

REACTION OF CARBENES WITH BICYCLO[2.1.0]PENTANE¹

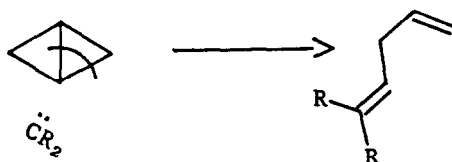
Gong-Huey Shiu, Ulf Misslitz, Xin-teng Ding,² and Maitland Jones, Jr.*

Department of Chemistry, Princeton University
Princeton, New Jersey 08544

Armin de Meijere
Institut für Organische Chemie und Biologie
Universität Hamburg
Federal Republic of Germany

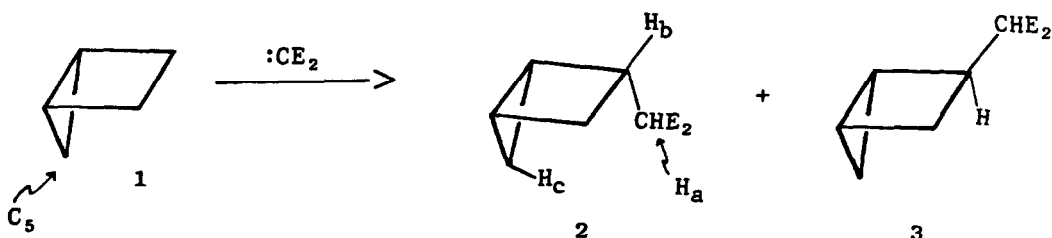
Summary: Bicyclo[2.1.0]pentane reacts with phenylcarbene and dicarbomethoxycarbene by simple insertion at the cyclobutane methylene position. By contrast, difluorocarbene reacts by two bond cleavage to give 1,1-difluoro-1,5-hexadiene.

BICYCLO[1.1.0]BUTANE reacts with carbenes to give 1,4-pentadienes as the major products.^{3,4} There is both experimental and theoretical support for the notion that this reaction involves a concerted two bond cleavage in which the central and one side bond are broken without intervening intermediates.⁴ Ordinary cyclopropanes do not undergo this



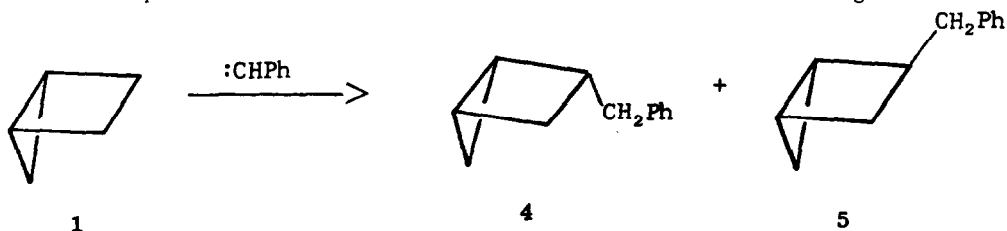
reaction⁵ even in strained systems⁶ and one is naturally led to wonder where the "break point" is. In particular, how bent must the central bond of the bicyclic system be in order for this reaction to occur? We describe here our work on the reaction of bicyclo[2.1.0]pentane (1) with carbenes.⁷

Irradiation of a degassed solution of methyl diazomalonate in 1 in a sealed quartz or Pyrex tube with a 450 watt medium pressure mercury arc led to two products (2,3) inseparable by gas chromatography. High resolution mass spectrometry showed them to be 1:1 adducts of dicarbomethoxycarbene and 1. ¹H NMR spectroscopy showed no vinyl hydrogens, and the presence of a three membered ring was revealed by multiplets integrating for 2H centered at δ 0.62 and 0.79 ppm (at 250 MHz 1 itself shows multiplets for hydrogen

