

The Role of Spin–Orbit Coupling and Symmetry in Oxadi- π -methane Rearrangements and Some Related Photochemical Reactions

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The spin–orbit coupling components in the effective one-electron Hamiltonian operator, with the inclusion of symmetry, have been used to formulate mechanisms of spin inversion in triplet reactions for the radiationless decay of triplet complexes to singlet ground state products. This has been applied to investigate the photochemical behavior of oxadi- π -methane rearrangement in β,γ -unsaturated carbonyl cyclic and acyclic systems. It is found that the 1,2-acyl-migrated endo isomer is the most favorable product due to its larger spin–orbit coupling expression as well as better initial overlaps (owing to the less atomic motion). Other related photorearrangements of some molecular systems, such as azadi- π -methane rearrangement, 4-aryl-substituted cyclopentenones, spirocyclic $\beta,\gamma,\delta,\epsilon$ -unsaturated ketones, and heavy atom effect, have also been investigated.

I. Introduction

As in ground state chemistry, in photochemistry the search for unifying principles has been of primary importance. With a very large number of examples of a given reaction, one can determine the minute details of the process, and our understanding of the theoretical basis of photochemistry can be enhanced.

The oxadi- π -methane (ODPM) rearrangement is one such reaction. It is well known that excited β,γ -unsaturated carbonyls undergo ODPM photorearrangement involving a formal 1,2-acyl ($\alpha \rightarrow \beta$) shift and three-membered ring formation through $\gamma \rightarrow \alpha$ bonding.^{1,2} Typical examples are illustrated in systems **1–9**,^{1,2} having an acyclic or a cyclic C=C bond.³ The results of a series of investigations permit the conclusion to be drawn that the ODPM rearrangement arises from the

$^3\pi\pi^*$ state of the enones, which is usually the lowest excited triplet state.^{1g,4} Three types of mechanisms including concerted and stepwise pathways have been suggested for ODPM photorearrangements.^{1e,2a} Mechanistic interpretations of these pathways have sometimes given ambiguous predictions, which are not consistent with experimental observations. The reason for this is presumably because those interpretations do not consider spin–orbit (SO) coupling effects. 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. This study is therefore concerned with the SO coupling terms, and simple group theory is used to explore the photochemical behavior and generality of these rearrangements.

To the author's knowledge, theoretical analyses of these crucial rearrangement reactions are still lacking.⁵ Recently, we have derived spin inversion mechanisms for triplet α,β -unsaturated cyclic ketone systems.⁶ There are several competitive mechanisms, and each may lead to a stereochemically unique product. The agreement with available experimental results was found to be very encouraging. Thus, we are able to understand the occurrence of stereospecific results in some photorearrangements of triplet cyclohexenones. We now apply these ideas to triplet excited β,γ -unsaturated carbonyl systems. Since competitive photochemistry is often encountered, a discussion on ODPM photoreactions will be presented first and then extended to examples where alternative reactivity is particularly relevant. Our aim is to search for a general theory of reactivity for such

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(1) For reviews, see: (a) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531–551. (b) Dauben, W. G.; Lodder, G.; Ipaktschi, J. *Top. Curr. Chem.* **1975**, *54*, 73–114. (c) Schaffner, K. *Tetrahedron* **1976**, *32*, 641–653. (d) Houk, K. N. *Chem. Rev.* **1976**, *76*, 1–74. (e) Schuster, D. I. *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 167–279. (f) Demuth, M. *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker, Inc.: New York, 1991; Vol. 11, pp 37–109 and references cited therein. (g) Demuth, M.; Schaffner, K. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 820–836. (h) Koppes, M. J. C. M.; Cerfontain, H. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 272–276 and references cited therein.

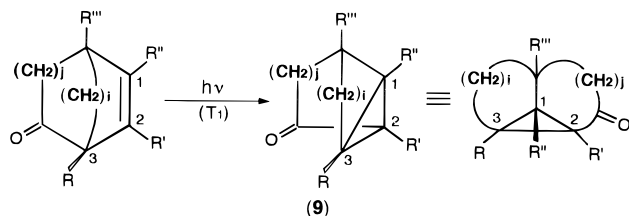
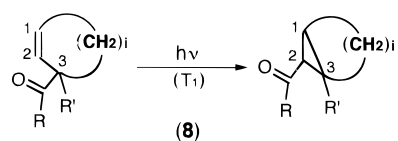
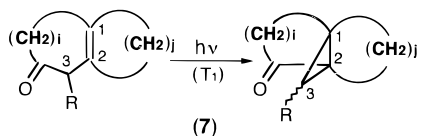
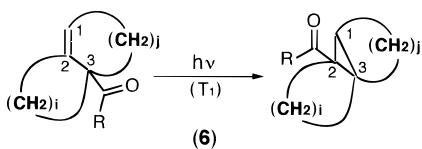
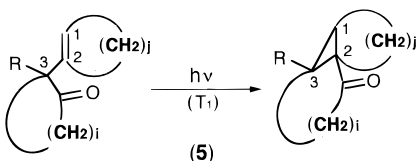
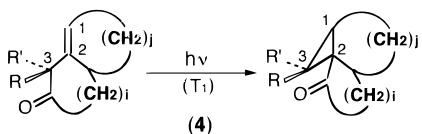
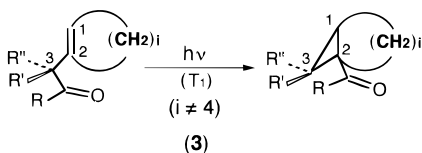
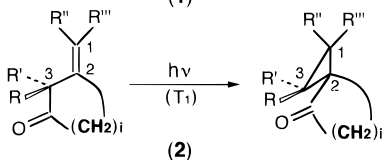
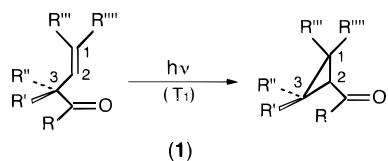
(2) (a) Dauben, W. G.; Kellogg, M. S.; Seeman, J. I.; Spitzer, W. A. *J. Am. Chem. Soc.* **1970**, *92*, 1786–1787. (b) Bellus, von D.; Kearns, D. R.; Schaffner, K. *Helv. Chim. Acta.* **1969**, *52*, 971–1009. (c) Engel, P. S.; Schexnayder, M. A.; Ziffer, H.; Seeman, J. I. *J. Am. Chem. Soc.* **1974**, *96*, 924–925. (d) Eckerley, T. J.; Rogers, N. A. J. *Tetrahedron* **1984**, *40*, 3759–3768. (e) Demuth, M.; Ritterskamp, P.; Schaffner, K. *Helv. Chim. Acta* **1984**, *67*, 2023–2027. (f) Uyehara, T.; Kabasawa, Y.; Kato, T. *Tetrahedron Lett.* **1985**, *26*, 2343–2346. (g) Schultz, A. G.; Lavieri, F. P.; Snead, T. E. *J. Org. Chem.* **1985**, *50*, 3086–3091. (h) Demuth, M.; Ritterskamp, P.; Weigt, E.; Schaffner, K. *J. Am. Chem. Soc.* **1986**, *108*, 4149–4154. (i) Reimann, B.; Sadler, D. E.; Schaffner, K. *J. Am. Chem. Soc.* **1986**, *108*, 5527–5530. (j) Singh, V.; Raju, B. N. S.; Deota, P. T. *Indian. J. Chem.* **1987**, *26B*, 301–304. (k) Ishii, K.; Hashimoto, T.; Sakamoto, M.; Taira, Z.; Asakawa, Y. *Chem. Lett.* **1988**, 609–612. (l) Koppes, M. J. C. M.; Cerfontain, H. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 549–562. (m) Koppes, M. J. C. M.; Crabbeband, A. M.; Cerfontain, H. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 676–683. (n) Singh, V.; Raju, B. N. S. *Synth. Commun.* **1988**, *18*, 1513–1514.

