



Pergamon

Tetrahedron Letters 39 (1998) 4433–4436

TETRAHEDRON
LETTERS

Bicyclo[2.2.1]heptan-1-ylcarbene Can Ring Expand¹

Rebecca T. Ruck and Maitland Jones, Jr. *

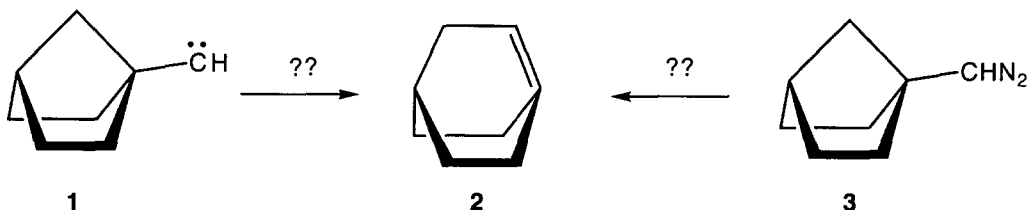
Department of Chemistry, Princeton University, Princeton, New Jersey 08544

Received 20 March 1998; revised 10 April 1998; accepted 14 April 1998

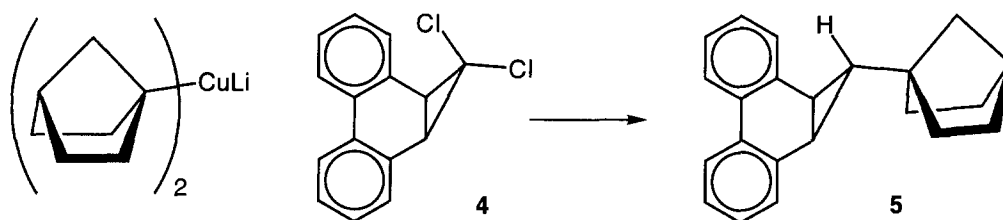
Abstract: Generation of bicyclo[2.2.1]heptan-1-ylcarbene from a hydrocarbon precursor avoids the problems that attend generation from nitrogenous molecules and allows the determination that such carbenes can ring expand to bridgehead alkenes. © 1998 Elsevier Science Ltd. All rights reserved.

Many years ago we used the pyrolysis of bridgehead-substituted diazo compounds to generate bridgehead alkenes.² We assumed at the time that the carbene was an intermediate. Nowadays, this presumption should surely be sharply questioned, as it is likely that the products of the photochemical decomposition of diazo compounds do not come entirely from the carbene, but derive in substantial measure from rearrangements of the nitrogen-containing precursors themselves.³ In particular, carbon-carbon insertion reactions, unknown in intermolecular chemistry of carbenes,⁴ are found to be at most minor pathways in the intramolecular chemistry of alkylcarbenes.⁵ Indeed, Frey, and Stevens,⁶ and Shechter⁷ had provided strong evidence long ago that such was the case. Although the thermal decomposition of simple alkyl-substituted diazo compounds seems to be free of similar complications,⁵⁻⁷ in strained systems such as cyclopropylcarbenes, even the thermal reactions do not involve pure carbene chemistry.⁸ Accordingly, the capacity of carbenes such as **1** to do the ring expansion to **2** comes into question,

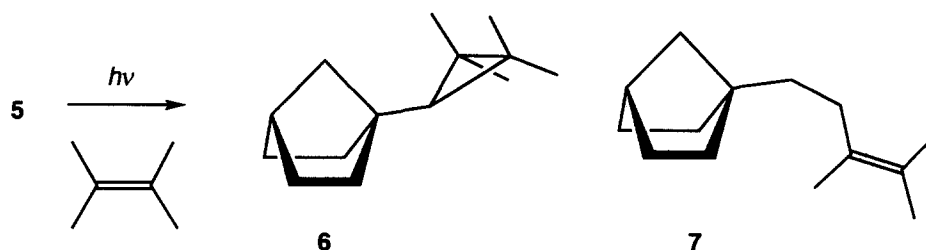
as the real precursor of the alkene might well be the diazo compound **3**. In this note, we show that at least one such carbene, bicyclo[2.2.1]heptan-1-ylcarbene (**1**), is capable of the ring expansion reaction.



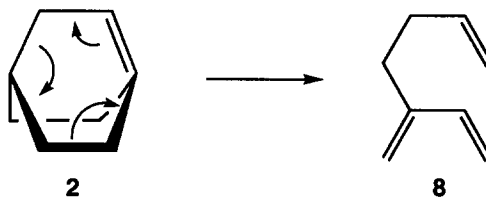
Our strategy was simple: generate **1** from a hydrocarbon precursor that would obviously be free of the complications introduced by diazo compounds and diazirines. Bicyclo[2.2.1]heptan-1-yllithium was generated from 1-chlorobicyclo[2.2.1]heptane by the method of Dimitrov, Thiele and Zschunke⁹ and coupled to dichlorocyclopropane **4**¹⁰ to give **5** though the modified procedure of Kitatani, Hiyama, and Nozaki.¹¹



Photolysis of **5** in 2,3-dimethyl-2-butene at 25 °C through quartz leads to much photoisomerisation of **5** (to other photoactive cyclopropanes) and to modest amounts of **6** and **7**, the products of capture of the carbene (ratio 2:1). For example, after complete photolysis of **5** and its photoisomers, **6** and **7** were present in 28% of the amount of phenanthrene formed. Bian had seen similar results from the photolysis of **3** in the 2-butenes.¹² Thus **5** (and its photoisomers) are capable of producing carbene **1**.



