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STEPWISE ADDITIONS OF SINGLET CARBENES[1]

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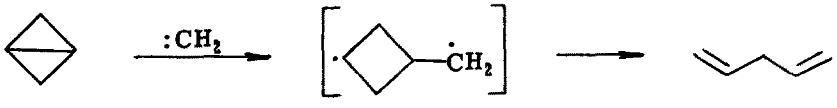
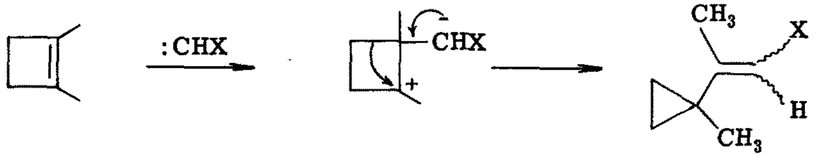
The concertedness of singlet carbene additions - at least in an operational sense - has been proved time and again.[2] However, over the past few years a few reports of apparently stepwise additions have crept into the literature. Despite the novelty of these reports they have received little attention. This Letter calls attention to these reactions and in some cases suggests alternative explanations.

As early as 1965 Doering and Coburn[3] and Wiberg and co-workers[4] described the formation of 1,4-pentadienes from the reaction of methylene with bicyclobutanes. Wiberg also discovered the similar reactions of dichlorocarbene,[4] and recently Applequist and Wheeler[5] found not only 1,4-pentadienes but also bicyclo[1.1.1]pentanes in the reaction of dichlorocarbene with substituted bicyclobutanes. The mechanism proposed involved the stepwise addition of the carbene across the central bond followed by rearrangement (eq 1). At the time these were the only examples of stepwise singlet reaction in a hydrocarbon system.[6]

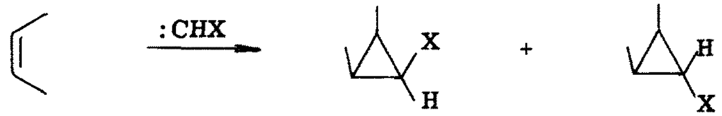


(1)

In 1968 Yang and Marolewski postulated another example in their report of the formation of vinylcyclopropanes on photolysis of iodoform or dichloroiodomethane in 1,2-dimethylcyclobutene.[9] Again the mechanism proposed involved a two-step singlet addition, although this time a polar process was postulated (eq 2).[10] In the most curious feature of the reaction, addition to *cis*-2-butene was stereospecific (eq 3), although addition to the cyclobutene proceeded with rearrangement.



(2)



(3)

Other possible stepwise additions of dihalocarbenes are described in the accompanying Letter by Lambert, Kobayashi, and Mueller.[13] Here too, rearranged products are accompanied by *stereospecific* addition.

Let us first consider the last two examples of halocarbene additions. The essential problem is that if one posits a two-step singlet reaction, there seems no way to accommodate the observed stereospecificity. One needs a rearrangement faster than rotation about a carbon-carbon single bond, which seems most unlikely. Similarly, if alternative explanations are advanced in which the singlet is replaced with the triplet, then a stereospecific triplet addition is required. Such has not been observed. However, it seems to us that an explanation involving two spin states is tenable, even though halocarbenes are known to have singlet ground states[14] and the triplets have never even been postulated as intermediates.

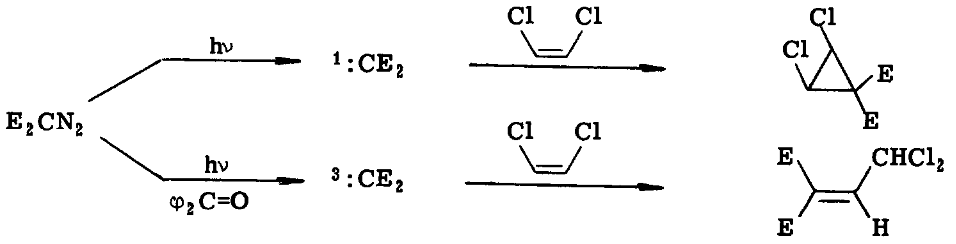
Given that the ground states are singlets, in order to postulate triplets in our reaction scheme, we need a combination of an accessible triplet - that is, the triplet must not be too far above the singlet in energy - and a sufficient rate of triplet reaction ($\underline{k}_T$ in the scheme).

$$\begin{tikzcd}
{}^{1}{:}CXY \arrow[r, "\text{alkene}", "\underline{k}_S"'] \arrow[d, shift left] & \text{stereospecific addition} \\
{}^{3}{:}CXY \arrow[r, "\text{alkene}", "\underline{k}_T"'] \arrow[u, shift left] & \text{rearrangement}
\end{tikzcd}$$

Both semiempirical and ab initio calculations of the singlet/triplet gaps in halocarbenes exist, although the former are somewhat unreliable and there are but two examples of the latter. If one "corrects" the semiempirical values (CHF -36.8,[15] -3.7,[16] or ca. 0;[17] CHCl -25.3;[15] CHBr -22.3;[15] CF_2 -82.8,[15] -34.6,[16] or -39;[17] CBr_2 -32.2;[15] CCl_2 -41.4[15] kcal/mol) by adjusting them by the amount they are "off" in calculating the singlet/triplet gap in methylene,[18] one arrives at values in good agreement with those calculated by ab initio methods. In this fashion we estimate -5 to -10 kcal/mol for CHF and -3 to -6 kcal/mol for CHBr, CHCl, and CBr_2. The calculations have yielded -45[21] or -47[22] for CF_2, -14 for CCl_2,[21] -9[21] or -11[22] for CHF, -2 for CHCl,[21] and +0.9 for CHBr.[21] Although there are no calculations at all for CHI, the triplet should be favored even more here. Thus we need only a small factor in triplet reactivity ($k_T > k_S$) to make the triplets potential intermediates in these cases. In the cases reported for halocarbenes this possibility seems not unreasonable to us. In Lambert's case[13] the dihaloalkene should be very slow in singlet reactions,[23] and the halogen will help stabilize its end of the diradical formed by triplet addition.

In Yang's reaction there seems no reasonable way that the triplet addition should be accelerated, but formation of the highly strained bicyclo[2.1.0] system by concerted singlet addition should be retarded. Cyclobutenes have not been used in competitive relative rate studies,[22] so direct evidence is lacking. It is known, however, that triplets add to cyclobutenes with rearrangement to give vinylcyclopropanes.[24],[25]

As a final piece of evidence to strengthen the plausibility of these arguments, we have verified that triplets give the appropriate rearrangement. Thus irradiation of methyl diazomalonate in cis-1,2-dichloroethylene gives cis-1,1-dicarbomethoxy-2,3-dichlorocyclopropane along with traces of the trans isomer. However, when the reaction is photosensitized, the major product (ca. 75%) is 1,1-dicarbomethoxy-3,3-dichloropropene.



We feel the evidence is quite strong in these reactions that triplet halocarbenes are involved. Potential tests abound and we hope by this Letter to provoke some.

The additions to bicyclobutanes present more problems. The singlet-triplet gap for CH_2 is at least 11 kcal/mol and that for CCl_2 doubtless even higher. It does not seem that an explanation involving triplets is possible in these cases. These reactions of Doering and Wiberg remain oddities, and, it seems to us, well worthy of further study.

REFERENCES AND NOTES

1. We thank the National Science Foundation for support of this work through grants CHE 77-10025 and CHE 77-08384. Our thanks also go to the many people who contributed to this work through discussions and suggestions. Among them were F. Bickelhaupt, W. T. Borden, B. Coleman, G. Klumpp, and S. L. Kammula.
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