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Cyclopropylmethylcarbene

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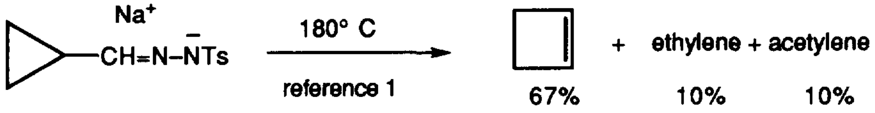
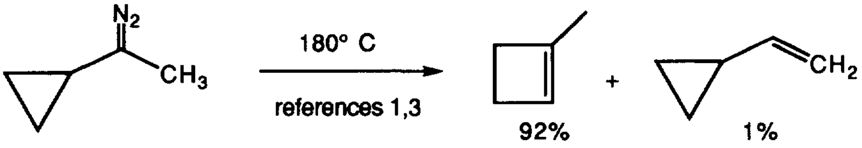
Abstract: In conflict with the dictates of conventional wisdom, cyclopropylmethylcarbene undergoes substantial 1,2-carbon-hydrogen insertion to give vinylcyclopropane.

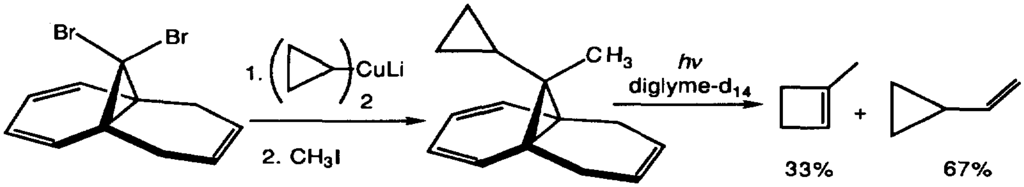
A paper on cyclopropylmethylcarbene may, at first sight, seem hopelessly anachronistic, as the cyclopropylcarbene rearrangement was discovered at The Ohio State University by Friedman and Shechter 36 years ago! Their early observations of extensive ring expansion to cyclobutenes set the pattern for much of what was to follow.[1] Cyclopropylmethylcarbenes have been reported many times, and the reactions of literally dozens of related cyclopropylcarbenes have been investigated.[2] There are two prominent reports on unsubstituted cyclopropylmethylcarbene. In each case, 92% 1-methylcyclobutene and only about 1% vinylcyclopropane was obtained.[1,3] In a series of decompositions of the tosylhydrazone salts of seven cyclopropylmethylcarbenes substituted in various ways on the ring, the sole product isomeric with the starting carbene was the ring-expanded cyclobutene.[2] There was no vinylcyclopropane at all. The lone exception to the ubiquitous formation of overwhelming amounts of ring-expanded product comes in the Dissertation of J. A. Smith of the Shechter group in 1964.[4] In this work, 33% of vinylcyclopropane was obtained on thermal decomposition of tosylhydrazone salt of cyclopropyl methyl ketone. It is not clear why so much more vinylcyclopropane was detected in 1964, four years *after* the original report of Friedman and Shechter, and two years *before* Kirmse's work, in which a mere 1% vinylcyclopropane was found.[1,3]





Quite early on in the study of carbene chemistry it became apparent, largely through the efforts of Frey, Stevens, and Shechter, that precursor chemistry was likely to be leading to some of the products attributed to carbenes.[5] In this paper we show that the chemistry of cyclopropylcarbenes has probably been misunderstood for decades. We suggest that much of the ring-expanded product, 1-methylcyclobutene, comes from reaction of the starting material, and the dominant reaction of the carbene is 1,2 carbon-hydrogen insertion to give vinylcyclopropane.

We examined two ways to make cyclopropylmethylcarbene that do not involve nitrogenous precursors. We first synthesized compound **1** from the known dibromide[6] through the route shown below. We have recently shown that similar alkylated cyclopropanes give carbenes on photolysis.[7] When **1** is photolyzed in diglyme, both 1-methylcyclobutene and vinylcyclopropane are formed, but, in contrast to all reactions involving nitrogenous starting materials, vinylcyclopropane is by far the major product. The product ratio is solvent-dependent; the more polar the solvent, the more vinylcyclopropane is formed. The yield of vinylcyclopropane is always very much greater than the approximately 1% reported in the early literature.[1,3] This solvent dependence is consistent with the notion that vinylcyclopropane is a carbene product, It is known that the transition state for the 1,2



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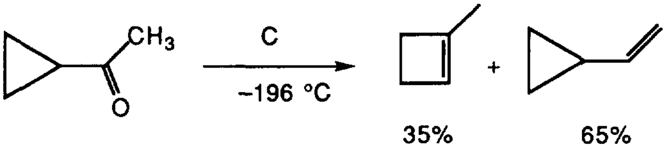
carbon-hydrogen insertion is polar, and is strongly favored by polar solvents.[8] Moreover, when the photolysis of **1** is run in 2,3-dimethyl-2-butene, a carbene trap, vinylcyclopropane diminishes.

