Novel Dissection Analysis of Spin-Orbit Coupling in the Type-B Cyclohexenone Photorearrangement. What Controls Photoreactivity? Mechanistic and Exploratory Organic Photochemistry\textsuperscript{1,2}

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Two main concepts have been invoked as controlling the course of organic photochemical reactions. One is the nature of the excited state hypersurface with reacting molecules following minimum energy pathways toward geometries of alternative photoproducts. The other is competitive excited state radiationless decay to the alternative ground state products by internal conversion of singlets or intersystem crossing of triplets. That such decay must occur is a truism; however, in our view decay controls the direction of excited state reactivity only for those simpler reactions where minimal geometric change occurs. More generally, when decay is a factor in a complex reaction it is far removed along the hypersurface.

In this paper we support this view and present important results in dealing with spin-orbit coupling\textsuperscript{6} control of intersystem crossing. The example of the type-B rearrangement of 4-arylcyclohexenones to afford 6-arylcyclohexanones is used. We report: (a) Ab initio spin-orbit coupling dissection at strategic points along the type-B reaction hypersurface. (b) Spin-orbit coupling is dominated by geminal interactions. (c) Evidence that HOMO–LUMO considerations lead to errors and a larger active space is required. (d) Energetics along the hypersurfaces leading from reactant to product. (e) The largest contributors to spin-orbit coupling for reactant and product ketones are oxygen p-π (i.e., n–π*) type. But, for the diradical intermediates, spin-orbit coupling is dominated by geminal hybrid interactions at the odd-electron centers. (f) The relatively low experimental quantum yields are due to intersystem crossing from the enone reactant triplet to ground state rather than along the reaction hypersurface. (g) Final product formation results from T\textsubscript{1} to S\textsubscript{0} intersystem crossing in the region past “diradical II” as the bicyclic structure is approached. (h) Evidence that for complex photochemical rearrangements, the reaction course is dictated by events on the excited state surface distant from the vertical excited state and controlled by the nature of the surface. Computations were run for the 4,4-diphenylcyclohexenone (1\textsuperscript{b}) and 4-methyl-4-vinylcyclohexenone (2\textsuperscript{i}) systems of reactant enone, diradical I, diradical II, and bicyclic photoproduct. Note eqs 1 and 2. For computational simplicity, a more complete study was carried out using the vinylene system where a more extended active space was possible. Ab initio energies, total spin-orbit coupling (SOC), and dissected SOC were obtained by methods we previously described.\textsuperscript{36}

Use of the commonly employed HOMO–LUMO approximation leads to errors. Note Table 1. Reactant and product ketones require an increased active space to provide complete SOC contributions, although intermediate reacting diradicals provided more complete SOC values with lesser active spaces. This is seen particularly clearly in the case of bicyclic ketone 5 where only MO's below HOMO contained appreciable p\textsubscript{i} (i.e., n*) weighting. The role of n–p* excitation in organic photochemistry has long literature precedent.\textsuperscript{3b,61}

Interestingly, the major contributions involve spin-orbit coupling between geminal orbital pairs with heavy weighting at the odd-electron centers. While anticipated for ketones with their oxygen n* (i.e., p\textsubscript{o}) and the p–π orbitals, past literature discussions have emphasized interactions between odd-electron centers. Interactions between orbitals at two different centers proved much smaller. Note Table 2 for the largest SOC contributions in the triplet species of interest. For example, in Table 2, the interaction between orbitals p\textsubscript{o} and p\textsubscript{π} is seen to be small.

We were also interested in the energetics of the type-B enone rearrangement. Figure 2 shows ab initio energies obtained at critical points along the hypersurface for the vinylene 2, namely the T\textsubscript{1} energies of enone 2, diradical

(1) This is publication 175 of our photochemical series and 238 of the general sequence.
(5) Spin-orbit coupling is most important in singlet–triplet interconversion.
(6) (a) Zimmerman, H. E.; Cowley, B. R.; Tsong, C.-Y.; Wilson, J. W. J. Org. Chem. 1984, 66, 2307–494. (b) Computations on the diphenylcyclohexene system proved parallel to the simple vinyl enone 2. The active space possible for the diphenyl system was limited to (6,6), which was sufficient for the two diradicals. Again, the large contributions were geminal.
(7) (a) The triplet type-B rearrangement of 4-phenyl-4-vinylcyclohexene has been reported by Swenton,\textsuperscript{79} and the corresponding reaction of 4-methyl-4-propenylcyclohexene is known from the research of Schaffner.\textsuperscript{78} (b) Swenton, J. S.; Blankenship, R. M.; Sanzera, R. J. Am. Chem. Soc. 1978, 100, 4941–4947. (c) Nobe, R.; Burger, L.; Schaffner, K. Helv. Chim. Acta 1977, 60, 1607–1628.
(8) AM1 was used for initial geometry optimization, GAMESS\textsuperscript{2} was employed for C.I. and total SOC. WISC SOC\textsuperscript{66} dissects overall spin-orbit coupling into two-basis orbital components, with Weinhold natural hybrid orbitals (NHO)\textsuperscript{10} being the choice basis. This required SOC integrals in an NHO basis. AO SOC integrals available in GAMESS were transformed to the NHO basis. An STO-3G basis set was used in order to avoid the ambiguity of adding 2p and 3p components.
The dependence of spin-orbit coupling on the relative large. Very small spin-orbit coupling was found for diradicals role, the major contributions are geminal at these centers.

I 1 and I 1 which follow on the triplet hypersurface. On the relatively low quantum yield in type B enone rear-

I 1 are minima on the reaction pathway. We note that rearrangements leading to enone radiationless triplet decay.

The point of decay seems to be near "closing species" (note Figure 1 for orbital numbering) with geometry optimization.

Interestingly, the increase in spin-orbit coupling in the n-π* enone triplet accounts for the relatively low quantum yields in type B enone rearrangements leading to enone radiationsless triplet decay. Very small spin-orbit coupling was found for diradicals I and II which follow on the triplet hypersurface. On the hypersurface, the triplet changes from n-π* to π-π* and back to n-π*; note Figure 1.

The energy barrier along with the observed large spin-orbit coupling in the n-π* enone triplet accounts for the low quantum yield in type B enone rearrangements leading to enone radiationless triplet decay. Very small spin-orbit coupling was found for diradicals I and II which follow on the triplet hypersurface. On the hypersurface, the triplet changes from n-π* to π-π* and back to n-π*; note Figure 1.

The point of decay seems to be near "closing species" (Table 1) which is between diradical I and bicyclic product. Triangles indicate T 1; squares indicate S 0.

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Supporting Information Available: Computational methodology and detailed results (81 pages).

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