Tetrahedron Letters No. 50, pp 5117 - 5120 , 1972. Pergamon Press. Printed in Great Britain.

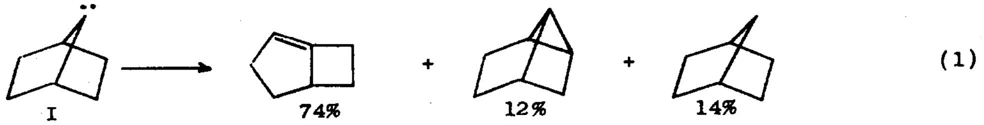
OLEFINIC CAPTURE OF 7-NORBORNANYLIDENE AND 7-NORBORNENYLIDENE

Robert A. Moss* and Ulf-Helge Dolling

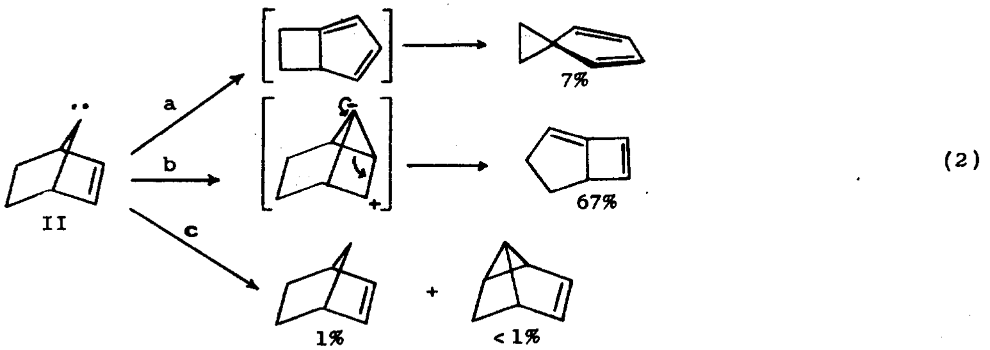
Wright Laboratory, School of Chemistry, Rutgers University,
The State University of New Jersey, New Brunswick, N.J. 08903

(Received in USA 27 August 1972; received in UK for publication 13 November 1972)

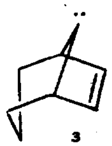
We have previously described the intramolecular chemistry of 7-norbornanylidene (I)[1] and 7-norbornenylidene (II)[2], eqns. (1) and (2). Bicyclo[3.2.0]heptadiene-1,6, the major product from II, was suggested to be the product of a rearrangement, initiated by interaction of the (singlet) carbene's vacant p orbital with its homoallylic π bond. Related processes, which could involve similar electronic interactions, appear to occur with carbenes III-VI. These attempts to generate "foiled methylenes,"[7] carbenes stabilized by interactions of their vacant p orbitals with non-adjacent, but nearby π or σ bonds, have thus led to

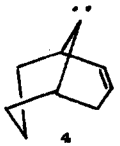


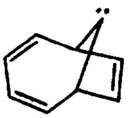
(1)

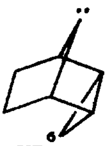


(2)


III[3]


IV[4]


V[5]

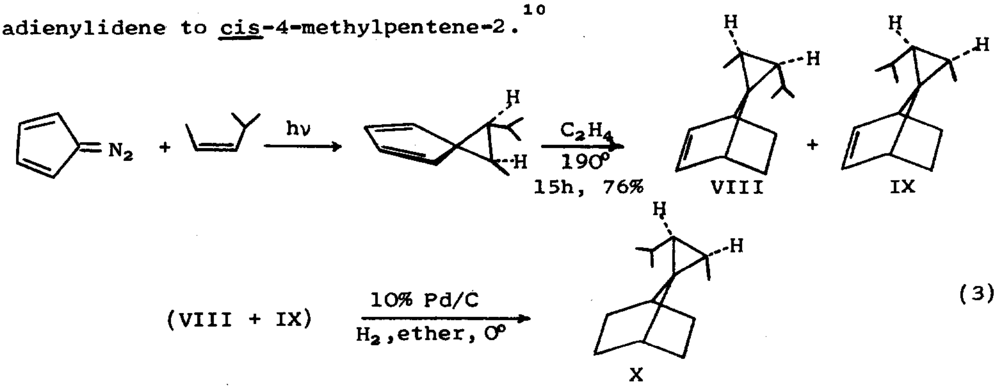

VI[6]

---

*Fellow of the Alfred P. Sloan Foundation facile intramolecular chemistry.[8]

We now describe the first olefin addition reactions of a "foiled methylene," II,[9] and comment briefly on the striking observation that its capture is much less efficient than that of its saturated analog, I.