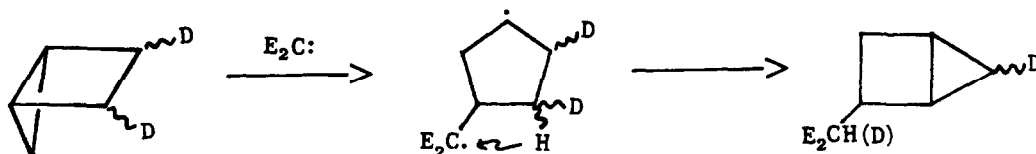


attached to C₅ centered at δ 0.50 and 0.65 ppm).⁸ Dicarbomethoxycarbene has apparently undergone only carbon-hydrogen insertion to give 2 and 3 in the ratio 2.7:1. The 250 MHz ¹H NMR spectrum of the major product 2 can be completely assigned from examination of the decoupled spectra, but the following details suffice to specify the endo structure for the major product. H_a appears as a sharp doublet at δ 3.28 ppm and decoupling experiments show that it is coupled to H_b at δ 3.08 ppm. That H_a is coupled to H_b shows that the carbene cannot be attached at the bridgehead, and the presence of two hydrogens at C₅ rules out insertion at that point. An NOE difference spectrum shows that H_a lies in proximity to one of the cyclopropane hydrogens (H_c, δ 0.62 ppm). The CH(COOCH₃)₂ group cannot be exo, as no NOE effect can be observed for either cyclopropane H in 3. Why is the major product endo? First of all, it is known that the endo 2-methoxy compound is thermodynamically favored,⁹ and it is reasonable for some of the preference for endo to be felt in the transition state for insertion. Bicyclo[2.1.0]pentanes are known to isomerize as low as 135° C,⁹ and our observed ratio of 2.7 may reflect some isomerization on preparative gas chromatography. Examination of the crude 250 MHz ¹H NMR spectrum, though complicated by many extraneous signals, shows that this ratio cannot be seriously in error; in particular the major product of the original insertion cannot be exo.

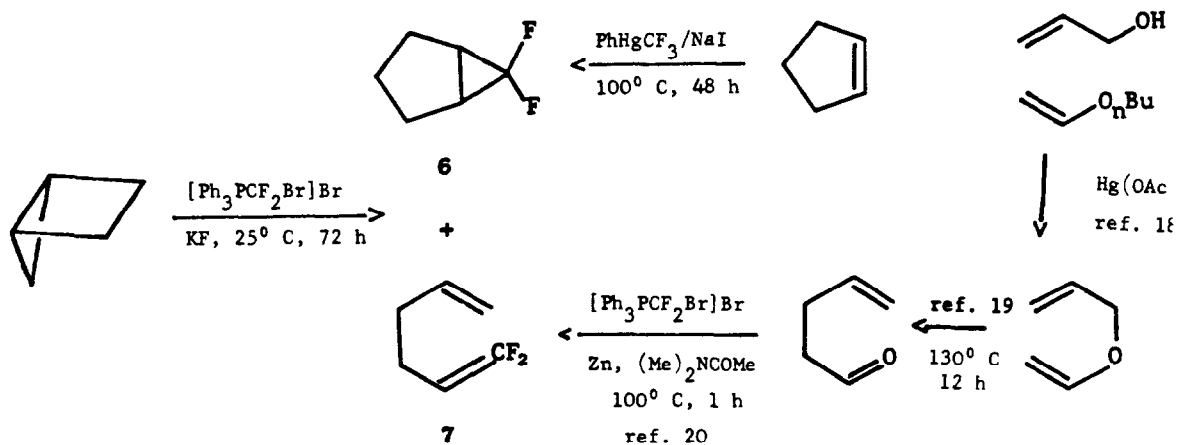
Irradiation of phenyldiazomethane in 1 leads to a similar picture. The products are 4 and 5 and the endo insertion product is favored by a factor of ca. 2.4. Once more the crude ¹H NMR spectrum shows that thermal interconversion cannot have changed the ratio much.



It has become quite fashionable to suggest stepwise mechanisms for reactions of singlet carbenes^{11,12} and some arguments (though by no means all!) are quite persuasive.¹³ One could write such a mechanism in this case, as shown below. However this exotic mechanism is eliminated by a labelling experiment. In an experiment in which a mixture of 71% endo,endo- and 29% exo,exo-2,3-dideuterio-1 was allowed to react with dicarbomethoxycarbene, ²H NMR spectroscopy showed that no deuterium appeared at C₅. No sign of two-bond cleavage reactions appears and therefore the formation of 2-5 involves a simple carbon-hydrogen insertion reaction.



