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The Mechanism of Photochemical Rearrangement of Vinylcyclopropanes to Cyclopentenes

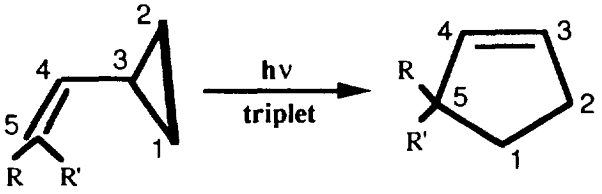
Ming-Der Su

DRAL Daresbury Laboratory, Warrington WA4 4AD, UK

Abstract: The spin-orbit coupling parts of the effective one-electron Hamiltonian operators, with the inclusion of symmetry, have been used to formulate the mechanism of spin inversion in triplet photoreaction for radiationless decay to singlet ground state product. This has been applied to investigate the photochemical behaviour of vinylcyclopropane. A reaction mechanism that satisfies the requirements of both spin-inversion and orbital symmetries is suggested.

INTRODUCTION

The photochemical rearrangement of vinylcyclopropanes to cyclopentenes as illustrated in (**1**) has been a subject of much interest over the past thirty years[1]. Such a ring expansion process can also apply to other bicycloalkene (with a three-membered ring) systems, producing products more complex than the reactant itself as shown in (**2**-**4**)[2].



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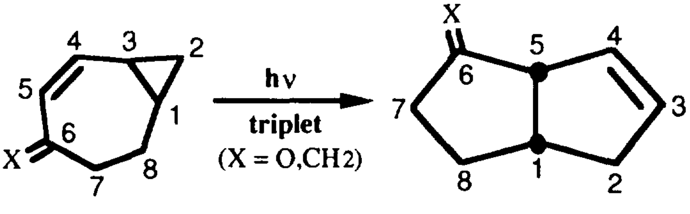

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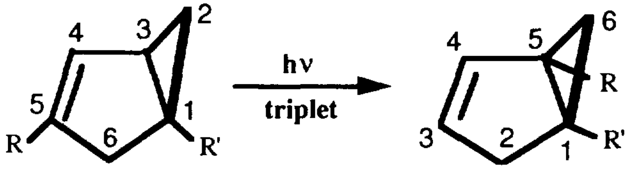

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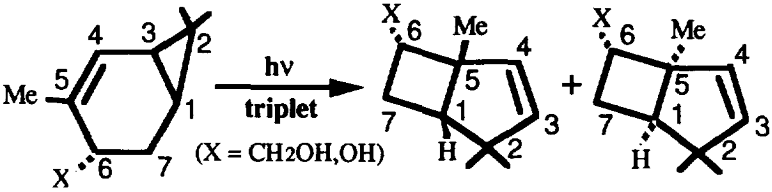


(4)

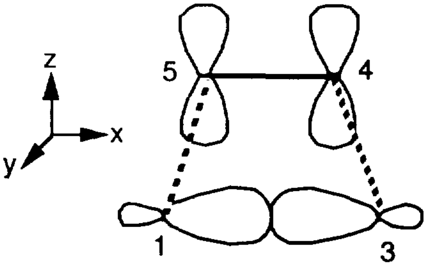
On the basis of classic sensitization and quenching studies, it was found that triplet excited states are exclusively responsible for the variety of those photoproducts[1,2]. In the case of a triplet reaction, a spin inversion process is required for the radiationless decay to either the ground singlet state reactants or products. To the author's knowledge, theoretical analyses of this crucial triplet cycloaddition reaction using the spin-orbit (SO) coupling method are still lacking. We therefore report our investigation of the photochemical behaviour of the vinylcyclopropanes and related systems from a unified point of view and delineate the significant role played by SO coupling and symmetry in controlling the mode of cycloaddition.

THEORY

The efficiency of spin inversion is proportional to the SO coupling matrix element $< T_1 \mid \hat{H}_{SO} \mid S_0 >$, and inversely proportional to the energy gap separating the singlet (S_0) and triplet (T_1) states[3]. Moreover, efficient spin inversion can be enhanced by motions, Q_k, which maximize the SO coupling matrix element and minimize the T_1-S_0 separation[4]. We then use group theory to search for potentially efficient spin inversion motions $(Q_k)^4$, thus

$$\Gamma(Q_k) = \Gamma(T_1^\nu)\times\Gamma(\mathbf{R_k})\times\Gamma(S_0) \qquad (k = x, y, z) \tag{1}$$

where $\Gamma(T_1{}^v)$ and $\Gamma(S_0)$ are the representations of the spatial part (v) of $T_1{}^v$ and S_0, respectively, and the $\Gamma(\mathbf{R_k})$ are the representations of the spin wave functions which transform as the rotation vectors $\mathbf{R_k}$ (k = x, y, z) in the point group of the triplet complex[3].

