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THE REACTION OF DICARBOMETHOXYCARBENE WITH CYCLOBUTENE. VINYLCYCLOPROPANE FORMATION FROM THE TRIPLET STATE[1]

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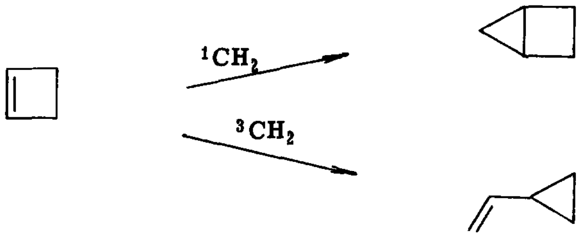
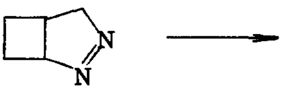
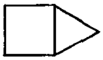
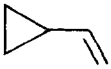
Although the stereochemical outcome of the addition of carbenes to alkenes is the most widely used diagnostic for spin state, in recent times other reactions have also come into use. For instance, rearrangements after reaction of 1,1-dicyclopropylethylene[2] or dihaloethylenes[3] with carbenes have been attributed to triplets. The latter example is more remarkable for its apparent detection of triplet dihalocarbenes.[4] There is yet another reaction, first noticed by Elliot and Frey,[5] that has been claimed to be capable of distinguishing singlets and triplets. Elliot and Frey noticed that singlet methylene reacted with cyclobutene to give only bicyclo[2.1.0]pentane, insertion products, and isomers formed by rearrangements of "hot" molecules, but triplet methylene formed by the mercury-sensitized photolysis of ketene gave almost entirely vinylcyclopropane.[6]

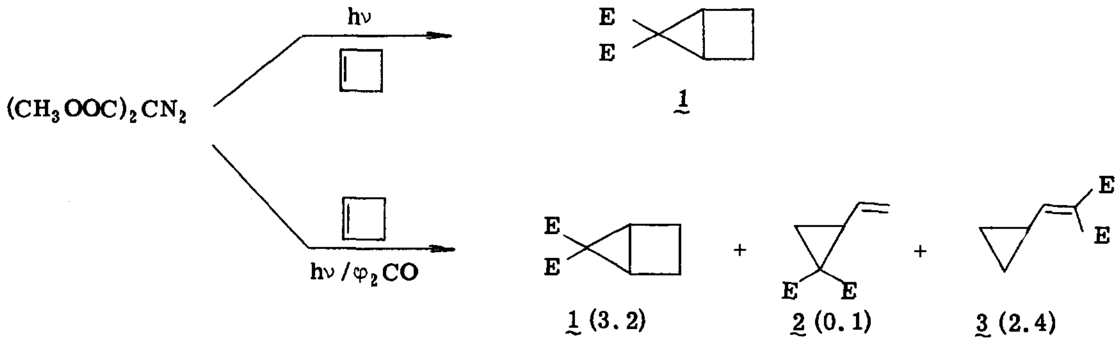


Some years later it was noted by White, Condit, and Bergman[8] that 2,3-diazobicyclo[3.2.0]hept-2-ene gave only traces of vinylcyclopropane on photosensitized decomposition (see Table I). The suggestion was made that in the work of Elliot and Frey the mercury may have served to convert some portion of the cyclobutene to butadiene, an efficient scavenger of triplet methylene.[9] It is the purpose of this Letter to describe a labeling experiment that supports the validity of Elliot and Frey's original interpretation and to suggest an explanation for the results of White, Condit, and Bergman.

Table I. Products (%) from the decomposition of 2,3-diazobicyclo[3.2.0]hept-2-ene[8]

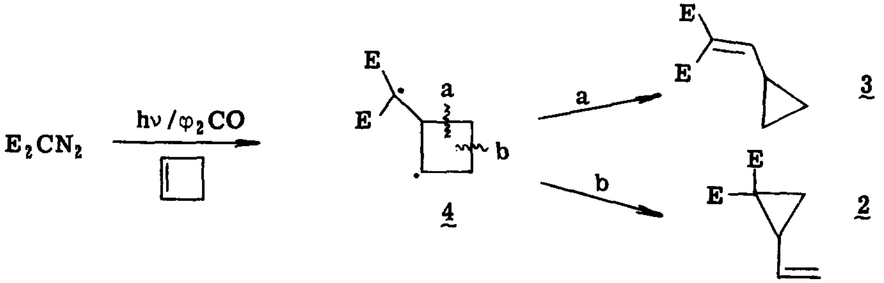
				Others
297 °C	72	15	5.9	6.9
hν	27	59	11	4
hν / sens	10	90	--	--

We have allowed singlet and triplet dicarbomethoxycarbene to react with cyclobutene.[10,11] The direct irradiation at room temperature through Pyrex of a 2% solution of methyl diazomalonate in cyclobutene[12] resulted in the formation of a single adduct in 55% yield. Elemental analysis and spectral data revealed the product to be the expected 5,5-dicarbomethoxybicyclo[2.1.0]pentane (1) [nmr (CCl_4) δ 3.78 (s, 3H), 3.70 (s, 3H), 2.1-2.6 (m, 4H), and 1.3-1.7 (m, 2H)]. Repetition of the photolysis in the presence of a two-fold excess of benzophenone as sensitizer gave three products in the ratio 3.2/0.1/2.4 in 68% overall yield. In addition to 1, the isomeric vinylcyclopropanes 2 and 3 were also formed.

