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REARRANGED ALKENE PRODUCTS IN THE ADDITION OF DIBROMOCARBENE TO 1,2-DIHALOETHYLENES. EVIDENCE FOR A POSSIBLE SINGLET-TRIPLET CARBENE INTERCONVERSION

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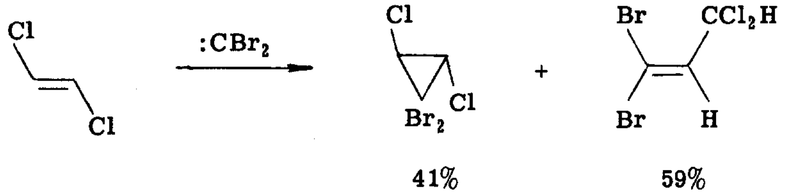
Whereas singlet carbenes normally produce cyclopropanes stereospecifically from alkenes, an equilibrium between singlet and triplet could give rise to a mixture of stereospecific and nonstereospecific products. This type of situation has been observed in the case of carbethoxynitrene.[2] We wish to report a reaction of dibromocarbene that is suggestive of a singlet-triplet equilibrium, although the existence of the triplet is not revealed by nonstereospecificity. The test for triplet carbene is provided here by the observation of certain rearrangement products. Similar observations have been made by Hendrick and Jones in quite a different system.[3] Reactions that fall into this general mold are discussed in an accompanying paper.[4]

Alkene products observed[5] in the reaction of the dichloroethylenes with dihalocarbenes have largely been ignored or attributed to instability of the product cyclopropanes. We have studied the reaction of dibromocarbene, formed by the decomposition of phenyltribromomethylmercury,[6] with the cis- and trans-dibromoethylenes and with trans-dichloroethylene. We have found that the alkene products arise from rearrangement of an intermediate prior to formation of the cyclopropane products, and not from the products themselves.

The reactions of the three substrates and their products are given in eq 1-3. The structural assignment of the tetrahalopropenes was based on comparison of spectroscopic data (IR, NMR) with reported data.[7] The stereochemistry of the tetrahalocyclopropanes was established from the magnitude of the vicinal proton-proton coupling constants measured from the ^{13}C satellites. The respective products from *trans*-dichloro- and -dibromoethylene had a coupling of about 5 Hz, in agreement with trans stereochemistry in the product cyclopropane, whereas the product from *cis*-dibromoethylene had a coupling of about 8 Hz.[8] Furthermore, reduction with tributyltin hydride of the product obtained from *trans*-dichloroethylene gave *trans*-1, 2-dichlorocyclopropane.



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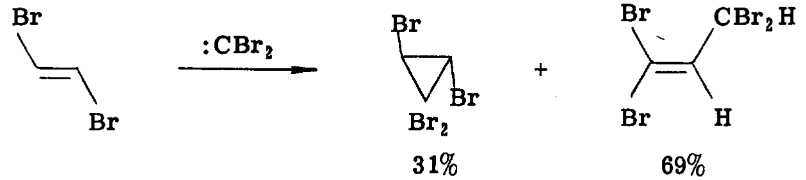

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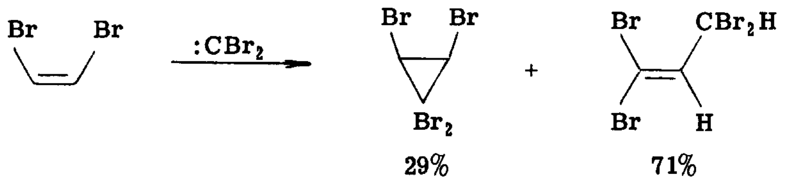
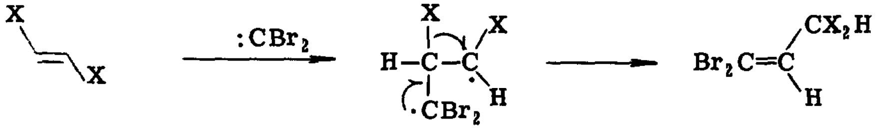


(3)

If the alkene products of the reactions were the result of decomposition of the product cyclopropane, the latter materials should rearrange when subjected to the conditions of the reaction. We found, however, that the cyclopropane products were stable under a variety of control conditions. Thus *trans*-1, 1-dibromo-2, 3-dichlorocyclopropane was recovered unchanged after two hours in refluxing benzene, both with and without phenyl(tribromomethyl)-mercury. Equimolar amounts of 1, 1-dibromo-2, 3-dichlorocyclopropane and phenyl(tribromomethyl)mercury were allowed to reflux in benzene in the presence of a ten-fold excess of cycloheptene, used to act as a surrogate alkene in the place of 1, 2-dichloroethylene. Again the cyclopropane was recovered unchanged, along with cycloheptene and its dibromocarbene adduct.

