Pergamon

Tetrahedron Letters, Vol. 37, No. 5, pp. 579-582, 1996

0040-4039/96 $15.00 + 0.00

0040-4039(95)02266-X

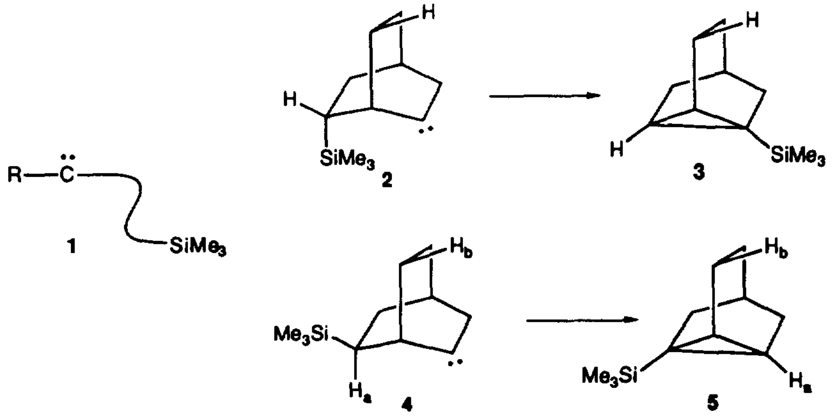
SILYL-SUBSTITUTED CYCLOPROPYL CARBENOIDS

Xavier Creary,* Ziqi Jiang, Mark Butchko, and Kathy McLean

Department of Chemistry and Biochemistry
University of Notre Dame, Notre Dame, IN 46556

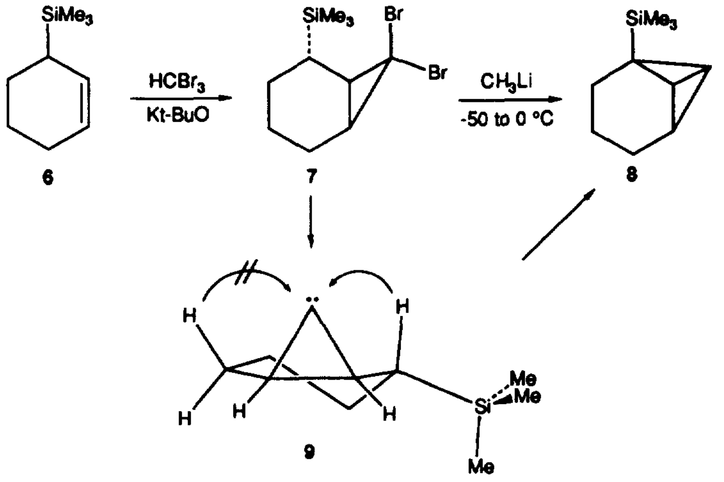
Abstract: Cyclopropyl carbeniods, generated from dibromocyclopropanes and methyllithium, insert preferentially into $SiMe_3$ activated C-H bonds. In other cases, allene formation remains the dominant process.

We have been interested in the chemistry of carbenes **1** containing silicon proximally disposed with respect to the divalent carbon center.[1] This interest grows out of our observation that silicon is prone to migrate to such centers as in carbene **2**.[2] Additionally, silicon appears to enhance the migratory aptitude of hydrogen in carbene **4**. We now wish to report on the chemistry of cyclopropyl carbenoids which contain silicon in close proximity to the carbenoid center.

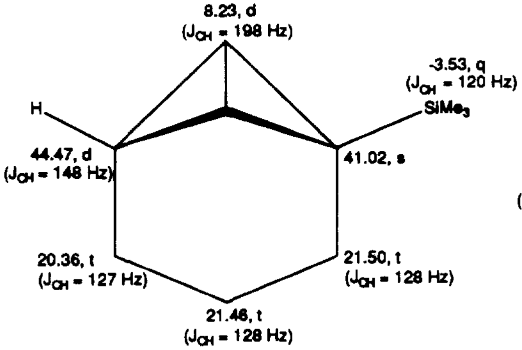


1 **2** **3** **4** **5**

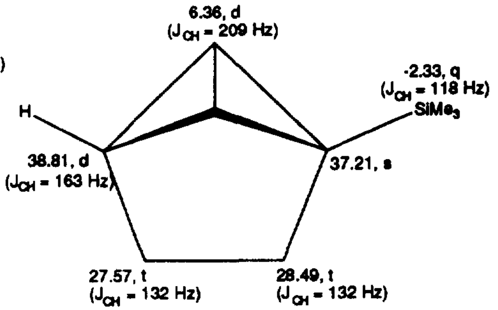
Cyclopropyl carbenoids can be generated when dibromocyclopropanes are reacted with methyllithium.[3] We have therefore added dibromocarbene to the allylsilane **6** and the resultant dibromocyclopropane **7** was treated with methyllithium. The sole product obtained (79 %) was the bicyclobutane **8**. The structure of