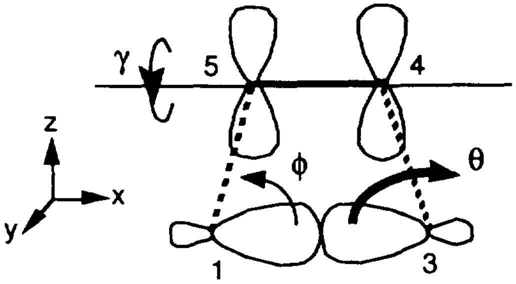


$\Gamma(S_0) = A'$
$\Gamma(T_1^v) = A'$
$\Gamma(R_x) = A''$
$\Gamma(R_y) = A''$
$\Gamma(R_z) = A'$

(5)

RESULTS AND DISCUSSIONS

We now use this principle to discover the motions that induce spin inversion in the $^3\pi\pi^*$ state of vinylcyclopropane. A system (5) consisting only of the reacting π and σ bonds will serve as a model to describe the stereochemical features of a spin-inversion mechanism. For simplicity, symmetries will be designed with respect to the molecular plane (xy) which bisects the π bond (the nodal plane). Using eq(1), we thus obtain the symmetries of the Q_k's in the C_s group as follows, $\Gamma(Q_x) = \Gamma(Q_y) = A' \times A'' \times A' = A''$ and $\Gamma(Q_z) = A' \times A' \times A' = A'$. Therefore, in order to maximize the y component of a two-centre SO coupling interaction, orthogonal p_x-p_z atomic orbitals (AOs) are required[5]. A motion that meets the above requirement is (6) which consists of the C-5 pπ orbital (γ, along the x axis) and a cleavage rotation of the C-1 pσ orbital (ϕ, along the z axis) as well as C-3 pσ orbital (θ, along the y axis).



(6)

Moreover, the relative SO coupling efficiency of the mechanisms can be estimated by evaluating the molecular orbital (MO) angular momentum ($\hat{l}_k$) matrix elements[6]:

$$\left\langle \hat{H}_{so} \right\rangle_k = C \cdot \left\langle HOMO \left| \frac{\hat{l}_k \cdot \hat{s}_k}{r^3} \right| LUMO \right\rangle \quad (k = x, y, z) \qquad (2)$$

where C is a constant[3]. HOMO and LUMO are the highest occupied and lowest unoccupied delocalized MOs of the molecular system, respectively. Further, the HOMO and the LUMO may be expressed as a function of the cleavage angles γ, ϕ, and θ as shown in (6)[7]. This leads to the following expression for the y component of the SO coupling ($a \approx b$):

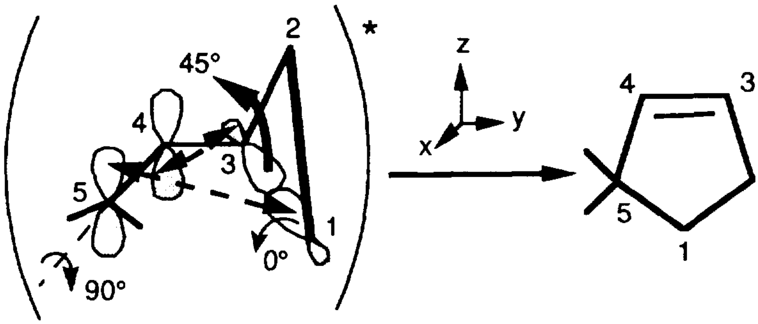
$$\left\langle \hat{H}_{so} \right\rangle_y = \frac{\hbar^2 C}{2\sqrt{2}} \cdot \left[\left(a^2 + b^2\right) V^{\pi}_{15} \cos\gamma \cos\phi \right.$$
$$\left. + \left(a^2 + b^2\right) V^{\pi}_{34} \cos\theta + ab(V^{\sigma}_{13} + V^{\pi}_{13}) \sin\theta \cos\phi\right] \qquad (3)$$