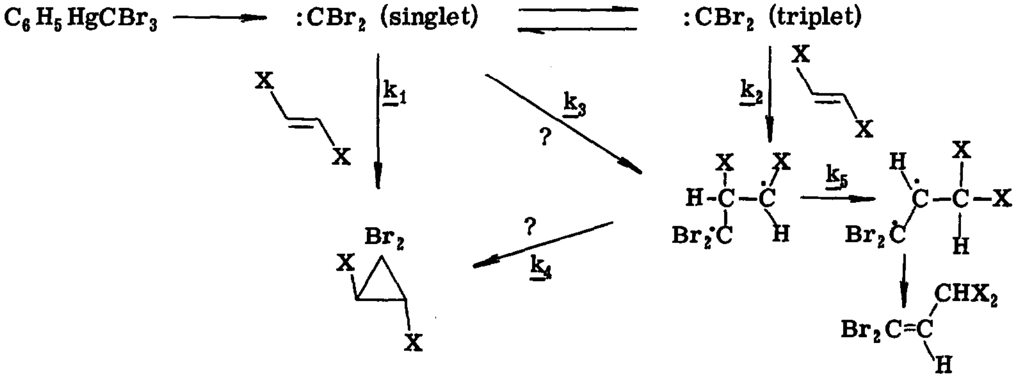
Since the alkenic material is not formed from product cyclopropane, it must arise from rearrangement of an intermediate, such as the diradical in eq 4.[9] The apparent paradox



(4)

of this mechanism, however, is that the cyclopropane products are formed with complete stereospecificity, a circumstance that is normally taken to indicate reactions of singlet carbenes without diradical intermediates. A mechanism that is not in contradiction with these facts is given in the Scheme. The carbene is formed as a singlet,[10] which reacts in the normal

SCHEME



fashion ($\underline{k}_1$) with the dihaloethylene to give the cyclopropane stereospecifically. The singlet is in equilibrium with a triplet, which reacts ($\underline{k}_2$) with the dihaloethylene to form the diradical of eq 4. This triplet diradical, rather than ring closing nonstereospecifically[2] to the cyclopropane, rearranges rapidly to the second diradical ($\underline{k}_5$), which ultimately intersystem-crosses and forms the alkene product. In a second mechanistic scenario, the initial diradical is a singlet, derived directly from the singlet carbene ($\underline{k}_3$). This diradical partitions rapidly between the products ($\underline{k}_4$, $\underline{k}_5$) before conformational equilibration can occur. Such a mechanism, however, is in considerable disagreement with accepted models for singlet carbene reactivity, in which singlet diradicals are thought not to intervene. In a third conceivable mechanism, both products could be formed from a triplet carbene that produces a triplet diradical (k_2, k_4, k_5). This mechanism would require the radical to intersystem-cross and give the two products faster than rotation can occur about the C-CHX bond.

Either alternative mechanism (all singlet, all triplet) requires arbitrary assumptions. We currently favor the singlet-triplet equilibrium, in which the cyclopropane is formed stereospecifically from the singlet (k_1) and the rearranged alkene from the triplet (k_2, k_5). Accurate spin state calculations on dibromocarbene are hampered by the large number of electrons.[10] If the singlet is the ground state, the triplet may still be appreciably populated at our reaction temperature (80 °C). Furthermore, even in an equilibrium strongly favoring the singlet, the triplet may react more rapidly than the singlet ($k_2 > k_1$). In this context, the halogen atoms on the substrate alkene may fulfill an important function by slowing the singlet reaction. The viability of these mechanistic hypotheses is discussed in terms of related systems in the accompanying paper.[4]

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REFERENCES AND NOTES

1. Petroleum Research Fund Postdoctoral Fellow, 1973-1975; present address, Department of Chemistry, College of General Education, University of Tokyo, Tokyo, Japan.
2. W. Lwowski and F. P. Woerner, *J. Am. Chem. Soc.*, **87**, 5491 (1965).
3. M. E. Hendrick and M. Jones, Jr., preceding Letter.
4. M. Jones, Jr., V. J. Tortorelli, P. P. Gaspar, and J. B. Lambert, following Letter
5. D. Seyferth, S. P. Hopper, and T. F. Jula, *J. Organomet. Chem.*, **17**, 193 (1969).
6. D. Seyferth and R. L. Lambert, Jr., *J. Organomet. Chem.*, **16**, 21 (1969).
7. C. Raulet and M. Levas, *Bull. Soc. Chim. Fr.*, 2147 (1963); B. J. Burreson and R. E. Moore, *Tetrahedron Lett.*, 473 (1975).
8. S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **88**, 2478 (1966).
9. An alternative mechanism to produce the rearranged material, suggested by a referee, is radical addition of $C_6H_5HgCBr_3$ to the alkene to form $C_6H_5HgCBr_2CHXCHXBr$, which then must somehow decompose to the observed product. Experiments currently in progress are designed to prove or disprove this pathway.
10. R. Hoffman, G. D. Zeiss, and G. W. Van Dine, *J. Am. Chem. Soc.*, **90**, 1485 (1968). More recent calculations suggest an even lower-energy triplet state: C. W. Bauschlicher, Jr., H. F. Schaefer III, and P. S. Bagus, *ibid.*, **99**, 7106 (1977).

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