. A.; Balyeat, J. R.; Wescott, L. D., Jr. *J. Org. Chem.* 1977, 42, 3356.

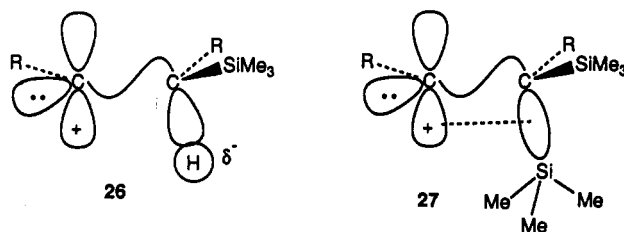
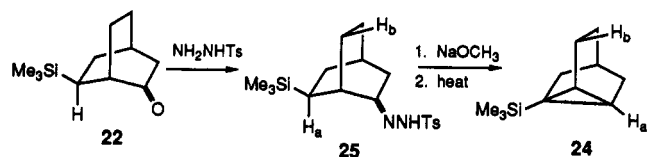
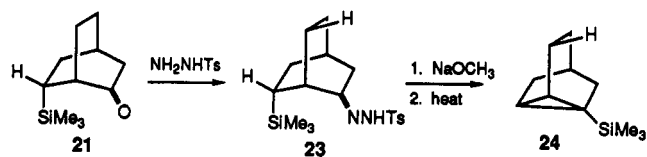
2-one,⁸ followed by selenoxide elimination, gave the unsaturated bromo ketone 18. Conversion to the silyl ketone 20 was accomplished as described below. Catalytic hydrogenation of 20 gave a mixture of 21 and 22, which were chromatographically separated. Conversion of 21



to the tosylhydrazone was followed by vacuum pyrolysis of the sodium salt of 23. The tricyclic derivative 24 was the only product formed. This indicates that the trimethylsilyl group of carbene 9 is much more prone to migrate to the carbenic center than the *syn*-7-hydrogen, which occupies the same position relative to the carbenic center as does the trimethylsilyl group.

The ketone 22 was also converted to the tosylhydrazone salt, and this salt was also vacuum pyrolyzed. The identical tricyclic product 24 was also formed. The silicon-perturbed hydrogen, H_a, has therefore migrated exclusively to the electron-deficient carbenic center in 10 despite the fact that H_b is similarly positioned with respect to the carbenic center. This preferential 1,3-migration of a "trimethylsilyl-activated" hydrogen atom is consistent with hydric character of H_a as shown in 26. Simultaneously, H_a is therefore more acidic as well as more hydric than H_b. Along these lines, long-range interactions of electron-deficient carbenic centers with silicon, as in 27, also account for the ease of trimethylsilyl migration in 9.

Finally, the question arises as to the involvement of actual carbenic intermediates 8–10, as opposed to excited



states of the corresponding diazocompounds.⁹ While we cannot rule out the possibility that rearrangement actually occurs in the excited state of diazocompounds, it should be kept in mind that these processes are thermally (rather than photochemically) initiated. Since the photochemical energy necessary to excite the diazocompounds is absent, a rearrangement involving excited states of diazocompounds is less probable. Studies are continuing on the effect of groups other than silicon and their effect on migratory aptitudes in carbenic systems.

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Supplementary Material Available: Experimental procedures and ¹H and ¹³C NMR spectra for the compounds described (27 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(8) Freeman, P. K.; Balls, D. M.; Brown, D. J. *J. Org. Chem.* 1968, 33, 2211.

(9) For recent examples of rearrangement occurring via excited states of diazocompounds and leading references, see: (a) Celebi, S.; Leyva, S.; Modarelli, D. A.; Platz, M. S. *J. Am. Chem. Soc.* 1993, 115, 8613. (b) White, W. R., III; Platz, M. S. *J. Org. Chem.* 1992, 57, 2841. (c) Modarelli, D. A.; Morgan, S.; Platz, M. S. *J. Am. Chem. Soc.* 1992, 114, 7034.