The products to be derived from the additions of I and II to *cis*-4-methylpentene-2 were synthesized in advance [eq. (3)]. The key reaction was a Diels-Alder addition (stainless steel bomb) of ethylene to *cis*-1-methyl-2-isopropylspiro[2.4]heptadiene-4,6, which was itself the product of the addition of cyclopentadienylidene to *cis*-4-methylpentene-2.[10]



(3)

Gc-purified (VIII + IX) and X gave satisfactory elemental analyses, mass spectral parent ions, ir and nmr spectra.[11] An analogous series of reactions, based on *trans*-1-methyl-2-isopropylspiro[2.4]heptadiene-4,6[10] gave the *trans* analogs of VIII, IX and X, which were similarly characterized.

Pyrolysis of the dry Li salt of 7-norbornanone tosylhydrazone in *cis*-4-methylpentene-2 (200°, 30 min., stainless steel bomb) gave 23% of adduct X as the only high-boiling product.[12] This reaction presumably represents an *intermolecular* addition of I, and was shown by gc to be >99% stereospecific. Photolysis of an olefinic suspension of the Li salt (Pyrex vessel, 3000 Å lamps, Rayonet reactor) gave 8.4% of X, based on the 71% evolved nitrogen. The photolytic reaction was also >99% stereospecific.

In contrast, an analogous pyrolytic generation of II gave a complex product mixture containing 0.067% of (VIII + IX), identified by gc[12] and nmr. The *trans* isomers of VIII and IX were not detectable.[13] Photolytic generation of II in *cis*-4-methylpentene-2 gave 0.24% of (VIII + IX), based on 40% nitrogen evolution.

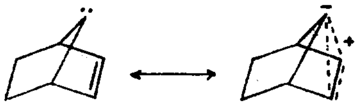
Adducts VIII, IX, and X were shown to be quantitatively stable to the reaction and analytical conditions.

Parallel pyrolytic experiments with substrate *trans*-4-methylpentene-2 gave the adduct of I (*trans*-X) in 11% yield, but the adducts of II (*trans*-VIII + IX) could not be detected. The addition reaction of I was >97% stereospecific.[13a]

Two conclusions can be elaborated. 7-Norbornanylidene (I) can be trapped by an olefin with unusual efficiency, considering that it is a carbene with well-characterized intramolecular escapes[1] available to it. Based on absolute product yields, 7-norbornenylidene (II) is 35 (photolytic) to 340 (pyrolytic) times less readily intercepted by *cis*-4-methylpentene-2 than is its saturated analog, I, under comparable conditions.

We attribute the unusual[14] and efficient capture of I to its reluctance to undergo intramolecular reactions which lead to highly strained products [see eq. (1)]. Its extended lifetime makes possible intermolecular interception. The carbenoid derived from 7,7-dibromonorcarane and methyllithium also exhibits intermolecular and intramolecular reactions,[15] and similar factors may be operative.

The intramolecular products derived from II[2] are even more strained than those formed from I [see eq. (2)], and we might have also anticipated efficient olefinic capture of 7-norbornenylidene. That the fact is quite the reverse must, we believe, be attributed to a crucial and dominant carbene-double bond interaction in II. This interaction could be simply the very facile addition of the 7-carbenic p orbital to the π bond, leading to a short-lived zwitterionic intermediate [*cf.*, eq. (2),b]. II could thus escape intermolecular capture, whereas its saturated analog, I, lacking the essential double bond, could not. Or, the interaction in II could be that of an idealized "foiled methylene,"[7] making II behave as a nucleophile during its lifetime,[16] and disdain addition to



simple dialkylethylene substrates.

A complete understanding could, of course, blend aspects of these two interpretations. However, the present results give powerful support to the notion that a homoallylic carbene-π interaction in 7-norbornenylidene is a major determinant of its chemistry. We are pressing related studies.

