Mechanism for the Photorearrangements of Cyclohexadienes

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Some time ago Zimmerman and Epling reported that sensitized irradiation of the 5,5-diphenyl-1,3-cyclohexadiene results in formations of the stereoisomeric *trans*-(**A**) and *cis*-5,6-diphenylbicyclo[3,1,0]hex-2-ene (**B**) and *trans*-4,5-diphenylcyclo[3,1,0]hex-2-ene (**C**) as shown in Scheme 1. This reaction is remarkably stereoselective, yielding the trans-5,6-bicyclic (**A**) olefin in preference to the *cis*-5,6-bicyclic olefin (**B**) in the ratio of 91:9, with the *trans*-4,5-bicyclic olefin (**C**) as the minor product. One important feature of such a photorearrangement is that the triplet excited state ($^3\pi\pi^*$) is exclusively responsible for the variety of previous mentioned photoproducts.[1] Thus, in the case of a triplet reaction, a spin inversion process is required for decay to either the ground singlet state reactants or products in a radiationless way. To our knowledge, there is no theoretical model or calculation which has explained such a crucial photorearrangement. Therefore, in this note we report our investigation of the photochemical behavior of 5,5-diphenyl-1,3-cyclohexadiene and delineate the significant role played by spin-orbit (SO) coupling and symmetry in controlling the mode of phenyl migration as well as cyclocontraction.

The theory can be traced back to previous papers by Lin, Salem, and Rowland as well as Epiotis and Shaik[3] and has been extensively applied in this work. The efficiency of spin inversion is proportional to the SO coupling matrix element $\langle T_1|\hat{H}_{SO}|S_0\rangle$, and inversely proportional to the energy gap separating the singlet (S_0) and triplet (T_1) states.[2] Moreover, efficient spin inversion can be enhanced by motions, Q_k, which maximize the SO coupling matrix element and minimized the T_1-S_0 separation.[3] We then use group theory to search for potentially efficient spin inversion motions (Q_k),[3] thus

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

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.[2]

Scheme 1

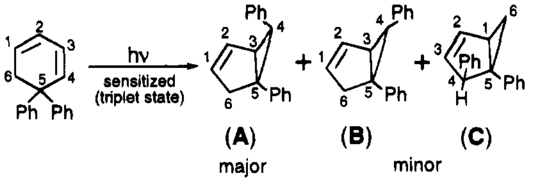


Chart 1

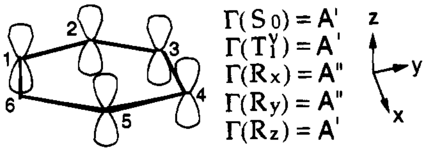
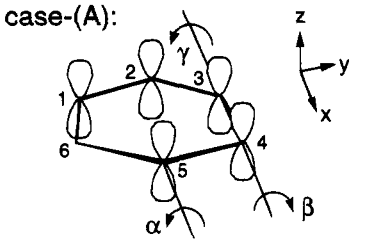


Chart 2



Firstly, we will investigate the 1,2-phenyl migration mechanism producing *trans*- (**A**) and *cis*-5,6-bicyclic olefin (**B**), which is called case-(A) as given in Chart 1. In this case there is one molecular plane (xy) which bisects the $p\pi$ orbitals of these C-1–C-5 atoms of cyclohexadiene (the nodal plane). Hence, the orbital (spatial) part of the $^3\pi\pi^*$ state is symmetric (A') with respect to this molecular 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 $\Gamma(Q_z) = A' \times A' \times A' = A'$. Hence, in order to maximize the x component of a two-center SO coupling interaction, a y, z perpendicular atomic orbital relationship is needed.[2,4] Further, a motion which meets the above requirement is shown in Chart 2 which consists of a disrotation of the C-3, C-4 $p\pi$ orbitals as well as a disrotation of the C-4, C-5 p orbitals, both rotations being based on the symmetry requirement and chemical intuition. Furthermore, the molecular orbitals (MOs) of the complex after rotation by α, β, γ in the direction shown in Chart 2 can be expressed as follows,[5]

$$\mathrm{HOMO} = a(p_{1z} - p_{2z} - p_{3z}\cos\gamma + p_{3y}\sin\gamma + p_{4z}\cos\beta + p_{4y}\sin\beta) + b(p_{5z}\cos\alpha - p_{5y}\sin\alpha) \quad (2)$$

$$\mathrm{LUMO} = b(p_{1z} + p_{2z} - p_{3z}\cos\gamma + p_{3y}\sin\gamma - p_{4z}\cos\beta - p_{4y}\sin\beta) + a(p_{5z}\cos\alpha - p_{5y}\sin\alpha) \quad (3)$$