For convenience, we use V^{σ} and V^{π} to describe σ- and π-interactions, respectively[4]. Thus

$$V^{\sigma}_{mn} = \left\langle p_{my}\left|\frac{1}{r_m^3}+\frac{1}{r_n^3}\right|p_{ny}\right\rangle,\ V^{\pi}_{mn} = \left\langle p_{mz}\left|\frac{1}{r_m^3}+\frac{1}{r_n^3}\right|p_{zn}\right\rangle, \ldots\ldots etc.$$

where *m* and *n* are positions of the atomic centres. Additionally, V^{σ} and V^{π} behave similarly to the corresponding atomic overlap integral such that $|V^{\sigma}| > V^{\pi} > 0$ and $V^{\sigma} < 0^4$. Hence, the last term in eq(3) is negative and is not added to the other terms.

At $\theta = \phi = 0°$ the SO coupling expression reaches a maximum when $\gamma = 90°$ where the olefinic moiety has a perpendicular conformation. In this geometry the system returns to its ground state reactant after a spin-inversion. Alternatively, it can reach a higher maximum SO coupling matrix element at $\gamma = 90°$, $\theta = 45°$, $\phi = 0°$. A schematic representation of a distortion complex corresponding to those angular characteristics is shown in (7) using the colouring convention of the p AOs to indicate the directional changes.



(7)

The double headed arrows indicate the bonds to be formed and the single headed arrows indicate the modes of π bond rotation and the σ bond cleavage. It begins with 1-4 bridging in the excited state, with the terminal carbon of the vinyl group bonding to the C-1 (or C-2) atom of the three-membered ring, accompanied by fission of the C-1 – C-3 (or C-2 – C-3) σ bond. Simultaneously, an inversion occurs at the C-3 atom to form a π bond between C-3 and C-4, producing the cyclopentene product. In addition, from (7), evidently this spin-inversion mechanism is identical with the formal photo-allowed pathway $[_{\sigma}2_a + _{\pi}2_a]^8$. Moreover, our mechanistic interpretation for such photorearrangements, which undergo a concerted process with internal bond fission, bears a similarity to the allylic biradical intermediate proposed by Jorgenson[2(a,b)], Zimmerman[2(f)], and Wilzbach[2(g)], although the latters apparently occur in a non-concerted process. Further, repeating the procedure for $<\hat{H}_{SO}>_x$ and $<\hat{H}_{SO}>_z$ leads to much smaller SO coupling expressions. Accordingly, spin inversion will occur faster only in the *y* sublevel.

In summary, the photorearrangement of the vinylcyclopropane to the cyclopentene is a case where spin-inversion and orbital-symmetry requirements conspire to produce the same product. It was proved that whenever both orbital-symmetry and spin-inversion requirements are met along the same reaction coordinate, the reaction can be stereospecific[4(c-e)]. It is therefore concluded that the photorearrangement discussed in this work is completely stereospecific and proceeds via a concerted process. This prediction has been verified in the case of vinylcyclopropane as well as bicycloalkene (with a three-membered ring) system as shown in (**1**-**4**)[1,2,9].

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(5) This view is also applicable to the x component situation, but we will not consider it further since the x component path is unable to lead to the experimentally-existing molecular conformations.

(6) For details see ref.(3,4) and M.-D. Su, Chem. Phys. Lett., in press.

(7) The valence molecular orbitals associated with this motion are given as follows,

$$HOMO = a(p_{1z}\cos\phi - p_{1y}\sin\phi - p_{3z}\cos\theta + p_{3z}\sin\theta) + b(p_{4z} + p_{5z}\cos\gamma + p_{5y}\sin\gamma) \text{ and } LUMO = b(p_{1z}\cos\phi - p_{1y}\sin\phi + p_{3z}\cos\theta - p_{3z}\sin\theta) + a(p_{4z} - p_{5z}\cos\gamma - p_{5y}\sin\gamma).$$

(8) Woodward, R. B. and Hoffmann, R., "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim, 1970; pp 65.

(9) It was found that the mechanistic interpretation for the photorearrangement of vinylcyclopropane can also apply to that of 3-vinylcyclopropene. For details see M.-D. Su, manuscript submitted.

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