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TRIPLET CYCLOPROPYLIDENE

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Singlet cyclopropylidenes are known both to add to olefins to form spiropentanes and undergo ring opening to allenes (2). However, the chemistry of the triplet species is almost unexplored. This communication reports theoretical predictions concerning its expected behavior.

In analogy with the singlet one might expect triplet cyclopropylidene to open to allene or undergo the usual reactions of a triplet carbene (3). A recent Pariser-Parr-Pople type calculation on allene (4) is relevant to deciding which of these alternatives should obtain. It predicts that the lowest triplet allene which retains the geometry of the ground state lies about 100 kcal./mole above it. A table of bond energies (5), the experimental strain energy of cyclopropane (6), and a semi-empirical value calculated for the energy difference between singlet and triplet methylene (7) allow one to estimate that triplet cyclopropylidene lies roughly 60 kcal. above the ground state of allene. Therefore, since the lowest triplet allene possessing the ground state geometry lies well above triplet cyclopropylidene, opening to an allene of this geometry is not expected on purely thermodynamic grounds.

However, the same theoretical treatment (4) shows that a geometry where substituents on the terminal carbons are coplanar is favored for the lowest triplet, a prediction which preliminary experiments with the sensitized irradiation of a suitably substituted optically active allene appear to confirm (8). The planar triplet is calculated to lie about 60 kcal./mole above the allene ground state; and the similarity of its energy to that computed for triplet cyclopropylidene suggests that transformation of the latter into the former by ring opening might occur, especially if the cyclopropylidene were generated with excess energy.

Three modes of opening the ring to yield the planar triplet can be envisaged--

conrotatory, disrotatory (9), and nonrotatory. In the latter process, as the C_2-C_3 bond cleaves, the orbitals on these carbon atoms would interact with the orbital on the central carbon in the plane of the ring (hereafter referred to as p_1). This process, as the name implies, does not require rotation, in contrast to the other two processes where the orbital perpendicular to the plane of the ring (p_2) is used to form the incipient allylic system. Correlation diagrams can be used to elucidate the consequences of each of these reaction modes, as has already been done for the cyclopropyl cation, radical, and anion (10). Table I shows the symmetry classification of the σ, σ^*, p_1, and p_2 orbitals in cyclopropylidene and the three allyl molecular orbitals and the lone p orbital in the planar allene for all three modes of opening. In Table II are listed the lowest triplet states of each symmetry class for each mode of opening.

TABLE I

Symmetry Classification of Orbitals in Cyclopropylidene and Planar Allene

Opening Mode	Symmetry	Cyclopropylidene	Planar Allene
Conrotatory	C_2: a	σ, p_1	p, Ψ_2
	b	p_2, σ^*	Ψ_1, Ψ_3
Disrotatory	C_s: a'	σ, p_1, p_2	Ψ_1, p, Ψ_3
	a''	σ^*	Ψ_2
Nonrotatory	C_{2v}: a_1	σ, p_1	Ψ_1, Ψ_3
	b_2	p_2	p
	b_1	σ^*	Ψ_2

TABLE II

Lowest Triplet States in Cyclopropylidene and Planar Allene

Opening Mode	Symmetry	Cyclopropylidene	Planar Allene
Conrotatory	C_2: A	$\sigma p_1 p_2^2$	$\Psi_1^2 p \Psi_2$
	B	$\sigma^2 p_1 p_2$	$\Psi_1 p^2 \Psi_2$
Disrotatory	C_s: A'	$\sigma^2 p_1 p_2$	$\Psi_1^2 p \Psi_3$
	A''	$\sigma^2 p_1 \sigma^*$	$\Psi_1^2 p \Psi_2$
Nonrotatory	C_{2v}: A_2	$\sigma^2 p_2 \sigma^*$	$\Psi_1^2 p \Psi_2$
	B_2	$\sigma^2 p_1 p_2$	$\Psi_1^2 p \Psi_3$

It is evident from Table II that the triplet ground state of cyclopropylidene, $\sigma^2 p_1 p_2$, is of different symmetry than that of the planar allene, $\Psi_1^2 p \Psi_2$, for all modes of opening. Thus, it will be strictly correlated with excited states of the planar allene which are calculated (4) to lie at least 60 kcal./mole above the lowest triplet; and opening of triplet cyclopropylidene to planar triplet allene is not expected to occur. Similarly, planar triplet allene is not expected to close to a triplet cyclopropylidene.

The only relevant experimental work relating to this subject is that of Skell and Engel on the addition of ^3p carbon atoms to olefins (11). They show that triplet cyclopropylidene is an intermediate and only spiropentanes are produced. Further experimental work on triplet planar allene and cyclopropylidene is in progress in this laboratory.

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