(3) In order to facilitate the discussion of the dependence of orbital interactions and photorearrangements on the geometries of the β,γ -unsaturated carbonyls and related systems, the numbering definition shown in **1–9** will be used throughout the whole study, unless stated otherwise. Thus, in this work, C-3 means C- α , C-2 means C- β , and C-1 means C- γ .

(4) (a) Gonzenbach, H. U.; Tegmo-Larson, I. M.; Grosdaude, J. P.; Schaffner, K. *Helv. Chim. Acta.* **1977**, *60*, 1091–1123. (b) Engel, P. S.; Schexnayder, M. A.; Phillips, W. V.; Ziffer, H.; Seeman, M. S. *Tetrahedron Lett.* **1975**, 1157–1160. (c) Dauben, W. G.; Kellogg, M. S.; Seeman, J. I.; Spitzer, W. A. *J. Am. Chem. Soc.* **1970**, *92*, 1786–1787. (d) Dauben, W. G.; Lodder, G.; Robbin, J. D. *J. Am. Chem. Soc.* **1976**, *98*, 3030–3031. (e) Kilger, R.; Korner, W.; Margaretha, P. *Helv. Chim. Acta.* **1984**, *67*, 1493–1495.

(5) Note the recent π -methane rearrangement computations, which are formally analogous to the ODPM rearrangement. (a) On a singlet reaction: Reguero, M.; Bernardi, F.; Jones, H.; Olivucci, M.; Ragazos, I. N.; Robb, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 2073–2074. (b) On a triplet reaction: Quenemoen, K.; Borden, W. T.; Davidson, E. R.; Feller, D. *J. Am. Chem. Soc.* **1985**, *107*, 5054–5059. (c) Zimmerman, H. E.; Kamath, A. *J. Am. Chem. Soc.* **1988**, *110*, 900–911.

(6) (a) Su, M.-D. *Chem. Phys. Lett.* **1995**, *237*, 317–322. (b) Su, M.-D. *J. Org. Chem.* **1995**, *60*, 6621–6623. (c) Su, M.-D. *Chem. Phys.* **1996**, in press.



rearrangement reactions from a unified point of view and to decide whether the photoproducts can be predicted through the qualitative understanding of the reaction mechanisms in the framework of the LCAO-MO (linear combination of atomic orbitals-molecular orbitals) theory.

We therefore proceed as follows. Section II briefly summarizes the SO coupling terms used. Section III is concerned with the investigation of the photochemical behaviors of the triplet β,γ -unsaturated carbonyls, to delineate the significant role played by SO coupling and symmetry in controlling the mode of acyl migration as well as three-membered ring formation. In section IV

we use our understanding of the mechanism of ODPM rearrangements to discuss and analyze some other related photorearrangement reactions, allowing us to determine the relative efficiency of the competitive reaction mechanisms. Finally, details of the SO coupling theory we used in this work are given in the Appendix.

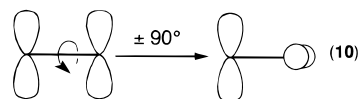
II. Theory

Since the theoretical background is described in the appendix and elsewhere,⁷⁻⁹ only a brief summary is given here. The theory can be traced back to previous papers by Lin,⁷ Salem, and Rowland,⁸ as well as Shaik and Epiotis⁹ and has been extensively applied in this work. It has to be pointed out that the concept of spin-inversion mechanisms in such triplet photoreactions was expressed for the first time by Shaik and Epiotis^{9a,c} and then by Shaik.^{9b} A very clear discussion of spin-orbit coupling in molecules has been provided by McGlynn *et al.*¹⁰

It was shown that 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.¹⁰ 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.⁷ We then use group theory to search for potentially efficient spin inversion motions (Q_k),⁹ thus

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

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.¹⁰ Further, in searching for the Q_k 's, it is suggested that archetype motions which create a strong SO coupling are usually rotations (see **10**).⁹ Moreover, it has to be mentioned that eq 1 was derived first and verified by Shaik.^{9b}



The relative SO coupling efficiency of the mechanisms may be estimated by evaluating the MO angular momentum (\hat{l}_k) matrix elements:⁹

$$\langle \hat{H}_{SO} \rangle_k = K \left\langle \text{HOMO} \left| \frac{\hat{l}_k \cdot \hat{s}_k}{r^3} \right| \text{LUMO} \right\rangle$$

$$\left(K = \frac{Z_N^* e^2}{2m^2 c^2}; k = x, y, z \right) \quad (2)$$

where HOMO and LUMO are the highest occupied and lowest unoccupied delocalized MOs of the molecular system.⁷ Inclusion of more configurations will certainly modify some features but will not alter the key conclusions since the HOMO and LUMO are supposed to be the crucial frontier MOs during the chemical reactions.

Additionally, for convenience, we use V^o and V^π to describe σ - and π -interactions, respectively.^{8,9} That is

(7) Lin, S. H. *J. Chem. Phys.* **1966**, *44*, 3759-3765.

(8) (a) Salem, L.; Rowland, C. *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 92-11. (b) Salem, L. *Pure Appl. Chem.* **1973**, *33*, 317-328.