Similarly, we may also examine the case-(B), which can lead to the *trans*-4,5-bicyclic olefin (**C**) photoproduct. Since the model of case-(B) is quite similar to that of case-(A), the symmetry requirements for the latter also apply to the former. Thus, the MOs of the complex, after a rotation by μ as well as disrotation by α and β in the direction shown in Chart 3, may be written as

$$\mathrm{HOMO} = a(p_{1z}\cos\mu - p_{1x}\sin\mu - p_{2z} - p_{3z} + p_{4z}\cos\beta + p_{4y}\sin\beta) + b(p_{5z}\cos\alpha - p_{5y}\sin\alpha) \quad (4)$$

$$\mathrm{LUMO} = b(p_{1z}\cos\mu - p_{1x}\sin\mu + p_{2z} - p_{3z} - p_{4z}\cos\beta - p_{4y}\sin\beta) + a(p_{5z}\cos\alpha - p_{5y}\sin\alpha) \quad (5)$$

The relative SO coupling efficiency of the mechanisms

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(1) (a) Zimmerman, H. E.; Epling, G. A. *J. Am. Chem. Soc.* **1970**, *92*, 1411–1412. (b) Swenton, J. S.; Crumrine, A. R.; Walker, T. J. *J. Am. Chem. Soc.* **1970**, *92*, 1406–1407. (c) Zimmerman, H. E.; Epling, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 8749–8761. (d) Zimmerman, H. E. Tetrahedron, **1974**, *30*, 1617–1628. (e) Hixson, S. S.; Mariaano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531–551. (f) Swenton, J. S.; Hyatt, J. A.; Walker, T. J.; Crumrine, A. L. *J. Am. Chem. Soc.* **1970**, *93*, 4808–4815.

(2) (a) McGlynn, S. O.; Azumi, T.; Kinoshita, M. *The Triplet State*; Prentice-Hall Inc.: New York, 1969; pp 190–198. (b) McGlym, S. O.; Vanquickenborne, L. G.; Kinoshita, M.; Carroll, D. G. *Introduction to Applied Quantum Chemistry*; Holt, Rinehart, and Winston: New York, 1972; Chapter 11.

(3) (a) Lin, S. H. *J. Chem. Phys.* **1966**, *44*, 3759–3765. (b) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92–111. (c) Shaik, S.; Epiotis, N. D. *J. Am. Chem. Soc.* **1978**, *100*, 18–29. (d) Shaik, S. *J. Am. Chem. Soc.* **1979**, *101*, 3184–3196. (e) Shaik, S.; Epiotis, N. D. *J. Am. Chem. Soc.* **1980**, *102*, 3184–3196. (f) Su, M.-D. *Tetrahedron* **1995**, *51*, 5871–5876. (g) Su, M.-D. *Chem. Phys.*, manuscript submitted.

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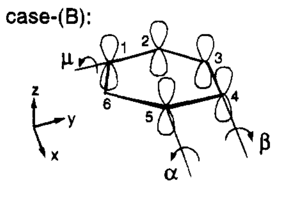
Chart 3



may be estimated by evaluating the MO angular momentum ($\hat{l}_k$) matrix elements:[3,6]

$$\langle \hat{H}_{SO}\rangle_k = C\left\langle \mathrm{HOMO}\left|\frac{\hat{l}_k\cdot\hat{s}_k}{r^3}\right|\mathrm{LUMO}\right\rangle \qquad \left(C = \frac{Z_N^*e^2}{2m^2c^2};\ k = x, y, z\right) \quad (6)$$

where HOMO and LUMO are the highest occupied and lowest unoccupied delocalized MOs of the molecular system.[7] Substituting eqs 2−5 in eq 6, the x components of the SO coupling matrix elements for case-(A) and case-(B) are given by

$$\text{case-}(A){:}\ \langle \hat{H}_{SO}\rangle_x = \frac{-i\hbar^2C}{4\sqrt{2}}[(a^2 - b^2)(V^\sigma_{35} + V^\pi_{35})\sin(\gamma-\alpha) + (a^2 + b^2)(V^\sigma_{45} + V^\pi_{45})\sin(\alpha + \beta) - 4abV^\pi_{34}\sin(\gamma + \beta)] \quad (7)$$

$$\text{case-(B)}{:}\ \langle \hat{H}_{SO}\rangle_x = \frac{-i\hbar^2C}{4\sqrt{2}}[(a^2 - b^2)(V^\sigma_{15} + V^\pi_{15})\sin\alpha\cos\mu + (a^2 + b^2)(V^\sigma_{45} + V^\pi_{45})\sin(\alpha + \beta) + 2ab(V^\sigma_{14} + V^\pi_{14})\sin\beta\cos\mu] \quad (8)$$

