

Electrostatic Control of the Regioselectivity in the Photoisomerization of *trans,trans*-1-Fluoro-2,4-hexadiene: Evidence for Competing Conical Intersections

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There have been many investigations exploring the decay channel of excited acyclic 1,3-dienes.^{1,2} The intermediacy of allylic-methylene zwitterions along the photoreaction pathway was used to explain the generally observed behavior of only one double bond isomerization occurring upon direct photolysis of 1,3-dienes^{1e-i} and the stereochemistry of ethylenecyclooctenes photochemical closure.^{1d} More recently, calculations suggest that conical intersections are extensively involved in 1,3-diene photoisomerization^{2a-c} and other photochemical reactions.^{2i-m}

We have reported the observation of at least a 20:1 rotational preference in the photoisomerization of the deuterium-substituted double bond over the methyl-substituted double bond in *cis*-*d*₁-1,3-pentadiene.^{1f} We postulated that this regiochemistry was the result of charge stabilization by the methyl substituent of the allylic cation portion of an allylic cation–methylene anion zwitterion. Our observations were reinterpreted on the basis of a pathway through an unsymmetrical tetraradicaloid species at a conical intersection.^{2b} It was suggested that in this case, and in general, the radicaloid nature of conical intersections^{2a-e,i,m} required that internal moments of inertia, rather than charge effects, control photoregioselectivity. Specifically, it was stated, that in our case the deuterium-substituted double bond preferentially photoisomerized simply because the deuterium was lighter than the methyl group. We felt that by examining the photoisomerization of an unsymmetrical 1,3-diene with an electron-withdrawing substituent the relative importance of charge vs internal momentum could be determined.

To this purpose we examined the photochemistry of *trans,trans*-1-fluoro-2,4-hexadiene (EE-FHD).³ We found, upon direct photolysis⁴ of a pentane solution of EE-FHD with 254-nm light, a 2.49 preference for isomerization about the double bond bearing the heavier CH₂F substituent (Figure 1) If the photoregioselectivity were controlled by internal rotational moments of inertia within the tetraradicaloids comprising a conical intersection, the double bond bearing the lighter methyl substituent would be expected to isomerize preferentially. Therefore, in this case, the regioselectivity of the photoisomerization is not controlled within a conical intersection.

However, the question arises whether FHD can be used as a general model for 1,3-dienes or if the CH₂F substituent introduces new chemistry. To check this, several tests were performed. MP2/6-31G* level calculations showed that the coefficients of the fluorine atom in the HOMO and LUMO B-orbitals of EE-FHD are negligible. The UV spectrum of EE-FHD is very similar to that of *trans,trans*-2,4-hexadiene (EE-HDE), showing the same maximum and general features.

In addition, we compared the general photochemistries of FHD and HDE in methylbutane and their photochemical trapping in methanol. The photochemistries of EE-HDE⁵ and EE-FHD were identical, with a rapid photoisomerization followed by slower ring closure and minor amounts of hydrogen-shift products. Furthermore,

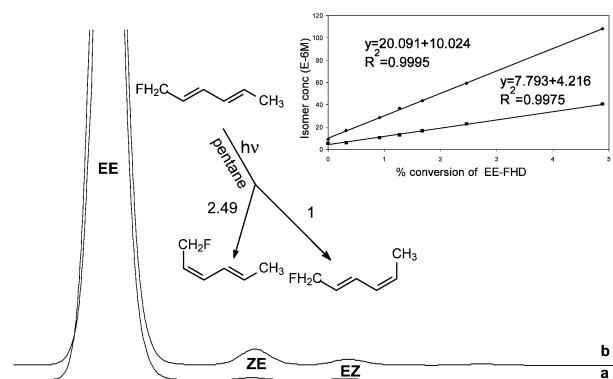


Figure 1. Photoisomerization of a 3.2 mM pentane solution of EE-FHD (a) initial GC, (b) after irradiation at 254 nm for 60 s.

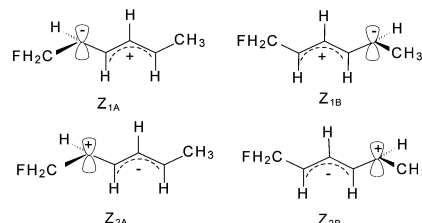


Figure 2. Electronic structures of the four allyl-methylene zwitterions of EE-FHD.

in carefully deacidified methanol neither diene showed methanol-trapping products even after prolonged photolysis, suggesting that the fluorine substituent does not induce participation of a charge-separated species along a different excited-state pathway than that traversed by HDE. It appears, then, that the photochemistry of FHD is typical of acyclic 1,3-dienes.

It is tempting to interpret our results as implying the presence of zwitterions along the photopathway, but that would not explain the substantial decrease in the regioselectivity as compared to the pentadiene system which is not as charge stabilized. That is, if *Z*_{1A} is lowest in energy of the four zwitterions (Figure 2), as calculations suggest,^{1h,6} then the production of ZE-FHD should not only predominate but should also be produced with a higher selectivity than the 20:1 of pentadiene-1-*d*₁ and not the 2.5:1 observed.