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

$$V_{mn}^{\sigma} = \left\langle p_{my} \left| \frac{1}{r_m^3} + \frac{1}{r_n^3} \right| p_{ny} \right\rangle, \quad V_{mn}^{\pi} = \left\langle p_{mz} \left| \frac{1}{r_m^3} + \frac{1}{r_n^3} \right| p_{nz} \right\rangle, \dots \text{etc.}$$

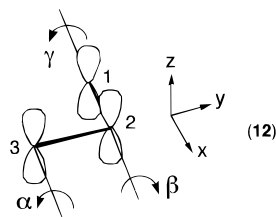
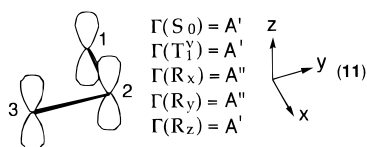
where m and n are atomic center positions. Moreover, V^{σ} and V^{π} behave similarly to the corresponding atomic overlap integral such that, in general, $|V_{mn}^{\sigma}| > V_{nm}^{\sigma} > 0$ and $V_{mn}^{\pi} < 0$.^{8,9} Hence, we shall assume a certain reaction coordinate and find the spin inversion pathways resulting from it and then compare the conclusions with available experimental data.

Before proceeding further, it must be emphasized that our focus on the stereochemical results of the spin inversion mechanisms does not imply that other factors (e.g., energy barriers, reaction intermediates, etc.) are not important. However, treating these effects along with spin-inversion would complicate the problem enormously. Hence, in order to reduce the complexity of the problem we have chosen an idealized system in which the determining variable is the efficiency of spin inversion. Other factors such as barriers to reorganization can be considered later as effects which may or may not modify the trend.

III. The Mechanism of the ODPM Rearrangements

In this section, we will use eq 1 to discover the motions which induce spin inversion in the $^3\pi\pi^*$ state of β,γ -unsaturated carbonyls.^{1g,4} A system (**11**) consisting only of the reacting p_z orbitals will serve as a model to describe the stereochemical features of spin-inversion mechanisms, which we call case A. In this model there is one molecular plane (xy) which bisects the p_z orbitals of these C-1–C-3 atoms (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 $\Gamma(Q_z) = A' \times A' \times A' = A'$. Thus, in order to maximize the x component of a two-center SO coupling interaction,¹¹ orthogonal p_y - p_z AOs are required.⁸⁻¹⁰ Therefore, **12** consists of a disrotation of the C-1, C-2 p_z orbitals as well as a disrotation of the C-2, C-3 p_z orbitals, both rotations being based on symmetry requirements and chemical intuition. This view is also applicable to the y component situation, but we will not consider it further since the y component path is unable to lead to the experimentally observed molecular conformations.

case-(A):



Furthermore, the HOMO and LUMO can be expressed as a function of rotation angles α , β , and γ in the direction

shown in ref 12. Thus one may obtain^{9,12}

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

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

After substitution of eqs 3 and 4 into eq 2, the x component of the SO coupling expression is given by

$$\langle \hat{H}_{\text{SO}} \rangle_x = \frac{-\hbar^2 K}{4\sqrt{2}} [(a^2 - b^2)(V_{13}^{\sigma} + V_{13}^{\pi}) \sin(\gamma - \alpha) + (a^2 + b^2)(V_{23}^{\sigma} + V_{23}^{\pi}) \sin(\alpha + \beta) - 4abV_{12}^{\pi} \sin(\beta + \gamma)] \quad (5)$$

Taking into account $|V^{\sigma}| > V^{\pi} > 0$ and $V^{\sigma} < 0$, the third term in eq 5 is therefore additive and may reach an extreme when the following conditions apply: (i) $\alpha = \beta = 0^\circ$, $\gamma = 90^\circ$, (ii) $\alpha = \beta = \gamma = 45^\circ$, and (iii) $\beta = \gamma = 45^\circ$, $\alpha = -45^\circ$. For path i, the system may either twist perpendicularly around the C=C bond resulting in *cis-trans* isomerization or invert a spin and then relax to a ground state reactant. This finding is in accordance with the experimentally observed photochemical behaviors of some acyclic β,γ -unsaturated aldehydes, where the vinyl group is less favorably substituted. Namely, when the C=C bond is not geometrically constrained (i.e., the bond is part of an acyclic system or not in a small ring), *cis-trans* isomerization can become so efficient that it is (almost) the only triplet process observed and the other triplet process do not complete.¹³

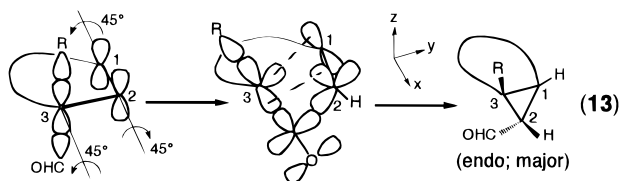
However, if either ii or iii are performed, the result may be an *endo* or an *exo* isomer, as shown in **13** and **14** respectively. For path ii, it can be seen that **13** is generated by disrotations of C-1 and C-2 as well as C-2 and C-3, which in turn undergo a disrotatory ring cleavage to a diradical complex containing two σ orbitals each on the C-2 and C-3 center. After rotating, these two σ lobes would subsequently recouple with the p orbitals of neighboring carbon atoms as shown by the dotted lines in **13**, indicating the bonds which are to be formed. Alternatively, the *exo*-product **14** would be accessible by a disrotatory motion at C-1 and C-2 as well as a conrotatory motion at C-2 and C-3 in a concerted process, producing a cyclization of the 3-membered ring accompanied by acyl migration. It must be pointed out that the stereochemistry of the transition complexes (**13** and **14**) will lead to inversion of configuration at C-3 due to the antarafacial interaction involving use of both σ and p lobes at C-3. Therefore, the preference for **13** may derive from better initial overlaps between the orbital lobes of the acyl group and the p lobes of 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. Note that, as seen in **13** and **14**, both ii and iii pathways are concerted with inversion of configuration at C-3 (C- α), which has been verified by

(11) The reason for ignoring the one-center SO coupling terms here is that the chemical bond formed arises from the overlap of orbitals at two centers and only the formation and breakage of chemical bonds are concerned in such rearrangements. Therefore, for simplicity, we did not consider the one-center effect. Even if the one-center SO coupling terms are considered, the key conclusions will not be altered.

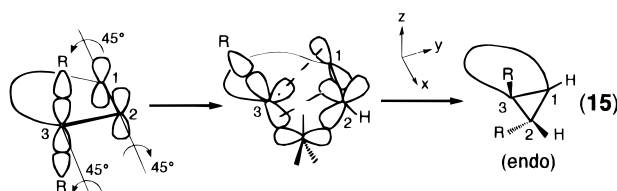
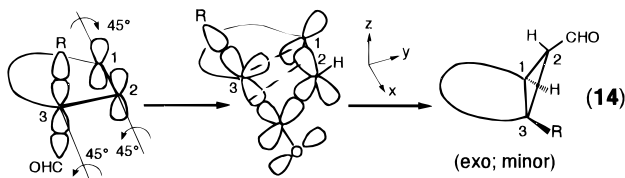
(12) A similar approach was used by: Trindle, C.; Pamuk, H. O. *Tetrahedron* **1978**, *34*, 747–752.