this product was established by ^{13}C NMR multiplicities as well as the characteristically large ^{13}C-H coupling constant (198 Hz) for the ring fused bridgehead carbons.[4] The isomeric bicyclobutanes that would have resulted from alternative migration processes were ruled out by the observed symmetry of the ^{13}C NMR spectrum. Addition of dibromocarbene to 3-trimethylsilylcyclopentene followed by reaction with CH_3Li led to formation of the analogous highly strained bicyclobutane **10**.[5]

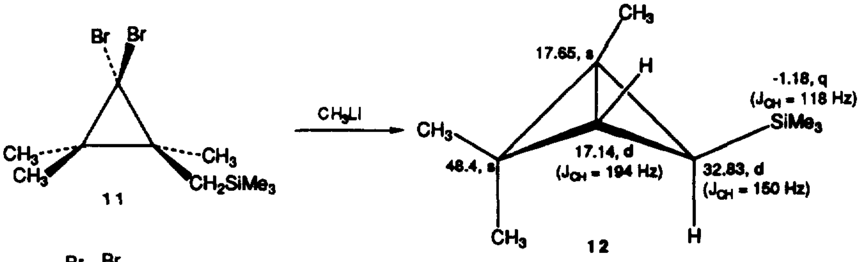


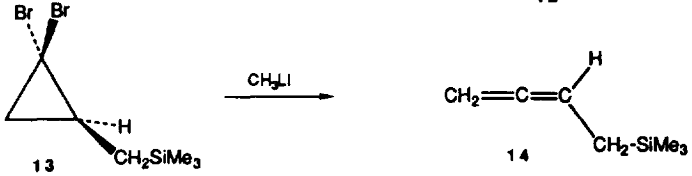
8

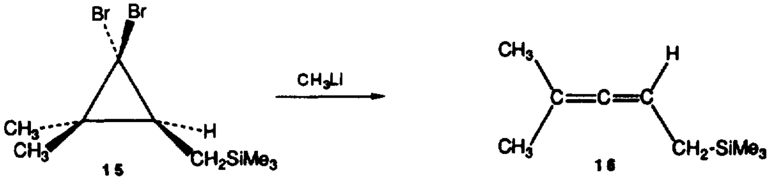


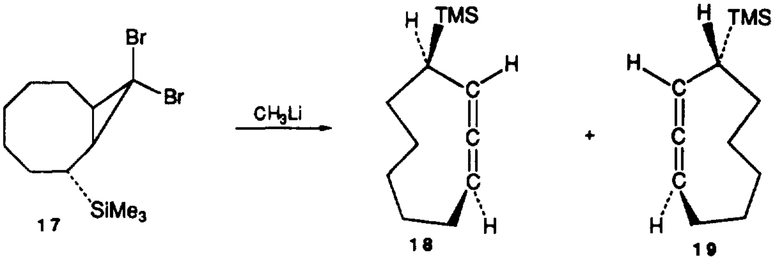
10

The formation of bicyclobutanes **8** and **10** as the exclusive products derived from the precursor cyclopropyl carbenoids suggests a high propensity for migration of "$SiMe_3$ activated" hydrogen as shown in **9**. In view of this facile entry into unusual bicyclobutane systems **8** and **10**, we have attempted to extend the scope of this reaction. The acyclic dibromocyclopropane **11** was reacted with methyllithium and the bicyclobutane **12** was formed. However, when dibromocyclopropanes **13** and **15** were treated with CH_3Li, the allenes **14** and **16** were the only products isolated.[6] The bicyclo[6.1.0]nonane **17** also