Acknowledgments. We thank the National Science Foundation and the National Institutes of Health for financial support. We are grateful to Dr. Dorothy Z. Denney for 100 MHz. nmr spectra.

References and Notes

(1) R. A. Moss and J. R. Whittle, *Chem. Commun.*, 341 (1969)

(2) R. A. Moss, U-H. Dolling, and J. R. Whittle, *Tetrahedron Letters*, 931 (1971).

(3) G. N. Fickes and C. B. Rose, *J. Org. Chem.*, in press. We thank these authors for a preprint.

(4) M. H. Fisch and H. D. Pierce, Jr., *Chem. Commun.*, 503 (1970).

(5) T. A. Antkowiak, D. C. Sanders, G. B. Trimitsis, J. B. Press, and H. Shechter, *J. Amer. Chem. Soc.*, **94**, 5366 (1972).

(6) P. K. Freeman, R. S. Raghavan, and D. G. Kuper, *ibid.*, **93**, 5288 (1971).

(7) R. Gleiter and R. Hoffmann, *ibid.*, **90**, 5457 (1968).

(8) Other carbenes which may possess extended electronic delocalization are cited by: R. G. Bergman and V. J. Rajadhyaksha, *ibid.*, **92**, 2163 (1970); G. W. Klumpp and P. M. v. Dijk, *Rec. Trav. Chim.*, **90**, 381 (1971); P. K. Freeman and K. B. Desai, *J. Org. Chem.*, **36**, 1544 (1971); and K. Geibel, *Chem. Ber.*, **103**, 1637 (1970).

(9) Lithium carbenoids corresponding to II and VI may react intermolecularly with CH_3Br: L. Skattebøl, *Tetrahedron*, **23**, 1107 (1967); M. S. Baird and C. B. Reese, *Chem. Commun.*, 523 (1972).

(10) R. A. Moss and J. R. Przybyla, *J. Org. Chem.*, **33**, 3816 (1968).

(11) Nmr of (VIII + IX), 100 MHz., $CHCl_3$, values in δ: 6.15, t, 2H, vinyl; 2.54 and 2.10, envelopes, 2H, bridgehead; 1.74, m, 2H, ethano; 1.60-0.8, m with sharp lines at 1.09, 1.03, 0.98, 0.92, 0.86, 12H, *i*-Pr and CH_3 plus 2 ethano; 0.56, m, 2H, cyclopropyl. Nmr of X, 100 MHz., 40% $CHCl_3/CCl_4$, δ: 1.81-1.23, m, 10H, 8 ethano and 2 bridgehead; m with lines at 1.07, 1.05, 1.02, 0.99, and 0.94, 9H, *i*-Pr methyls and methyl (consistent with 3 overlapping doublets, J = 6.5-6.8 and 5.1 Hz.); 0.78, m, 1H, *i*-Pr carbinyl, 0.56, AB, 2H, cyclopropyl.

(12) We used a 100' Apiezon-L Golay column and a f.i. detector for analytical work. Yields were measured against a dodecane internal standard. Intramolecular rearrangement products of the carbenes [eqns. (1) or (2)][1,2] presumably account for the balance of the starting material. Though detected, they could not be quantitatively determined in the presence of the large excess of olefin because all of the gc retention times were similar.

(13) Nor was *cis*-1-methyl-2-isopropylspiro[2.4]heptadiene-4,6 in evidence. Fragmentation to ethylene and cyclopentadienylidene is excluded as a major reaction of II (*cf.*, Ref. 2); the former is readily captured by *cis*-4-methylpentene-2.[16]

(13a) About 2.5% of a product with the retention time of X was detected, but its identity has not been proven.

(14) "With few exceptions it can be stated that if a singlet carbene has an internal insertion or cycloaddition available, it will not be possible to trap it with an external reagent," W. J. Baron, *et. al.*, in "Carbenes," M. Jones, Jr., and R. A. Moss, Eds., Wiley, New York, N.Y., *in press*, Chapt. 1.

(15) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Amer. Chem. Soc.*, **83**, 2019 (1961).

(16) See the elegant study of cycloheptatrienylidene by L. W. Christensen, E. E. Waali, and W. M. Jones, *ibid.*, **94**, 2118 (1972).