(13) (a) Reference 1b,f. (b) Engel, P. S.; Schexnayder, M. A. *J. Am. Chem. Soc.* **1975**, *97*, 145–153. (c) Reference 15g,h. (d) Koppes, M. J. C. M.; Cerfontain, H. *Recl. Trav. Chim. Pays-Bas.* **1988**, *107*, 313–324.

Path (ii):



Path (iii):



many experiments.^{1d,e,2,14} Further, repeating the procedure for $\langle \hat{H}_{SO} \rangle_y$ and $\langle \hat{H}_{SO} \rangle_z$ for the model **12** leads to much smaller SO coupling expressions. Accordingly, spin inversion will occur faster only in the x sublevel.

Furthermore, it is constructive to reexamine the SO coupling expressions of each path and show that

path ii ($\alpha = \beta = \gamma = 45^\circ$):

$$\langle \hat{H}_{SO} \rangle_x = \frac{-\hbar^2 K}{4\sqrt{2}} [(a^2) + (b^2)(V_{23}^\sigma + V_{23}^\pi) - 4abV_{12}^\pi] \quad (6)$$

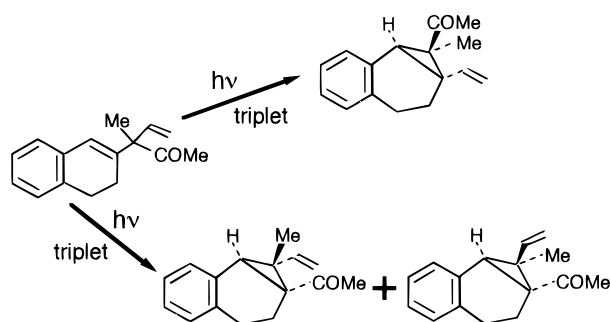
path iii ($\beta = \gamma = -\alpha = 45^\circ$):

$$\langle \hat{H}_{SO} \rangle_x = \frac{-\hbar^2 K}{4\sqrt{2}} [(a^2 - b^2)(V_{13}^\sigma + V_{13}^\pi) - 4abV_{12}^\pi] \quad (7)$$

It is obvious that $|(eq\ 6)^2| > |(eq\ 7)^2|$. Consequently, we conclude that *the endo isomer is expected, in general, to be kinetically more favored than the exo isomer as a result of the larger SO coupling expression as well as the better initial orbital overlaps (owing to less atomic motion), if both isomers exist in the photorearrangements of β,γ -unsaturated carbonyls.* This model conclusion is based on the assumption that other controlling factors are constant and is in very good agreement with experimental results as shown in (**1-9**).^{1,2,4a}

Moreover, as seen in **13** and **14**, the 1,2-acyl migration is favorable because the migrating center can utilize both its $sp^2 - \sigma$ orbital and the orthogonal $p - \pi$ orbitals to obtain better overlaps with orbital lobes of C-2 and C-3 which facilitate the transfer. Hence, in addition to acyl groups, the nature of the migration and the rationale behind it may be readily extended to any substituent which has an $sp^2 - \sigma$ orbital as well as an orthogonal

Scheme 1



$p - \pi$ orbital. For example, the valence orbitals of aryl, vinyl, and imino groups are topologically analogous to the acyl $sp^2 - \sigma$ and $p - \pi$ orbitals. It is therefore expected that *the aryl, vinyl, and imino substituent at C-3 (C- α) should also easily migrate to the C-2 center and the endo isomer photoproduct would predominate.* Supporting evidence comes from the fact that triplet excited oxime esters (β,γ -enamines) undergo the so-called azadi- π -methane (ADPM) rearrangements.¹⁵

Further, one may wonder why only the acyl group is capable of undergoing the 1,2-migration while the alkyl group is not. This can be easily understood by the 3-dimensional picture (**15**). In other words, this 1,2-shift, by way of a six-electron three-center transition state, can also be viewed as an example of an $[\pi 2 + \sigma 2 + \sigma 2]$ reaction.¹⁶ 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 **15**. This is obviously impossible for the migration of hydrogen and the alkyl group since either the poor orbital overlap or extreme crowding in the transition state make the shift exceedingly unlikely.¹⁶ It is therefore suggested that *only the substituent with its $sp^2 - \sigma$ orbital and an orthogonal $p - \pi$ orbital (rather than hydrogen and the alkyl groups) at C-3 is capable of undergoing the 1,2-migration.* Many confirming examples can be found in refs 1, 2, 15, and 17. Further supporting evidence comes from the fact that triplet-sensitized irradiation of the dienone yields the di- π -methane (DPM) product and two isomeric ODPM compounds as shown in Scheme 1,^{5,18} a competition between the acyl and the vinyl groups in an enone. However, the authors claim that the preference for the DPM process

(15) (a) Armesto, D.; Horspool, W. M.; Langa, F. *J. Chem. Soc., Chem. Commun.* **1987**, 1874-1875. (b) Armesto, D.; Horspool, W. M.; Langa, F.; Perez-Ossorio, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1039-1042. (c) Armesto, D.; Gallego, M. G.; Horspool, W. M. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2663-2666. (d) Armesto, D.; Horspool, W. M.; Langa, F.; Gallego, M. G.; Agarrabeitia, A. R. *J. Chem. Soc., Chem Commun.* **1990**, 934-936. (e) Armesto, D.; Horspool, W. M.; Manchano, W. J.; Ortiz J. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2348-2349. (f) Armesto, D.; Gallego, M. G.; Horspool, W. M. *Tetrahedron Lett.* **1990**, 31, 2475-2478. (g) Armesto, D.; Gallego, M. G.; Horspool, W. M. *Tetrahedron* **1990**, 46, 6185-6192. (h) Armesto, D.; Horspool, W. M.; Langa, F.; Ramos, A. *J. Chem. Soc., Perkin Trans. 1* **1991**, 223-228. (i) Armesto, D.; Gallego, M. G.; Agarrabeitia, R. A. *J. Chem. Soc., Perkin Trans. 1* **1992**, 163-169.

(16) (a) Gilchrist, T. L.; Storr, R. C. *Organic Reactions and Orbital Symmetry*, 2nd ed.; Cambridge University Press: Cambridge, 1979; pp 245-265. (b) Gill, G. B.; Willis, M. R. *Pericyclic Reactions*; Chapman and Hall: London, 1974; pp 178-181.

(17) This prediction is also strongly confirmed by the photorearrangements of triplet cyclohexenone systems, which occur by migration of the aryl group from C- γ to C- β and formation of a new bond between C- α and C- γ . For details see ref 6.

