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NONSTEREOSPECIFIC, NONTRIPLET CYCLOPROPANATIONS WITH DIBROMOMETHYLENE

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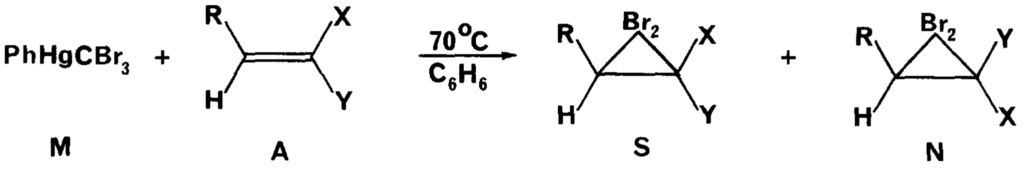
Summary The Seyferth reagent $PhHgCBr_3$ generates singlet CBr_2 that adds nonstereospecifically to styrene and fumaronitrile via a carbene complex.

Nonstereospecificity has been the hallmark for identifying triplet spin character of carbenes in their cycloaddition reactions with alkenes.[1] We wish to report two parallel examples of nonstereospecific addition of dibromomethylene (CBr_2), generated by the Seyferth procedure. These examples appear not to involve triplet carbenes, but instead take place via reversibly formed carbene complexes.

Phenyl(tribromomethyl)mercury, the Seyferth reagent,[2] reacts with either fumaronitrile (trans-dicyanoethene) or styrene-cis-2-d to give a high yield of the cyclopropane adduct, eq. 1. In both cases the reaction is stereoselective but not stereospecific, and the reagents and products are all stable under reaction conditions. Typically, [N]/[S] by ^1H NMR integration is 0.1-0.6, depending



(1)

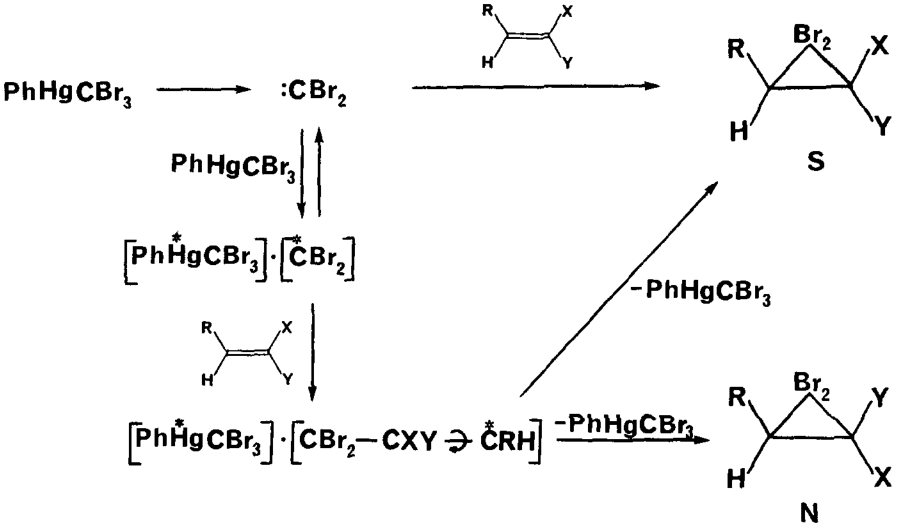
R = CN, X = H, Y = CN
R = Ph, X = D, Y = H

on reactant concentrations. At first glance, the loss of stereochemistry might be attributed to intervention of triplet dibromomethylene. The nonstereospecific reaction of diphenylmethylene with styrene, for example, has been interpreted in terms of the triplet ground state of this carbene.[3] Dibromomethylene, however, has a singlet ground state, the triplet being several kcal/mol higher in energy.[4]