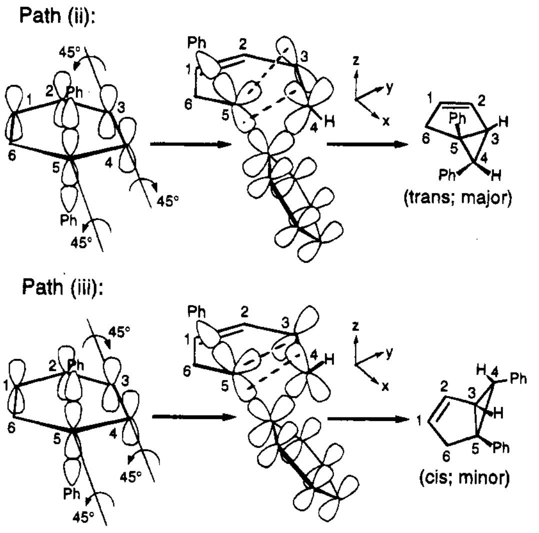
For convenience, we use V^σ and V^π to describe σ- and π-interactions, respectively[3c−e] That is,

$$V^\sigma_{mn} = \left\langle p_{my}\left|\frac{1}{r_m^3} + \frac{1}{r_n^3}\right|p_{ny}\right\rangle, \qquad V^\pi_{mn} = \left\langle p_{mz}\left|\frac{1}{r_m^3} + \frac{1}{r_n^3}\right|p_{nz}\right\rangle, \ldots\ldots \textit{etc.}$$

where m and n are atomic centers position. Additionally, V^σ and V^π behave similarly to the corresponding atomic overlap integral such that, in general, $|V^\sigma| > V^\pi > 0$ and $V^\sigma < 0$.[3d]

For case-(A) the third term in eq 7 is therefore additive and may reach an extreme when the following conditions apply: (i) $\alpha = \beta = 0°$, $\gamma = 90°$, (ii) $\alpha = \beta = \gamma = 45°$, and (iii) $\beta = \gamma = 45°$, $\alpha = -45°$. For path i, where the olefinic moiety has a perpendicular conformation, the system thus inverts a spin and relaxes to a ground-state reactant. The 3-dimensional diagrams of the mechanisms during the phenyl migration from C-5 to C-4 for path ii and path iii, which may lead to a *trans* or a *cis* isomer, are shown in Scheme 2. For path ii, it can be seen that the *trans*-product is generated by disrotations of C-3 and C-4 as well as C-4 and C-5, which in turn undergoes a disrotatory ring cleavage to a diradical complex containing two σ orbitals each on C-4 and C-5 center, simultaneously followed by bond-recoupling as shown by the dotted lines in path ii, indicating the bonds which are to be formed. Alternatively, the *cis*-product would be accessible by a conrotatory motion at C-4 and C-5 as well as a disrotatory motion at C-3 and C-4 in a concerted process, producing a cyclization of the three-membered ring by concomitant phenyl migration. It should be noted that the stereochemistry given in *trans*- and *cis*-products obviously involves use of both σ and p lobes at C-5 and thus leads to inversion of configuration at C-5. Therefore, the preference for path ii may derive from better initial overlaps between the σ orbital lobes and the p lobes on interacting carbons and/or the requirement for less motion of the two σ−p coupling orbitals on the path to the transition state leading to full bonding.

Scheme 2



Conversely, for case-(B), eq 8 reaches a maximum at $\alpha = \beta = 45°$, $\mu = 0°$, when the 1,2-phenyl migration occurs. Then the system either returns to a ground-state reactant after a spin-inversion or forms a allyl−benzyl diradical intermediate and subsequently leads to a singlet product (**C**) via a ring closure.[8] This complex corresponding to the angular characteristics is illustrated in Scheme 3. Further, repeating the procedure for $\langle \hat{H}_{SO}\rangle_y$ and $\langle \hat{H}_{SO}\rangle_z$ for both case-(A) and case-(B) leads to much smaller SO coupling expressions. Accordingly, spin inversion will occur faster merely in x sublevel.

Moreover, since the case-(A) mechanism competes with the case-(B) one, we may reexamine their SO coupling matrix expressions and show that

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[4] This view is also applicable to the y component situation, but we will not discuss it here since the y component path is unable to lead to the experimentally-existing molecular conformations.