(18) (a) Van der Veen, R. H.; Kruk, C.; Cerfontain, H. *Recl. Trav. Chim. Pays-Bas* **1982**, 101, 272-276; (b) *J. Am. Chem. Soc.* **1983**, 105, 4367-4372.

(14) One reviewer has pointed out that the triplet biradicals were found to be involved in a few cases for ODPM rearrangement in his laboratory. Nevertheless, those observations could be special cases since, to our knowledge, those photoreactions occur so fast (below 1 ps) that experimentalists are exceedingly unlikely to detect the reactions directly. As a result, it is reasonable to believe that, in general, ODPM rearrangements should occur in a concerted manner.

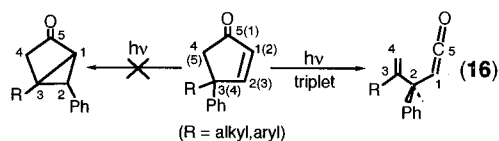
is thought to be due to the involvement of the weaker ethylenic π -system, and the formation of only one DPM isomer is ascribed to charge-transfer stabilization of the 1,3-diradical.

Furthermore, two points need to be mentioned here. First, intuitively, one may predict that a *small size substituent, which has the $sp^2 - \sigma$ orbital and an orthogonal $p-\pi$ orbital*, should be favorable in the 1,2-migration for the ODPM rearrangements. For instance, presumably the 1,2-vinyl migration should be in preference to the 1,2-phenyl migration and affords the main product. Second, it is anticipated that the 1,2-aryl migration through the six-electron three-center transition state should have the transferring trend as follows: *electron-withdrawing phenyl substituent > phenyl > electron-releasing phenyl substituent*.^{6c} We are eagerly awaiting experimental results.

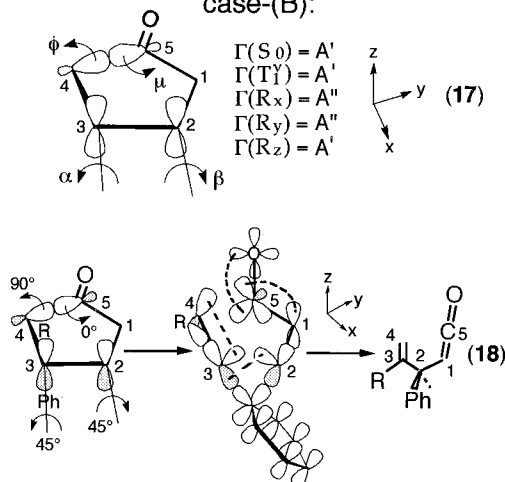
IV. Miscellaneous Reactions

In this section we shall discuss a series of photoreactions of some intriguing molecular systems, which are related to the ODPM rearrangement reactions.

(1) Rearrangement to Ketenes. Two decades ago, Zimmerman, Agosta, and co-workers¹⁹ reported that room-temperature irradiation of 4,4-diphenyl- and 4-methyl-4-phenylcyclopentenone led to a very efficient production of a ketene rearrangement product rather than bicyclic ketones,³ characteristic of the ODPM rearrangements,²⁰ as shown in **16**. Those rearrangements are known to proceed via a triplet excited state.¹⁹ Here again, we will use eq 1 to investigate the possible mechanisms, which induce spin inversion in the triplet excited state of cyclopentenones.



case-(B):



In **17** we examine the reaction mechanism for the formation of ketene. Only the reacting σ and π MOs are

(19) (a) Zimmerman, H. E.; Little, R. D. *J. Chem. Soc., Chem. Commun.* **1972**, 698–700; (b) *J. Am. Chem. Soc.* **1974**, *96*, 4623–4628. (c) Wolff, S.; Agosta, W. C. *J. Chem. Soc., Chem. Commun.* **1972**, 226–227.

(20) For a recent review see: Schuster, D. I. In *The Chemistry of Enones*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons, Ltd: Chichester, England, 1989; pp 623–756. (b) Reference 6.

given in **17**, which is called case B. For consistency with the previous model of the ODPM rearrangement **11**, symmetries will be designed with respect to the molecular plane xy (the nodal plane). Therefore, the symmetry requirements for the case A mechanism **11** also apply to the case B mechanism **17**. In contrast, the distortion for the latter mechanism may involve a disrotation of the π bond and a conrotatory cleavage of the σ bond. The HOMO and LUMO can be expressed as a function of the rotation angle α and β (π bond) and the cleavage angle ϕ and μ (σ bond) with respect to the mirror plane (xz) as shown in **17**. That is,

$$\text{HOMO} = a(p_{2z} \cos \beta + p_{2y} \sin \beta + p_{3z} \cos \alpha - p_{3y} \sin \alpha) - b(p_{5y} \cos \mu + p_{5z} \sin \mu - p_{4y} \cos \phi - p_{4z} \sin \phi) \quad (8)$$

$$\text{LUMO} = b(p_{2z} \cos \beta + p_{2y} \sin \beta - p_{3z} \cos \alpha + p_{3y} \sin \alpha) + \alpha(p_{5y} \cos \mu + p_{5z} \sin \mu + p_{4y} \cos \phi + p_{4z} \sin \phi) \quad (9)$$

After substitution into eq 4, one obtains

$$\langle \hat{H}_{\text{SO}} \rangle_x = \frac{\hbar^2 K}{4\sqrt{2}} [(a^2 - b^2)(V_{24}^\sigma + V_{24}^\pi) \cos(\beta + \phi) + 2ab(V_{23}^\sigma + V_{23}^\pi) \sin(\alpha + \beta) + (a^2 - b^2)(V_{35}^\sigma + V_{35}^\pi) \cos(\mu - \alpha) + 2ab(V_{45}^\sigma + V_{45}^\pi) \sin(\phi - \mu) + 2(a^2 + b^2)V_{34}^\pi \cos(\phi - \alpha) + 2(a^2 + b^2)V_{25}^\pi \cos(\beta + \mu)] \quad (10)$$

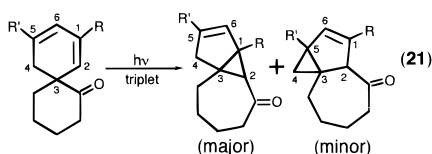
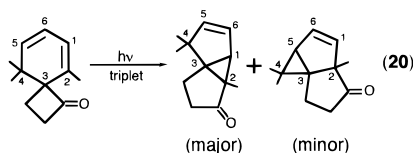
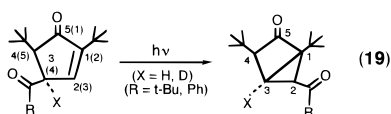
Thus, a maximum value may be reached at $\alpha = \beta = 45^\circ$, $\phi = 90^\circ$, $\mu = 0^\circ$. That is

$$\langle \hat{H}_{\text{SO}} \rangle_x = \frac{\hbar^2 K}{8\sqrt{2}} [\sqrt{2}(a^2 - b^2)] [(V_{35}^\sigma + V_{35}^\pi) - (V_{24}^\sigma + V_{24}^\pi)] + 4ab[(V_{23}^\sigma + V_{23}^\pi) + (V_{45}^\sigma + V_{45}^\pi)] + 2\sqrt{2}(a^2 + b^2)(V_{34}^\pi + V_{25}^\pi) \quad (11)$$