We applied a standard kinetic test for the presence of two (or more) consecutively formed intermediates that give distinct products[5-8] and obtained positive results for both styrene and fumaronitrile. These results are what would be expected for any two intermediates, such as in a singlet-triplet equilibrium, as observed for example for carboxynitrene.[9] However, we further observed that the ratio of products from the second intermediate to those from the first for styrene[7,10] or fumaronitrile[8,10] is directly proportional to the concentration of the Seyferth reagent. This kinetic dependence requires an additional molecule of $PhHgCBr_3$ as a homogeneous catalyst for the conversion of the first intermediate to the second and is not reasonable for a singlet to triplet process. In other words, loss of stereospecificity is directly proportional to the concentration of $PhHgCBr_3$, an unprecedented observation. We propose that the second intermediate is a complex between singlet dibromomethylene and the Seyferth reagent. This complex reacts with alkene to give a diradical, or its equivalent, that undergoes internal rotation to produce the cyclopropane nonstereospecifically (N + S). Complexes (ylides) have been observed between carbenes and a wide variety of Lewis bases, including aldehydes, ketones,[11] nitriles,[12] ethers, sulfides, amines, and iodides.[13]

Our results can be explained by the mechanism given in Scheme I. The first-formed singlet carbene reacts stereospecifically with alkene to give the cyclopropane S. The carbene also reacts with a molecule of $PhHgCBr_3$ to form a complex, shown in brackets. If the carbene acts as an electrophile ($\underline{m}$ = 0.65 for CBr_2, within the electrophilic range[14]), the basic site on the Seyferth reagent may be either the phenyl-mercury bond or the aromatic π electrons. The complexed carbene then adds to the alkene to give the linear intermediate, also shown in brackets, in which free rotation can occur. Charge type or diradical character (plus, minus, or dot) is not defined and is represented by asterisks. The linear intermediate then loses the catalytic molecule of $PhHgCBr_3$, probably to form the simple diradical $\cdot CHRCXYCBr_2\cdot$, which can ring-close to give both N and S. The mechanism in Scheme I correctly requires that the ratio of products from the two pathways is directly proportional to the concentration of Seyferth reagent and is inversely proportional to the concentration of alkene.

Scheme I



In summary, we have observed that dibromomethylene undergoes nonstereospecific cycloaddition to the alkenes styrene and fumaronitrile without the intervention of the triplet state. An intermediate resembling the diradical normally expected from the triplet, $\cdot CBr_2CXYCHR\cdot$, is generated through a catalyzed pathway that is signified by the observed direct proportionality between the concentration of $PhHgCBr_3$ and the ratio of products from the nonstereospecific and stereospecific pathways. The nonstereospecific pathway is observed when Seyferth reagent can compete successfully with alkene for reaction with the singlet carbene and is favored when R, X, or Y is electron withdrawing.

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7. For styrene the test is a plot of $2[N]/([S]-[N])$ vs. $[\text{alkene}]^{-1}$. The numerator represents material from the second intermediate (double the concentration of N, since half the products have isomerized to S). The denominator is material from the first intermediate (the contribution from the second intermediate [N] is subtracted from [S]). The correlation coefficient was 0.97.
8. For fumaronitrile there is no a priori method for calculating the amount of S that comes from the second intermediate. A plot of $[N]/[S]$ vs. $[\text{alkene}]^{-1}$ assumes no contribution to [S] from the second intermediate, i.e., that both pathways are stereospecific. We also made plots that assumed that the second intermediate went randomly[7] to N and S (nonstereoselective), i.e., $2[N]/([S]-[N])$ vs. $[\text{alkene}]^{-1}$, and that the second intermediate split 1/3 to S and 2/3 to N (stereoselective but nonstereospecific), i.e., $3[N]/(2[S]-[N])$ vs. $[\text{alkene}]^{-1}$. All three plots were linear, corr. coeff. 0.97, 0.994, 0.993. We concluded that the method is not particularly sensitive to the contribution of the nonstereospecific pathway to [S].
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10. For styrene, the plot is of $[N]/[S]$ vs. $[\text{PhHgCBr}_3]$ (corr. coeff. 0.993). For fumaronitrile, again[8] three plots were examined (corr. coeff. 0.997, 0.992, 0.98).
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