[5] Both HOMO and LUMO can be expressed as a function of the rotation and bending angles, see ref 3c−e.

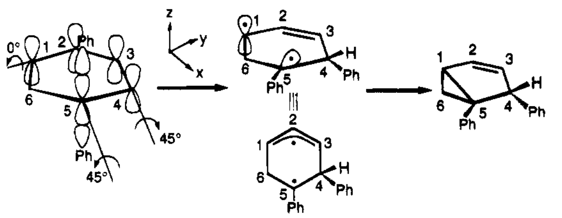
[6] For instance, consider a SO matrix element connecting a singlet state S_0 with a triplet state T_1, where S_0 is derived from a configuration [ ]a^2 and where T_1 is derived from a configuration [ ]a^1b^1. The brackets denote filled MOs and a and b are valence MOs. In this case, one can obtain $\langle S_0|\hat{H}_{SO}|T_1\rangle = N\langle \alpha\beta|\hat{h}_{SO}|b\alpha\rangle$ where $\hat{h}_{SO}$ is the one-electron SO operator and N is a constant. α and β stand for spin-up and spin-down, respectively. From this simple result, one can see that S_0 and T_1 configurations must differ in the occupancy number of not more than one molecular orbital.

[7] Z_N^* stands for the effective nuclear charge of nucleus N. The r_{iN} stands for the distance between electron i and nucleus N. The $\hat{l}(i)$ and $\hat{s}(i)$ are the orbital and spin angular momentum operators for electron i, respectively.

[8] This common allylic diradical may then decay to those three observed products with different rates. Nevertheless, as discussed in this work, the path ii (*trans*-isomer) will occur preferentially than the case-(B) (allyl−benzyl diradical).

[9] (a) Gilchrist, T. L.; Storr, R. C. *Organic Reactions and Orbital Symmetry*, 2nd. ed.; Cambridge University Press: Cambridge, 1979; pp 242−265. (b) Gill, G. B.; Willis, M. R. *Pericyclic Reactions*; Chapman and Hall: London, 1974; pp 178−181.

Scheme 3



path ii (α = $\beta = \gamma$ = 45°):

$$\langle \hat{H}_{\mathrm{SO}} \rangle_x = \frac{-i\hbar^2 C}{4\sqrt{2}}[(a^2 + b^2)(V_{45}^{\sigma} + V_{45}^{\pi}) - 4abV_{34}^{\pi}] \tag{9}$$

path iii ($\beta = \gamma$ = −α = 45°):

$$\langle \hat{H}_{\mathrm{SO}} \rangle_x = \frac{-i\hbar^2 C}{4\sqrt{2}}[(a^2 - b^2)(V_{45}^{\sigma} + V_{45}^{\pi}) - 4abV_{34}^{\pi}] \tag{10}$$

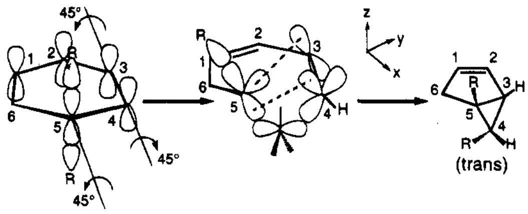
case-(B) (α = β = 45°, μ = 0°):

$$\langle \hat{H}_{\mathrm{SO}} \rangle_x = \frac{-i\hbar^2 C}{4\sqrt{2}}[0.71(a^2 - b^2)(V_{15}^{\sigma} + V_{15}^{\pi}) + (a^2 + b^2)(V_{45}^{\sigma} + V_{45}^{\pi}) + 1.41ab(V_{14}^{\sigma} + V_{14}^{\pi})] \tag{11}$$

It is apparent that $|(\text{eq } 9)^2| \gtrsim |(\text{eq } 11)^2| > |(\text{eq } 10)^2|$ since $2V_{34}^{\pi} > (V_{15}^{\sigma} + V_{15}^{\pi}) > (V_{14}^{\sigma} + V_{14}^{\pi})$.[3b] Consequently, we conclude that *the trans-5,6-bicyclic olefin (**A**) is expected, in general, to be kinetically more favored than other competing 1,2 phenyl-migrated bicyclic olefins (**B**, **C**) as a result of the larger SO coupling expression as well as the better initial orbital overlaps (owing to the less geometric motion).* This is exactly what is observed experimentally.[1]