The distortion complex corresponding to these angular characteristics of this route is illustrated in **18**. The coloring convention of the p orbitals is used to indicate directional changes following distortion, and the dotted lines indicate the newly forming bonds. As we see from **18**, the phenyl group may use its $p-\pi$ orbitals to obtain better overlap with the $p-\pi$ orbitals of C-2, resulting in the 1,2-phenyl migration. Simultaneously, the σ bond between C-4 and C-5 may undergo a conrotatory cleavage, forming π bonds between C-3 and C-4 as well as between the O atom, C-5, and C-1, so that the conformer rearranges to lead to a ketene. Further, repeating the procedure for $\langle \hat{H}_{\text{SO}} \rangle_y$ and $\langle \hat{H}_{\text{SO}} \rangle_z$ for the case B mechanism leads to much smaller SO coupling expressions. Accordingly, spin inversion will occur faster only in the x sublevel.

Since the ODPM rearrangement competes with the formation of ketene, it is constructive to compare their SO coupling expressions as given in eqs 6 and 11, respectively. Taking into account the relationships $V_{35}^\sigma + V_{35}^\pi \approx V_{24}^\sigma + V_{24}^\pi$, $V_{23}^\sigma + V_{23}^\pi \approx V_{45}^\sigma + V_{45}^\pi$, and $V_{12}^\pi > V_{34}^\pi$, it is readily shown that $|\langle \text{eq 11} \rangle| > |\langle \text{eq 6} \rangle|$. This leads to the conclusion that *because of the larger SO coupling expression as well as the smaller geometric strain, the formation of ketene should be more efficient than that of endo-bicyclic ketone in the photorearrange-*

ment of 4-aryl-substituted cyclopentenones. This conclusion is based on the model we used here as well as on the assumption that other reaction conditions are equal. Our theoretical finding has been confirmed by available experiments.^{19,21} Nevertheless, it was found that 4-acyl-2,5-di-*tert*-butylcyclopentenones rearranged to bicyclo[2.1.0]pentanones as illustrated in **19**.²² Mechanistically, this is an ODPM photorearrangement which is characteristic of β,γ -unsaturated carbonyls as discussed in section III. Unfortunately, there have been no further experimental mechanistic studies including determination of reactive excited state multiplicity reported on this system. If this system (**19**) occurs via a triplet excited state, then the reason for producing the ODPM rearrangement rather than the formation of ketene is presumably that two *tert*-butyl groups occupy the C-2 and C-5 positions resulting in a preference for the former due to the steric effect.



(2) Rearrangement to ODPM Isomers. Spirocyclic $\beta,\gamma,\delta,\epsilon$ -unsaturated ketones have been shown to be astonishingly versatile substrates which can serve as useful precursors in the synthesis of compounds with polycyclic rings.^{23–25} Upon irradiation with ultraviolet light, this system undergoes 1,2-acyl migration during the photocyclic reaction, producing products considerably more complex than the reactant itself as in **20** and **21**. The major compound is formed by a normal ODPM rearrangement (i.e., involving only one double bond of the diene system), whereas the minor product results from vinylogous ring closure. These photochemical reactions are known to proceed via a triplet excited state. Again, we will use eq 1 to determine the motions which

(21) However, at low temperature ($-140\text{ }^\circ\text{C}$) a bicyclo[2.1.0]pentanone intermediate was observed; see ref 19b. Nevertheless, Zimmerman and Little also questioned that whether this is sufficient evidence that this is the mechanism followed at room temperature since reaction mechanisms may well be temperature dependent.

(22) (a) Matsuura, T.; Ogura, K. *J. Am. Chem. Soc.* **1967**, *89*, 3850–3857; (b) *J. Chem. Soc., Chem. Commun.* **1967**, 1247–1248; (c) *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3187–3194.

(23) In the case of spirocyclic $\beta,\gamma,\delta,\epsilon$ -unsaturated carbonyl systems, the methane carbon (i.e., C-3 in **20** and **21**) represents a spiro center.

(24) (a) Lyle, T. A.; Frei, B. *Helv. Chim. Acta.* **1981**, *64*, 2598–2612. (b) Lyle, T. A.; Meryala, H. B.; Pascual, A.; Frei, B. *Helv. Chim. Acta* **1984**, *67*, 774–788.

(25) (a) Zizuashvili, J.; Abramson, S.; Shmueli, U.; Fuchs, B. *J. Chem. Soc., Chem. Commun.* **1982**, 1375–1378. (b) Oren, J.; Schleifer, L.; Shmueli, U.; Fuchs, B. *Tetrahedron Lett.* **1984**, *25*, 981–984. (c) Viskin, R.; Fuchs, B. *Tetrahedron Lett.* **1985**, *26*, 2365–2368. (d) Oren, J.; Fuchs, B. *J. Am. Chem. Soc.* **1986**, *108*, 4881–4887.

induce spin inversion in the $^3\pi\pi^*$ state of $\beta,\gamma,\delta,\epsilon$ -unsaturated carbonyls.

The spin-inversion mechanism of the ODPM rearrangement has been discussed in section III. Similarly, we also examine case C, which can lead to the minor photoproduct as shown in **20** and **21**. Since the model of case C is analogous to that of case A, the symmetry requirements for the latter also apply to the former. Therefore, the MOs of the complex, after a rotation by μ as well as disrotation by α and β in the direction shown in **22**, may be written as

$$\text{HOMO} = -a(p_{2z} \cos \beta + p_{2y} \sin \beta + p_{1z} - p_{6z} - p_{5z} \cos \mu + p_{5x} \sin \mu) + b(p_{3z} \cos \alpha - p_{3y} \sin \alpha) \quad (12)$$

$$\text{LUMO} = b(p_{2z} \cos \beta + p_{2y} \sin \beta - p_{1z} - p_{6z} + p_{5z} \cos \mu - p_{5x} \sin \mu) + a(p_{3z} \cos \alpha - p_{3y} \sin \alpha) \quad (13)$$