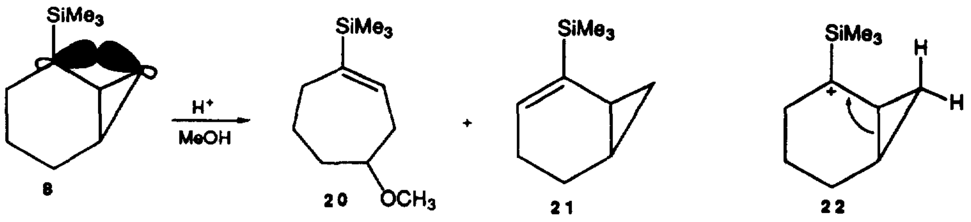




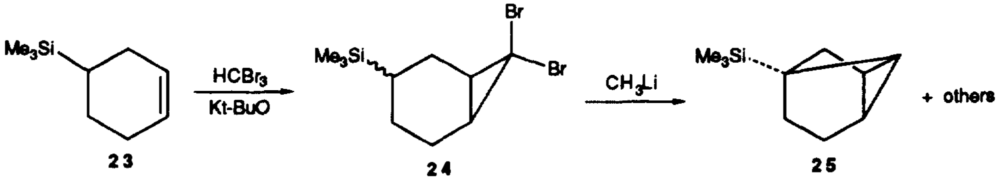


gave exclusively allene products, with the diastereomeric allenes **18** and **19** being formed exclusively in essentially equal amounts.[7]

The bicyclobutane **8** is a relatively sensitive compound, and rearranges readily on treatment with a trace of acid in methanol to give **20** as the major product along with a trace of **21**. This rearrangement presumably occurs via edge protonation of the strained bicyclobutane bond of **8** to give the cyclopropylcarbinyl cation **22**, followed by further rearrangement of cation **22**.[8]



Finally, the dibromocyclopropanes **24** were prepared as an inseparable mixture of isomers by dibromocarbene addition to **23**. Treatment of this mixture with CH_3Li gave the tricyclic product **25** as the major product, along with smaller amounts of uncharacterized products. The product **25** is undoubtedly derived from cyclopropyl carbenoid insertion into the trimethylsilyl activated C-H bond.



In summary, cyclopropyl carbenoid insertion into trimethylsilyl activated C-H bonds can lead to highly strained cyclopropyl systems. However, when allene formation is a possibility, this may offset the $SiMe_3$ activated C-H insertion reaction.

Acknowledgment is made to the National Science Foundation for support of this research.

References and Notes

1) Creary, X.; Wang, Y.-X. *Tetrahedron Lett.* **1989**, 30, 2493. See also Kirmse, W.; Konrad, W.; Schnitzler, D. *J. Org. Chem.* **1994**, 59, 3821.
2) Creary, X.; Wang, Y.-X. *J. Org. Chem.* **1994**, 59, 1604.
3) a) Moore, W. R.; Ward, H. R.; Merritt, RT. F. *J. Am. Chem. Soc.* **1961**, 83, 2019. b) Skattebøl, L. *Tetrahedron*, **1967**, 23, 1107, and references therein.
4) For typical examples, see a) Wiberg, K. B.; Lampman, G. M.; Cuila, R. P.; Connor, D. S.; Schertler, P.; Lavanish, J. *Tetrahedron* **1965**, 21, 2749. (b) Wüthrich, K.; Metboom, S.; Snyder, L. C. *J. Chem. Phys.* **1970**, 52, 230. (c) Pomerantz, M.; Hillenbrand, D. F. *J. Am. Chem. Soc.* **1974**, 96, 17.
5) No bicyclobutane is observed when 6,6-dibromobicyclo[3.1.0]hexane reacts with CH_3Li. See Moore, W. R.; Moser, W. R. *J. Org. Chem.* **1970**, 35, 908.
6) For leading references, see *Carbene Chemistry, Second Edition,* Kirmse, W.; Academic Press: New York, 1971, p 462.
7) For the analogous reaction of dibromobicyclo[6.1.0]nonane, see Skattebøl, L.; Solomon, S. *Org. Synth. Coll. Vol. V* **1973**, 306.
8) For an analogous acid catalyzed rearrangement, see reference 3a. See also Wiberg, K. B.; Lampman, G. M.; Ciula, R. P.; Connor, D. S.; Schertler, P.; Lavanish, J. *Tetrahedron* **1965**, 21, 2749.

(*Received in USA* 16 *October* 1995; *revised* 16 *November* 1995; *accepted* 21 *November* 1995)