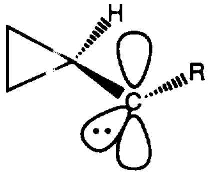
In a second approach, we have used carbon atoms to deoxygenate cyclopropyl methyl ketone at −196 °C, a procedure that has been shown to give real carbenes.[9] The deoxygenation of cyclopropyl methyl ketone was reported many years ago by Skell and Plonka,[10] who found vinylcyclopropane and 1-methylcyclobutene in the ratio of 30:70. This was very early work, and we have repeated it under conditions likely to minimize complications introduced by gas phase chemistry. When we inject carbon atoms into a layer of cyclopropyl methyl ketone at −196 °C, we find a 65:35 mixture of vinylcyclopropane and 1-methylcyclobutene, an exact turnabout from the earlier results. If care is not taken to minimize gas phase chemistry, more 1-methylcyclobutene appears, along with isoprene and cyclopentene, the rearrangement products of 1-methylcyclobutene and vinylcyclopropane. As with **1**, there is always far more vinylcyclopropane in the deoxygenation reaction than the 0-1% traditionally found in decompositions of diazo compounds.

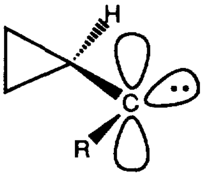


We suggest that 1,2 carbon-hydrogen insertion is the dominant reaction of cyclopropylmethylcarbene, and, at least at relatively low temperature, ring expansion is a minor process. At higher temperature, ring expansion may become more important, and such a temperature dependence may be at the heart of the difference between our results and the earlier reports,[1,3] as low temperature does favor carbon-hydrogen insertion.[7,9] In accord with our suggestion are the results reported in the accompanying Letter in which Platz and Huang show that ring expansion is not an important reaction of *trans*-2-*tert*-butylcyclopropylcarbene.[11]

Shevlin and McKee have calculated that there is a rather large difference in the ability of the two possible conformations of cyclopropylcarbene to undergo ring expansion. The cis conformation **2a** favors ring expansion ($\Delta H^{\#}$ = 5 kcal/mol), whereas the trans conformation **3a** favors fragmentation over ring expansion ($\Delta H^{\#}$ = 20.4 kcal/mol).[12]

2a, R = H
2b, R = CH_3





3a, R = H
3b, R = CH_3

Might we be generating cyclopropylmethylcarbene in a less stable trans conformation **3b** in which ring expansion is relatively difficult? The barrier to 1,2-carbon-hydrogen insertion in methylcarbene itself is only 0.9 kcal/mol,[13] although it rises to about 5 kcal/mol in dimethylcarbene.[14] The calculated barrier to rotation in **2a** is 14.9 kcal/mol.[12] Might the barrier for equilibration of **2b** and **3b** be sufficiently high so that carbon-hydrogen insertion in **3b** overwhelms rotation to the cis form in which ring expansion is easier? The quantitative similarity between the hydrocarbon source and the deoxygenation at very low temperature, along with Huang and Platz' work,[11] leads us to prefer the idea that we are seeing a difference between a mixture of precursor and carbene chemistry in the tosylhydrazone salt decompositions and pure carbene chemistry in our reactions.

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References

1. Friedman, L; Shechter, H. *J. Am. Chem. Soc.* **1960**, *82*, 1002.
2. Arct, J.; Brinker, U. H. In *Methoden der Organische Chemie (Houben-Weyl)*; M. Regitz, Ed.; G. Thieme Verlag: Stuttgart, 1989; Vol. E19b, pp 337-375.
3. Kirmse, W.; von Bülow, B. G.; Schepp, H. *Justus Liebigs Ann. Chem.* **1966**, *691*, 41. Kirmse also reports the Shapiro reaction of cyclopropyl methyl ketone tosylhydrazone which gives vinylcyclopropane almost exclusively.
4. Smith, J. A. *Dissertation Abstracts*, **1965**, *XXV*, 4.
5. Frey, H. M. *Pure and Appl. Chem.* **1964**, *9*, 527, and references therein. Mansoor A. M.; Stevens, I. D. R. *Tetrahedron Lett.*, **1966**, 1733. Chang, K.-T.; Shechter, H. *J. Am. Chem. Soc.*, **1979**, *101*, 5082.
6. Hartwig, J. F.; Jones, M., Jr. ; Moss, R. A.; Lawrynowicz, W. *Tetrahedron Lett.* **1986**, *27*, 5907. Lambert, J. G.; Ziemnicka-Merchant, B. T. *J. Org. Chem.* **1990**, *55*, 3460.
7. Glick, H.; Likhotvorik, I. R.; Jones, M., Jr. *Tetrahedron Lett.* **1995**, *36*, 5715.
8. Platz, M. S.; Modarelli, D. A.; Morgan, S.; White, W. R.; Mulins, M.; Celebi, S.; Toscano, J. P. *Prog. React. Kinetics* **1994**, *19*, 93.
9. Armstrong, B. M.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 3685.
10. Skell, P. S.; Plonka,J. H. *Tetrahedron*, **1972**, *28*, 3571.
11. Huang, H.; Platz, M. S. accompanying communication.
12. Shevlin, P. B.; McKee, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 519.
13. Evenseck, J. D.; Houk, K. N. *J. Phys. Chem.* **1990**, *94*, 5518.
14. Evenseck. J. D.: Houk. K. N. *J. Am. Chem. Soc.* **1990**. *112*. 9148.

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