On substitution of eqs 12 and 13 into eq 2, the x component of the SO coupling expression for the case C mechanism is given by

$$\langle \hat{H}_{\text{SO}} \rangle_x = \frac{-\hbar^2 K}{4\sqrt{2}} [(a^2 - b^2)(V_{35}^\sigma + V_{35}^\pi) \sin \alpha \cos \mu + 2ab(V_{25}^\sigma + V_{25}^\pi) \sin \beta \cos \mu + (a^2 + b^2)(V_{23}^\sigma + V_{23}^\pi) \sin(\alpha + \beta)] \quad (14)$$

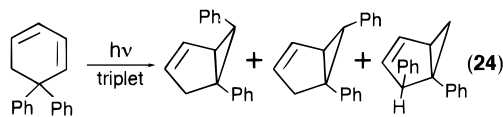
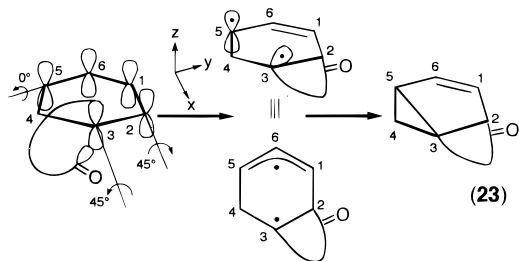
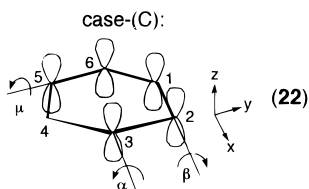
It is apparent that eq 14 reaches a maximum at $\alpha = \beta = 45^\circ$, $\mu = 0^\circ$. That is

$$\langle \hat{H}_{\text{SO}} \rangle_x = \frac{-\hbar^2 K}{8\sqrt{2}} [\sqrt{2}(a^2 - b^2)(V_{35}^\sigma + V_{35}^\pi) + 2\sqrt{2}ab(V_{25}^\sigma + V_{25}^\pi) + 2(a^2 + b^2)(V_{23}^\sigma + V_{23}^\pi)] \quad (15)$$

A schematic representation of a distortion complex corresponding to these angular characteristics is shown in **23**. In such a complex the disrotation of C-2 and C-3 may lead to the 1,2-acyl migration, the same as that found in the ODPM rearrangement as discussed in section III. It then forms a common allylbenzyl diradical which subsequently leads to a singlet product via a ring closure.²⁶ Further, repeating the procedure for $\langle \hat{H}_{\text{SO}} \rangle_y$ and $\langle \hat{H}_{\text{SO}} \rangle_z$ for the case C mechanism leads to much smaller SO coupling expressions. Accordingly, spin inversion will occur faster only in the x sublevel.

Moreover, since there is competition between the case A (i.e., ODPM rearrangement) and case C mechanisms, we reexamine their SO coupling matrix expressions. Comparing eqs 6 and 15, it is apparent that $|(eq\ 6)^2| > |(eq\ 15)^2|$ since $2V_{12}^\sigma > (V_{35}^\sigma + V_{35}^\pi) > (V_{25}^\sigma + V_{25}^\pi)$.⁸ Consequently, it is concluded that the *endo-bicyclic olefin* (i.e., ODPM rearrangement) is expected, in general, to be kinetically more favored than the other competing 1,2-acyl-migrated bicyclic olefins (the minor product) as a result of the larger SO coupling expression as well as the better initial orbital overlaps (owing to the less atomic motion). This conclusion is based on the assumption that other controlling factors are equal. Our theoretical finding is in good agreement with experimental observations.^{24,25} It should be noted that since spirocyclic $\beta,\gamma,\delta,\epsilon$ -

(26) This allylic diradical intermediate may then decay to those two observed photoproducts (see **20** and **21**) with different rates. Nevertheless, as discussed in this work, the ODPM rearrangement (endo isomer) will take place preferentially than the case C pathway.



unsaturated carbonyls are topologically similar to the 5,5-diphenyl-1,3-cyclohexadiene system (see **24**), the mechanistic interpretation for the former should also apply to the latter, which is in accordance with several available experimental findings.²⁷

(3) The Heavy Atom Effect. One important factor which is known to affect triplet-singlet radiationless decay is the heavy atom effect.^{8,28,29} This can be easily seen from eq 2 (or eq A-1); the SO coupling matrix element is directly proportional to the atomic number of an atom. Thus, whenever a reactant contains a heavy atom center which is not necessarily directly involved in the direction, a strong SO coupling may be obtained. In other words, the system, via the agency of the heavy atom, can enhance the probability of a spin-forbidden transition occurring through coupling of spin and orbital angular momenta. This, in turn, can provide the necessary orthogonal AO interactions without any need for distortions. It is therefore expected that *introduction of the heavy atom increases the importance of the radiationless decay processes for the triplet complex.*

Although there are insufficient photophysical studies for the ODPM reactions, the conclusion based upon the above model has been verified by Givens and co-work-

ers.³⁰ The triplet-sensitized experiments which result in the formation of the product (tricyclo[3.2.1]octan-3-one) from bicyclo[3.2.1]oct-2-en-7-one show a decrease in efficiency as the substituent is changed from hydrogen, through chlorine, to bromine. Thus, the authors conclude that the introduction of the heavy-atom substituent results in enhanced radiationless decay.³⁰ Indeed, there is evidence to suggest that a complex formed between the sensitizer and the enone is involved in the reaction and the heavy-atom substituent increases the radiationless decay from this complex.

In this work we present a coherent theoretical framework which facilitates a rational approach to the photorearrangements of triplet reactants. It is important to stress that those mechanisms proposed in this work (case A–case C) are not necessarily the energy minima on the T_1 potential surface of those molecular systems, but rather represent the conformations for which $T_1 - S_0$ radiationless decay are predicted to be optimal. Despite its simplifications and some mathematical approximations, our theoretical findings are verified by experiments in many cases. Indeed, the actual formation of the rearrangement photoproduct is always one of several competitive reactions. We admit the complexity of the problem, and indeed our model must be used with caution especially when applied to some complicated reaction systems. In spite of its simplicity, our approach proves to be rather effective and can provide chemists with important insights into the factors controlling the photoreactions of molecules, thus allowing a better understanding of the nature of such systems as well as a number of predictions to be made.

It is hoped that our study will stimulate for further research into the subject.

Acknowledgment. I wish to thank Professor Michael A. Robb (King's College, University of London, U.K.) for his encouragement and support. I gratefully acknowledge the hospitality of Dr. Paul Sherwood at the DRAL Daresbury Laboratory in U. K., where this paper was prepared. I am also grateful to the reviewers for useful remarks and suggestions.