The next step was to remove efficient carbene traps such as alkenes from the photolysis mixture to see if evidence of ring expansion would appear. When the photolysis of **5** was carried out in benzene, a molecule impervious to **1**, GC/MS revealed five compounds isomeric with dimers of **1**. Analysis of the mixture by ^1H NMR spectroscopy shows that the alkenes formed by formal dimerization of the carbene are not present, as the appropriate vinyl hydrogens are not detectable. Presumably, these dimeric compounds include the cyclobutanes formed from $2 + 2$ dimerization of the bridgehead alkene, **2**. Our inability to separate and identify these dimers makes them useless as firm diagnostics for the presence of the ring-expanded carbene, bicyclo[2.2.2]oct-1-ene (**2**). However, in earlier work we had shown that **2** underwent a reverse Diels-Alder reaction at high temperature to give triene **8**.²



Authentic **8**, synthesized afresh, was conspicuous by its absence from the reaction products. However, when the photolysis was carried out at $60\text{ }^\circ\text{C}$, compound **8** made up 15% of the products, and at ca. $100\text{ }^\circ\text{C}$, it became the sole product. Although we now know that carbene **1** can indeed undergo the ring expansion reaction, we still do not know whether it is the active ingredient in the

formation of **2** and **8** in the pyrolysis of the diazo compound **3**. Nor can we be certain about the temperature effect on the appearance of **8** in the photolysis of **5**. Is it the ring expansion or the reverse Diels-Alder that does not take place at low temperature? The formation of the large number of dimeric products makes it likely that the latter situation applies, but a final resolution of this matter awaits further work.

Acknowledgements: It is a pleasure to acknowledge the assistance of Dr. Dasan M. Thamattoor in the early stages of this work. Conversations with Professors Hideo Tomioka and Matthew S. Platz have been especially helpful.

References:

1. Support of this work by the National Science Foundation through grant CHE-9702823 is gratefully acknowledged. RTR thanks Pfizer, Inc. for a Pfizer Undergraduate Research Fellowship.
2. Wolf, A. D.; Jones, M., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 8209. For a review, see: Jones, M. Jr. *Adv. Carbene Chem.* **1998**, *2*, in the press.
3. (a) Modarelli, D. A.; Morgan, S. C.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 7034. (b) White, W. R.; Platz, M. S. *J. Org. Chem.* **1992**, *57*, 2841. (c) Celebi, S.; Leyva, S.; Modarelli, D. A.; Platz, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 8613. Moss, R. A.; Ho, G.-J. *J. Phys. Org. Chem.* **1993**, *6*, 126. Tomioka, H.; Kitagawa, H.; Izawa, Y. *J. Org. Chem.* **1979**, *44*, 3072. See also, Seburg, R. A.; McMahon, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 7183 and Yamamoto, N.; Bernardi, F.; Bottoni, A.; Olivucci, M.; Robb, M. A.; Wilsey, S. *J. Am. Chem. Soc.* **1994**, *116*, 2064.
4. Wu, G.; Jones, M. Jr.; Doering, W. von E.; Knox, L. H. *Tetrahedron* **1997**, *53*, 9913.
5. Glick, H.; Likhovorik, I. R.; Jones, M., Jr. *Tetrahedron Lett.* **1995**, *36*, 5715. For a summary of the *tert*-butylcarbene story and relevant calculations, see: Armstrong, B. M.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 3685.
6. Frey, H. M. *Pure and Appl. Chem.* **1964**, *9*, 527, and references therein. Mansoor, A. M.; Stevens, I. D. R. *Tetrahedron Lett.* **1966**, 1733.
7. Chang, K.-T.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 5082.
8. Thamattoor, D. M.; Jones, M. Jr.; Pan, W.; Shevlin, P. B. *Tetrahedron Lett.* **1996**, *37*, 8333.
9. Dimitrov, V. V.; Thiele, K. H.; Zschunke, A. *Anorg. All. Chem.* **1982**, *494*, 144.
10. Chateaneuf, J. E.; Johnson, R. P.; Kirchhoff, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 3217.
11. Kitatani, K.; Hiyama, T.; Nozaki, H. *J. Am. Chem. Soc.* **1976**, *98*, 2364, *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1600.
12. Bian, N.; Jones, M. Jr. *Tetrahedron Lett.* **1993**, *34*, 3967.