Several intriguing points are noteworthy. Firstly, as seen in Scheme 2, the 1,2-migration of phenyl group is favorable because the migrating center can utilize both its sp^2-σ orbital as well as an orthogonal p-π orbital to obtain better overlaps with orbital lobes of C-4 and C-5 which facilitate the transfer. Hence, in addition to aromatic groups (e.g., phenyl, naphthyl, etc.), the migration nature and rationale behind it may be readily extended to any substituent which has an sp^2-σ orbital as well as an orthogonal p-π orbital. For example, the valence orbitals of vinyl and acyl groups play the same role and are topologically analogous to the phenyl sp^2-σ and p-π orbitals. It is therefore expected that *the vinyl and acyl substituents at C-5 should easily migrate to the C-4 center and the trans-5,6-bicyclic olefin would be a predominant photoproduct.* Secondly, this 1,2-shift, by way of a six-electron three-center transition state, can also be viewed as an $[_{\pi}2 + {}_{\sigma}2 + {}_{\sigma}2]$ reaction.[9] Hence, it was suggested that an antra-supra-supra interaction is required for electronic stability, and geometry requires that the inversion occurs at the migrating group rather than at the migration terminus as shown in Scheme 4. This is, clearly, impossible for the migration of hydrogen as well as alkyl groups since either the poor orbital overlap or extreme crowding in the transition state make the shift exceedingly unlikely.[9] Accordingly, it is predicted that *only aryl, vinyl, and acyl groups at C-5 are capable of undergoing the 1,2-migration rather than the proton as well as the alkyl groups.*[10] Thirdly, it has been proved that the 1,2-phenyl migration through the four-electron three-center transition state may show the following order of tendency to transfer: *electron-withdrawing phenyl substituents* > *phenyl* > *electron-releasing phenyl substituents*, which is probably due to the more effective delocalization of extra electron densities.[11] This prediction is based on the substrate, solvent system, and other reaction conditions being the same or nearly the same for the cases studied. Fourthly, considering the case where a $\approx b$ (and thus $2ab \approx a^2 + b^2$),[3d] which corresponds to the interacting MOs in eqs 2 and 3 and eqs 4 and 5 being electronically similar, one can see that only eq 9 still reaches the maximum. This implies that *path ii (i.e., the trans-5,6-bicyclic olefin (**A**)) is preferred in a nonpolar solvent.* On the other hand, if the MOs become polarized with $a > b$, then $(a^2 + b^2)$ becomes larger than $2ab$. In the extreme case, the MO polarization makes $2ab \rightarrow 0$ while $(a^2 + b^2)$ approaches unity. Hence, the SO coupling expression in eqs 10 and 11 will lead to an extreme when $a > b$ (but not a $\gg b$). It is therefore anticipated that *the formation of cis-5,6-bicyclic olefin (**B**) and trans-4,5-bicyclic olefin (**C**) will take place preferentially in a polar (but not highly polar) solvent.* Fifthly, it is well-known that introduction of the heavy atom increases the radiationless decay rate for the triplet state.[2,12] In other words, the system, via the agency of the heavy atom, can provide the needed orthogonal atomic orbitals' interactions without any need of distortions. It is therefore predicted that *the efficiencies of photorearrangements of the sensitized cyclohexadienes will reflect the same trend for heavy-atom substitution (for instance, H, Cl, Br, etc.).* Unfortunately, there is insufficient stereochemical data for 5,5-disubstituted-1,3-cyclohexadiene to prove or disprove our above predictions.

Scheme 4



In summary, this work represents an attempt to apply group theory to search for the motions which lead to spin inversion and then evaluate their relative efficiency using delocalized MOs as the semiquantitative tool. A mechanistic interpretation for such photorearrangements in terms of a concerted process via diradicals is satisfactorily reconciled with the stereochemical results[13] and allows a number of predictions to be made. It is hoped that our study will simulate further research into the subject.

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(11) Phelan, N. N.; Jaffe, H. H.; Orchin, M. *J. Chem. Educ.* **1967**, *44*, 626–635.

(12) (a) El-Sayed, M. A. *Acc. Chem. Res.* **1968**, *1*, 18–16. (b) El-Sayed, M. A. *J. Chem. Phys.* **1963**, *38*, 2834–2838. (c) A related experiment can be found: Givens, R. S.; Chae, W. K.; Matuszewski, B. *J. Am. Chem. Soc.*, **1982**, *104*, 2456–2466.

(13) It must be emphasized that our focus on the stereochemcal results of the spin inversion mechanisms does not imply that other factors (e.g., energy barriers, reaction intermediates, etc.) are not important. Other factors such as barriers to regoranization can be considered latter as effects which may or may not modify the trend.