Appendix

Consider a reaction system on a triplet surface (T_1). After completing a sequence of events (e.g., bond reorganization) the reaction system reaches a region where it inverts a spin and relaxes to the ground state (S_0) in a radiationless manner. The SO coupling operator can be written as a double sum over the interaction of all electrons, i , with all nuclei, N^{10}

$$\hat{H}_{SO} = \sum_i \sum_N \frac{Z_N^* e^2}{2m^2 c^2} \frac{\hat{l}(i) \cdot \hat{s}(i)}{r_{iN}^3} = \sum_i \sum_N K \frac{\hat{l}(i) \cdot \hat{s}(i)}{r_{iN}^3} \quad \left(K = \frac{Z_N^* e^2}{2m^2 c^2} \right) \quad (\text{A-1})$$

where Z_N^* represents the effective nuclear charge of nucleus N and r_{iN} represents the distance between electron i and nucleus N . The $\hat{l}(i)$ and $\hat{s}(i)$ are the orbital

(27) (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) Reference 1a. (f) Swenton, J. S.; Hyatt, J. A.; Walker, T. J.; Crumrine, A. L. *J. Am. Chem. Soc.* **1970**, *92*, 4808–4815. (g) Su, M.-D. *J. Org. Chem.* **1995**, *60*, 6621–6623.

(28) (a) For a lucid summary of the mechanistic and spectroscopic studies, see: Turro, N. J. *Modern Molecular Photochemistry*; The Benjamin/Cummings Co.: Menlo Park, CA, 1978; Chapter 6. (b) El-Sayed, M. A. *Acc. Chem. Res.* **1968**, *1*, 8–16. (c) *J. Chem. Phys.* **1963**, *38*, 2834–2838.

(29) Other factors which are known to affect singlet-triplet inter-system crossing include the following: (1) the magnitude of the singlet-triplet energy difference between the two states; (2) the configuration of the initial and of the final states; and (3) vibronic or Frank-Condon factors. See: (a) References 8 and 25. (b) Robinson, G. W.; Frosch, R. P. *J. Chem. Phys.* **1962**, *37*, 1962–1973; (c) *J. Chem. Phys.* **1963**, *38*, 1187–1203. (d) Borkman, R. F. *Mol. Photochem.* **1972**, *4*, 453–471.

(30) (a) Givens, R. S.; Chae, W. K. *J. Am. Chem. Soc.* **1978**, *100*, 6278–6280. (b) Givens, R. S.; Chae, W. K.; Matuszewski, B. *J. Am. Chem. Soc.* **1982**, 2456–2466.

and spin angular momentum operators for electron i , respectively.

We note that the SO coupling operator (eq A-1) is also a sum of one-electron operators. It is therefore easily verified that the SO matrix elements vanish if the two configurations involved differ by more than one pair of MOs. 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. Accordingly, the SO coupling matrix element can be reduced to the evaluation of the matrix elements of the HOMO and LUMO of the reaction complex as shown in eq 2. The reason for choosing HOMO and LUMO is that they are supposed to be the most important frontier MOs during the chemical reactions.

In evaluating the magnitude of SO coupling matrix elements, we shall use the Cartesian operators and real atomic wave functions since they are familiar to the organic chemists. In Cartesian space, the $\hat{l}\cdot\hat{s}$ operator is expanded as shown by

$$\hat{l}\cdot\hat{s} = \hat{l}_x\hat{s}_x + \hat{l}_y\hat{s}_y + \hat{l}_z\hat{s}_z \quad (\text{A-2})$$

In this equation the \hat{l} components operate only on the spatial (orbital) parts and \hat{s} components only on the spin parts of the wave functions.

On the other hand, the SO coupling matrix element of the two states (here we are interested in only two particular states T_1 and S_0) can be expanded as

$$\hat{H}_{SO} = \hat{H}_{SO}^0 + \left(\frac{\partial\hat{H}_{SO}}{\partial Q_k}\right) Q_k + \dots \quad (\text{A-3})$$

where Q_k stands for the normal coordinate of the k th vibrational mode. This leads to the final form of the SO coupling matrix element as follows

$$\langle T_1|\hat{H}_{SO}|S_0\rangle = \langle T_1^0|\hat{H}_{SO}^0|S_0^0\rangle Q_k + \left\langle T_1^0\left|\frac{\partial\hat{H}_{SO}}{\partial Q_k}\right|S_0^0\right\rangle + \dots \quad (\text{A-4})$$

We may therefore obtain the intersystem crossing rule as^{7,9b}

$$\langle T_1^0|\hat{H}_{SO}|S_0^0\rangle \rightarrow \Gamma(T_1^{0,\nu}) \times \Gamma(\mathbf{R}_k) \times \Gamma(S_0) = A \quad (k = x, y, z) \quad (\text{A-5})$$

$$\left\langle T_1^0\left|\frac{\partial\hat{H}_{SO}}{\partial Q_k}\right|S_0^0\right\rangle \rightarrow \Gamma(T_1^{0,\nu}) \times \Gamma(\mathbf{R}_k) \times \Gamma(S_0) \times \Gamma(Q_k) = A \quad (k = x, y, z) \quad (\text{A-6})$$

where $\Gamma(\xi)$ represents the symmetry species of the argument ξ , which may be either a function or an operator. The letter A in eqs A-5 and A-6 stands for the phrase, "the totally symmetric species of the point group" and $\Gamma(T_1^{0,\nu})$ is the representation of the spatial part of T_1^0 . In addition, the superscript zero in eq A-4 denotes the zero-order solutions for the fixed reference system. Since $(\partial\hat{H}_{SO}/\partial Q_k)Q_k$ is part of the Hamiltonian, the direct product $\Gamma(\partial\hat{H}_{SO}/\partial Q_k)\cdot\Gamma(Q_k)$ must therefore be totally symmetric, or $\Gamma(Q_k)$ must be identical to $\Gamma(\partial\hat{H}_{SO}/\partial Q_k)$. Obviously, these two equations (eqs A-5 and A-6) define the basis for the set of selection rules for the process known as intersystem crossing. Equation A-5 states the condition for the nonvanishing SO coupling intersection in the fixed reference system and eq A-6 describes the conditions for creating the SO coupling interaction upon a distortion Q_k .^{9b} Hence, the representations of the motions (Q_k) which couple the sublevels of the triplet state with the ground state and promote spin inversion in eq A-6 may be rewritten as

$$\Gamma(Q_k) = \Gamma(T_1^{\nu}) \times \Gamma(\mathbf{R}_k) \times \Gamma(S_0) \quad (k = x, y, z) \quad (\text{A-7})$$

This rule, eq A-7, is valid whenever the eq A-5 requirement is not met and a distortion (Q_k) is needed. In other words, this analysis is reduced to finding motions (Q_k) which can efficiently couple S_0 with one of the components of T_1 . We may therefore use group theory to search for the potentially efficient spin inversion motions.

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