Another argument against direct participation of zwitterions is the effect of solvent on the photoregioselectivity. For the solvent series pentane, ether, methanol, and propionitrile, the preference for the ZE isomer decreases from 2.49 to 3.34, 3.70, and 3.99, respectively. Figure 3 shows the relationship between the selectivity and the *E*₁ value⁷ of a mixed hexane/propionitrile solvent. Thus, as the polarity of the solvent increases, the regioselectivity is seen to increase. However, polar solvent mitigation of the charge-stabilizing ability of substituents is a long-established phenomenon.⁸ Polar solvents should decrease the charge-stabilizing effects of polar

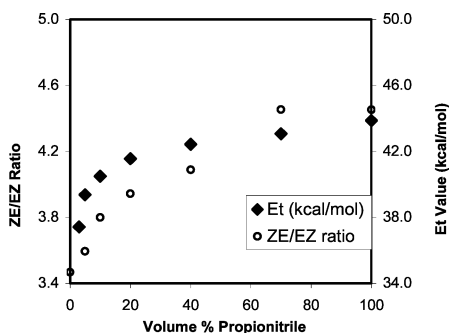


Figure 3. Photoregioselectivity of EE-FHD (254 nm) and E_1 value of a mixed propionitrile-hexane solvent system.

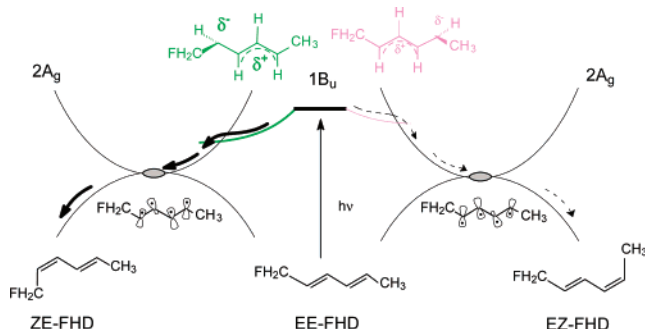


Figure 4. Proposed pathways from $1B_u$ state showing differing polarizations and leading to two different conical intersections.

substituents on the zwitterions and thus reduce the energy differences between zwitterions. This reduction would result in a decrease, not the observed increase in the photoregioselectivity.

The magnitude and solvent dependence of the regiophotomerization and lack of any methanol-trapping products strongly suggest that a picture of this photochemistry involving a simple traverse via zwitterions to ground state cannot be the case. However, this system certainly shows a charge effect not consistent with a simple conical intersection picture. An amalgam of these two mechanisms seems necessary, one that can explain the lower regioselectivity, the absence of any methanol trapping, and the observed solvent effect.

Calculations^{2a} describe the formation of an unsymmetrical tetraradicaloid as butadiene proceeds through a conical intersection with substantial twisting occurring about the double bond involved in a "three-carbon kink" but with only a small amount of twist about the bond not directly included in the "kink". Therefore, unsymmetrical dienes must have two distinct conical intersections each having substantial rotation about one or the other of the two double bonds.^{2b} We suggest that the regiochemistry of the photoisomerization is determined not within the conical intersection but rather by the relative efficiencies of the entryways leading to the two conical intersections. In fact Zilberg⁹ has shown that the phase-change theorem of Longuet-Higgins¹⁰ demands that separate conical intersections must be responsible for the production of the two double bond isomers.

From the Franck-Condon region of the initially obtained $1B_u$ state, bifurcation into two pathways leading to the two conical intersections must occur, and it is at this point that the final ratio of the double bond isomers is determined (Figure 4). We believe that species traversing these two pathways have differing polarizations and that, while this polarization disappears upon transition to the A-state surface, it is ultimately responsible for determining the relative populations of the two conical intersections and therefore the photoregioselectivity.

The 1,3-diene short-lived¹¹ $1B_u$ state is a resonance hybrid of Z_1 - and Z_2 -like planar allyl-methylene zwitterions. As such it is not polarized, but it has the potential to be polarized when the symmetry is lowered and is described therefore as the "ionic" state.¹² In the case of unsymmetrical dienes, the species along the two pathways leading from the Franck-Condon area of this state would be polarized unequally (different mixes of the respective Z_1 - and Z_2 -like species). Indeed, of the two the pathways toward the ZE-FHD conical intersection should be more polarized due to the match of the polarization and the charge-stabilizing characteristics of the substituents. This difference in polarization explains the solvent effect with the more polarized pathway more favored in polar solvents. The very short $1B_u$ state lifetime would preclude the addition of methanol and limit the degree of polarization occurring on this state. The magnitude of the regioselectivity of the photoisomerization will depend strongly on this lifetime and therefore on the position of the A-B conical intersection. Thus, in this system there is an interplay of a charge effect and dynamics on the potential energy surface that controls the direction and the magnitude of the rotational preference.

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- (3) EE-FHD was prepared by fluorination of *trans,trans*-1-bromo-2,4-hexadiene-1-ol (97%, Aldrich) with phosphorous bromide. The product mixture (ca. 70% EE-FHD) was purified by preparative gas-phase chromatography ($6' \times 1/8''$ column packed with Chromosorb W coated with 10% OV-17) to yield a pure sample of EE-FHD (99.5%).
- (4) A 2 mM EE-FHD solution was photolyzed at 0° in capillary quartz tubes with low-pressure Hg lamps (G258). The photoreaction was monitored using analytical GC (30 m \times 0.25 μ m \times 0.25 mm AT-50 capillary column). Regioselectivities were determined by measuring the yields of ZE and EZ-FHD at times corresponding to less than 6% conversion of EE-FHD.
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