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CARBENE-CARBENE REARRANGEMENTS: MULTIPLICITY OF THE REARRANGED CARBENE

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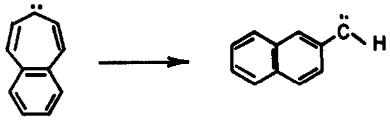
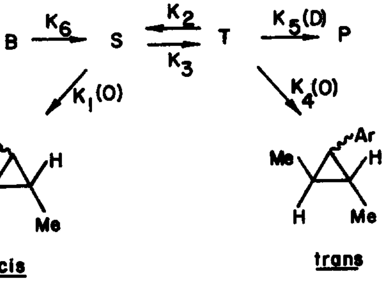
The stereochemistry of the addition of carbenes to alkenes has been used to probe both the multiplicity of carbenes at the instant of their addition to alkenes[1] and the interconversion of singlet and triplet carbenes.[2] Furthermore, in cases where addition of the triplet carbene competes with its reversal to the singlet, the effect of olefin concentration has also identified the multiplicity of the carbene at its inception.[3] At this time, we would like to report the use of the effect of added scavenger on the stereochemistry of addition as a method to probe the multiplicity of a carbene at its inception[3] in a system where the method of variations in olefin concentration is ineffective. This question was of interest to us in our attempts to understand the mechanism of carbene-carbene rearrangements and was applied to the conversion of benzocycloheptatrienylidene to 2-naphthylcarbene.[4]



Consider the following scheme, for the moment disregarding step $k_5(D)$. If the carbene enters the singlet-triplet manifold at S and if k_2 is greater than $k_4(O)$,[2] a simple steady state

Scheme I



B = Benzocycloheptatrienylidene

S = Singlet naphthylcarbene

T = Triplet

D = 2,4-Hexadiene

O = cis-2-Butene

P = 2,4-Hexadiene-carbene product

treatment with elimination of time as a variable leads to $\frac{\text{cis}}{\text{trans}} = \frac{k_1k_2}{k_3k_4}$ and the stereochemistry of the reaction should be independent of the concentration of olefin. By similar reasoning, the same relationship obtains if the carbene enters at T and $k_3(S)$ is greater than $k_1(O)$. In other words, singlet-triplet reversibility[2] vitiates variations in stereochemistry with olefin concentration as a viable probe of the point of entry of the carbene into the singlet-triplet manifold.

From the results in Table 1, this is apparently the case in the rearrangement of benzocycloheptatrienylidene to β-naphthylcarbene. From the results in Table 1, it is also apparent that, as is typical,[3] the singlet carbene adds to the alkene faster than the triplet (although the triplet is probably in higher concentration at equilibrium).

Consider now Scheme 1 with inclusion of $k_5(D)$ and assume k_5 is greater than k_4 (i.e. triplet reacts faster with diene than with monoene).[1,3] Further, assume $k_5(D)>k_2$ (i.e. diene traps triplet before it can return to singlet). Finally, assume the carbene enters the manifold at S and that some singlet is trapped before it can cross to triplet. In this extreme case, only cis cyclopropane should be formed. Or, in steady state terms, with no restrictions:

$$\frac{\text{cis}}{\text{trans}} = \frac{k_1k_2 + k_1k_4(O) + k_1k_5(D)}{k_3k_4}$$

but, if $k_5(D)>k_4(O)$ and $k_5(D)>k_2$: $\frac{\text{cis}}{\text{trans}} = \frac{k_1k_5(D)}{k_3k_4}$ and the ratio of cis to trans cyclopropane should increase with diene concentration (although the yield of cyclopropane would obviously be drastically reduced). Although the stereochemistry of the reaction in the absence of diene was already heavily toward the stereospecific side, from the data in Table 1 it is clear that hexadiene essentially eliminates trans-cyclopropane and oxygen -- another known triplet scavenger[1,3] -- may also increase the stereospecificity of the reaction.

In contrast to the above, if the manifold is entered at the triplet in the presence of a singlet scavenger and if restraints similar to those above are applied, the cis:trans ratio is predicted to be inversely proportional to the scavenger concentration.

Finally, it should be mentioned that the gross results predicted above are not affected if the triplet scavenger also reacts with singlet carbene (or singlet scavenger with triplet) nor if the triplet carbene gives some *cis*-cyclopropane as well as *trans*. The effect of scavenger on stereochemistry will depend only on the point of entry into the manifold and the degree to which the various restrictions are met.

Thus from the results in Table 1, it is clear that β-naphthylcarbene from rearrangement of benzocycloheptatrienylidene enters the singlet-triplet manifold as a singlet.

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4. Cf. W. M. Jones, R. C. Joines, J. A. Myers, T. Mitsuhashi, K. E. Krajca, E. E. Waali, T. L. Davis and A. B. Turner, J. Amer. Chem. Soc., **95**, 826 (1973).

Table 1

Stereochemistry of Addition of β-Naphthylcarbene

to *cis*-2-Butene[a]

Tosylhydrazone Sodium Salt Solvent System (molar ratio)	% "Wrong Isomer"[b,c]
Naphthaldehyde *cis*-2-butene	10[d]
Benzotropone *cis*-2-butene	7

Benzotropone *cis*-2-butene/benzene (1:3)	6
Benzotropone *cis*-2-butene/perfluorocyclobutane (1:2)	6
Benzotropone *cis*-2-butene/perfluorocyclobutane (1:6)	6
Benzotropone *cis*-2-butene/oxygen (saturated)	4
Benzotropone *cis*-2-butene/2,4-hexadiene (1.0:1.5)	1

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[a] research grade 99.94 mole %

[b] 1-(2-naphthyl)-*trans*-2,3-dimethylcyclopropane

[c] standard deviations were typically ± 1

[d] datum only approximate due to interfering material