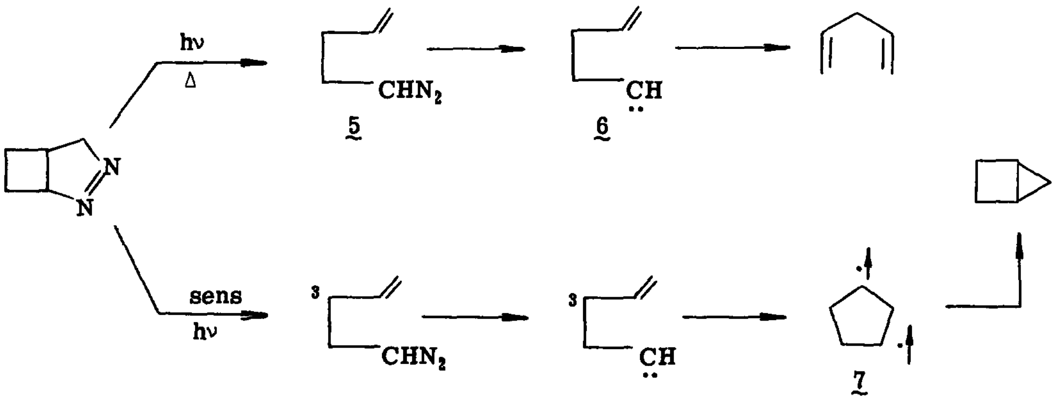


Isomer 2 was identical to material previously described[10] and could be synthesized from dimethyl malonate and trans-1,4-dichloro-2-butene. The structure of 3 follows from elemental analysis and examination of spectra [ir (neat) 3004, 1715, and 1631 cm^{-1}; nmr (CCl$_4$) δ 6.29 (d, 11 Hz, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 1.7-2.3 (m, 1H), and 0.6-1.3 (m, 4H)]. All three products were stable to irradiation with or without benzophenone and diazomalonic ester, and hence are primary products.

The formation of adduct 3 clearly demonstrates that vinylcyclopropane formation is a primary product of the triplet carbene and not an artifact of butadiene formation. Product 2 is another matter. An enticing explanation for its formation involves 3,4 cleavage (b) of the diradical 4. However, the involvement of minute amounts of butadiene formed during the reaction cannot be conclusively ruled out.[13]



What of the results of White, Condit, and Bergman[8] (see Table I)? These authors have demonstrated that an important process in the thermal and direct photochemical reactions of 2,3-diazobicyclo[3.2.0]hept-2-ene is the retro-1,3-dipolar addition to give the diazo compound 5. This material serves as a source of carbene 6 and of the 1,4-pentadiene. We



suggest that the photosensitized reaction may yield triplet 5 and thus triplet 6. The triplet carbene can then undergo intramolecular cycloaddition to give diradical 7. Triplet 7 has been made and shown to rearrange to bicyclo[2.1.0]pentane.[14]

References and Notes

1. Support of this work by the National Science Foundation is gratefully acknowledged. We are additionally in debt to Professor W. R. Roth for weighty discussions.
2. N. Shimizu and S. Nishida, J. Am. Chem. Soc., 96, 6451 (1974).
3. J. B. Lambert, K. Kobayashi, and P. H. Mueller, following Letter.
4. M. Jones, Jr., V. J. Tortorelli, P. P. Gaspar, and J. B. Lambert, accompanying Letter.
5. C. S. Elliot and H. M. Frey, Trans. Faraday Soc., 64, 2352 (1968).
6. There is another example of vinylcyclopropane formation from the reaction of a carbene and cyclobutene.[7] Here rearrangement was attributed to the stepwise addition of singlet iodocarbene. We suggest in the accompanying Letter[4] that the triplet may be responsible.
7. N. C. Yang and T. A. Marolewski, J. Am. Chem. Soc., 90, 5644 (1968).
8. D. H. White, P. B. Condit, and R. G. Bergman, J. Am. Chem. Soc., 94, 1348 (1972).
9. See R. A. Moss, Chapter II, in "Carbenes," Vol. 1, M. Jones, Jr. and R. A. Moss, Eds., Wiley, New York, N.Y., 1973.
10. M. Jones, Jr., W. Ando, M. E. Hendrick, A. Kulczycki, Jr., P. M. Howley, K. F. Hummel, and D. S. Malament, J. Am. Chem. Soc., 94, 7469 (1972).
11. For an exposition of the thesis that carbenes are not involved in the direct irradiation of diazomalonic ester see D. S. Wulfman, B. Poling, and R. S. McDaniel, Tetrahedron Lett., 4519 (1975).
12. Butadiene was carefully removed by fractional distillation, low-temperature reaction with 4-phenyl-1,2,4-triazoline-3,5-dione, and repeated distillation. Analysis by glpc showed no butadiene.
13. Analysis of the recovered cyclobutene revealed no butadiene, however.
14. S. L. Buchwalter and G. L. Closs, J. Am. Chem. Soc., 97, 3857 (1975). We a referee for bringing this article to our attention.

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