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REACTION OF DICARBOMETHOXYCARBENE WITH QUADRICYCLANE[1,2]

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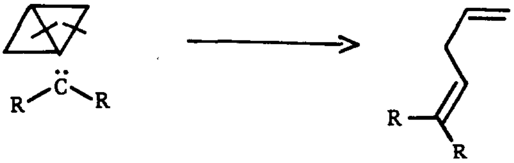
SUMMARY: Dicarbomethoxycarbene reacts with quadricyclane to give mainly 3,3-dicarbomethoxy-exo-tricyclo[3.2.1.0^{2,4}]oct-6-ene. Although this is the same major product as formed by reaction of the carbene with norbornadiene, it is shown that reaction with quadricyclane is direct and does not involve prior isomerization to the diene.

The reluctance of carbenes to attack the carbon-carbon single bond stands in contrast to the ease of reaction with the carbon-hydrogen bond and all manner of π systems.[3] Only the bicyclo[1.1.0] system is generally reactive[4,5] and even here, it has been suggested that the process resembles addition to a π system more than it does reaction with a single bond.[6] The postulated[6] simultaneous cleavage of both central and side bonds finds analogy in the well-known fragmentation reaction of cyclopropylcarbenes.[3,7] There is some experimental evidence that the two-step reaction originally suggested[4] should be replaced with the concerted variant, which resembles the olefin addition process.[6]



We wondered if the bicyclo[2.1.0]system would behave similarly, and thus undertook an examination of the reaction of carbenes with tetracyclo[3.2.0.0.^{2,7}0^{4,6}]heptane ("quadricyclane," 1). The reaction of dichlorocarbene and difluorocarbene with 1 has been described previously.[8] As our results with the former carbene were different from those reported[8,9] and as "dihalocarbene" products can be precursor-dependent[10] we decided to examine the reaction of dicarbomethoxycarbene with 1.

Irradiation of diazomalonic ester in quadricyclane led to four products, 2-5.[11] Norbornadiene is reported to produce 3 and 5 and we have verified that 2 and 4 are formed as well (table). Although it seems unlikely that 1 could rearrange to norbornadiene (6) under our reaction conditions, the nature of the products makes it imperative that this possibility be carefully considered. Although the products from 1 and 6 are the same, they are produced in quite different ratios (table). The conclusion is inescapable that isomerization of 1 to 6 does not preceed product formation.

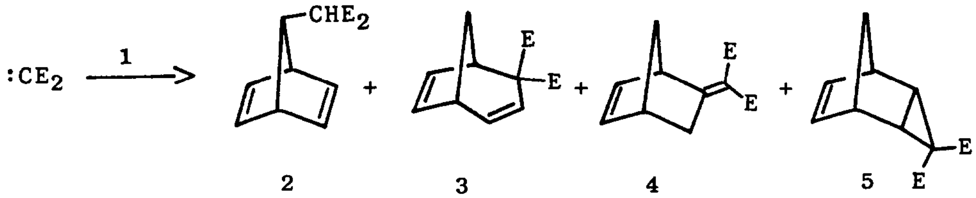
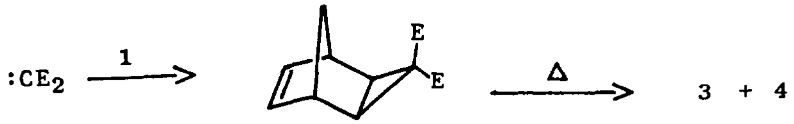


Table. Reaction of Dicarbomethoxycarbene with 1 and 6.

Substrate	Relative Percent			
	2	3	4	5
1	15	70	11	4
6	trace	57	8	35

Compound 3 is known to be a product of pyrolysis of *exo*-cyclopropane 7.[12] We have shown that 4 is formed as well.[13] Cyclopropane 7, though very prone to rearrangement on gas chromatography can be isolated along with 5 from reaction of 6 with dicarbomethoxycarbene followed by chromatography on silica gel. Thus we are able to examine the crude reaction mixtures of 1 and dicarbomethoxycarbene and identify 7 as a primary product.



7

Quadricyclane is known to undergo a concerted, stereospecific 6 electron thermal cycloaddition reaction with olefins.[14] Other similar cycloadditions with acetylenes[15] and ketones[16] are known, although, in these cases, stereochemical information is not available. We, too, lack the stereochemical label necessary for proof of concert in the reaction of carbenes with 1. Yet it does not seem unreasonable to suggest that the formation of 7 represents a new example of the concerted reaction of divalent carbon with two σ bonds.

Carbenes seem to behave much as do double bonds in their reactions with 1 and 6. Both olefins and carbenes react with 6 to give homo-*endo*-1,4 addition. Carbenes, of course, also react normally with the double bonds of 6. Quadricyclane reacts with double bonds in a different fashion to give products of *exo*-cycloaddition, and carbenes follow suit.

REFERENCES AND NOTES

(1) Support from the National Science Foundation through grant CHE-81-01212 is gratefully acknowledged.

(2) This work is taken from the A.B. Thesis of M.L.T., Princeton University, 1983.

(3) For general references see W. Kirmse, "Carbene Chemistry," Academic Press, Inc., New York, 1971, 2nd Ed., and M. Jones, Jr. and R. A. Moss, Eds., "Carbenes," Vol. 1, Wiley-Interscience, New York, 1973, Chapter 3.

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(9) Our results will be reported in detail in a forthcoming Tetrahedron Symposium in Print.

(10) See for instance, R. A. Moss, Chapter 2 in "Carbenes" Vol. 1, Wiley, New York, 1973, M. Jones, Jr. and R. A. Moss, Eds.

(11) Compounds **3** and **5** are known;[12] we synthesized authentic **4** from dehydronorcamphor, and the structure of **2** rests upon elemental analysis and inspection of its ^1H NMR spectrum.

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(13) M. L. Tetef, unpublished work. We will shortly report upon the thermal reaction of **7** and **5**. For a summary of related work see J. J. Gajewski, "Hydrocarbon Thermal Rearrangements" Academic Press, Inc., New York, 1981, p. 265-266.

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