In reactions with quadricyclane we have shown that difluorocarbene gives the product of two-bond cleavage when other carbenes do not.⁷ Moreover, products of carbon-hydrogen insertions of $:CF_2$ are unlikely to dominate. Reaction of 1 with difluorocarbene generated by the method of Burton¹⁴ led to two products, 6 and 7, albeit in only ca. 2% overall yield. Compound 6 is probably the result of reaction of $:CF_2$ with the 0.3% cyclopentene present as a contaminant in 1, although we cannot absolutely rule out a more interesting origin. Compound 7 however is the expected product of two bond cleavage. Both 6 and 7 were identified by comparison of spectra with those of authentic samples. Cyclopropane 6 is known,¹⁵ though published details are scanty. We synthesized an authentic sample from cyclopentene and $PhHgCF_3/NaI$.¹⁶ Diene 7 could be made through the indicated sequence.¹⁷⁻²¹



The reaction with difluorocarbene shows that the limit of the two bond cleavage reaction has not quite been reached with 1, but clearly this reaction will be restricted to unusual molecules.

REFERENCES AND NOTES

- (1) We thank the National Science Foundation for support of this work through Grant CHE 8118345. We also thank the Studienstiftung des deutschen Volkes for a Fellowship for UM.
- (2) On leave from the Department of Chemistry, Fudan University, Shanghai, People's Republic of China.
- (3) (a) W. von Doering and J. F. Coburn, Jr., Tetrahedron Lett., **991** (1965). (b) K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler and J. Lavanish, Tetrahedron **21**, 2749 (1965). (c) D. E. Applequist and J. W. Wheeler, Tetrahedron Lett., **3411** (1977).
- (4) G. B. Mock and M. Jones, Jr., Tetrahedron Lett., **22**, 3819 (1981), J. E. Jackson, G. B. Mock, M. L. Tetef, G.-x. Zheng and M. Jones, Jr., Tetrahedron, **41**, 1453 (1985).
- (5) W. Kirmse, "Carbene Chemistry," 2nd Ed., Academic Press, 1971.
- (6) R. R. Sauers and R. J. Kiesel, J. Am. Chem. Soc., **89**, 4695 (1967).
- (7) For our work on the related quadricyclane see the accompanying paper. For work by others on quadricyclane differing in both mechanistic interpretation and experimental observation from our work see, first: (a) C. W. Jefford, J.-C. E. Gehret and V. de los Heros, Bull. Soc. Chim. Belg., **88**, 973 (1979), then (b) C. W. Jefford, J. Roussilhe and M. Papadopoulos, In Press.
- (8) P. G. Gassman and K. T. Mansfield, Org. Syn. Coll. Vol. V, 96, Wiley, New York, 1973, report δ 0.3-0.8 at an unspecified field strength.
- (9) E. L. Alired and R. L. Smith, J. Am. Chem. Soc., **91**, 6766 (1969). It had earlier been assumed by Chesick¹⁰ that the more stable 2-methyl isomer was the exo. Chesick made his assumption clear in the paper, however.
- (10) J. P. Chesick, J. Am. Chem. Soc., **84**, 3250 (1962).
- (11) See references cited in ref. 4.
- (12) E. V. Dehmlow and R. Kramer, Angew. Chem. Internat. Ed. Engl., **23**, 706 (1984).
- (13) C. W. Jefford, G. Bernardinelli, J.-C. Rossien and J. A. Zuber, Helv. Chim. Acta, **65**, 1467 (1982).
- (14) D. J. Burton and D. G. Naeae, J. Am. Chem. Soc., **95**, 8467 (1973).
- (15) O. M. Nefedov and A. A. Ivashenko, Nov. Khim. Karbenov, Mater. Vses. Soveshch. Khim. Karbenov Ikh. Analogov., 1st, 145 (1972) [Pub. 1973]. Chem. Abstr., **82**, 72584j.
- (16) D. Seyferth, S. P. Hopper and G. J. Murphy, J. Organometal. Chem., **46**, 201 (1972).
- (17) We thank Dr. R. W. Creekmore and R. Fischer of the FMC Company and M. W. Baum of Princeton for most generous help in determining the ¹⁹F NMR spectra.
- (18) W. H. Watanabe and L. E. Conlon, J. Am. Chem. Soc., **79**, 2828 (1957).
- (19) L. K. Montgomery and J. W. Matt, J. Am. Chem. Soc., **89**, 6556 (1967).
- (20) S. Hayashi, T. Nakai, N. Ishikawa, D. J. Burton, D. G. Naeae and H. S. Kesling, Chem. Lett., 983 (1979).
- (21) W. R. Dolbier, Jr., K. S. Medinger, A. Greenberg, and J. F. Liebman, Tetrahedron, **38**, 2415 (1982).

(Received in USA 24 June 1985)