Tetrahedron Vol 49, No 43, pp 9699-9712, 1993
Printed in Great Britain

0040-4020/93 $6 00+ 00

Mechanistic Investigation of [2 + 2] Photoannulations of Enones and Olefins

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(*Received in USA* 27 *January* 1993, *accepted* 23 *August* 1993)

Key Words [2+2] photoannulation, UHF, triplet acrolein, condensation stereoselectivity, biradicals

Abstract: The photoinitiated [2 + 2] cycloaddition reaction between acrolein and ethylene is investigated using ***ab initio*** molecular orbital calculations RHF and UHF geometry optimizations with the 6-31G* basis set are reported for ethylene, acrolein, triplet acrolein, *gauche* and *trans* triplet biradical intermediates, and formylcyclobutane, and are used to address the issues of reactivity and selectivity in enone-olefin photoannulations In contrast to a model in which regioselectivity arises from the alignment of dipoles in the excited state, calculated dipole moments and electrostatic potentials show no basis for such an assignment. It is striking that the proposed dipole as well as FMO based selectivity models in the literature used to explain observed product distributions are inadequate, leaving open the question of the mechanistic significance of a triplet exciplex in determining regioselectivity

INTRODUCTION

A long standing question in organic chemistry involves the mechanism of thermal and photoinitiated [2 + 2] cycloaddition reactions of olefins Proposed mechanisms include stepwise pathways that involve biradical and zwitterionic intermediates and as well a synchronous concerted mechanism.[1] Whereas extensive theoretical and experimental investigation of the thermal reaction has been reported,[1] photochemically initiated [2 + 2] cycloadditions, and in particular those involving enones and olefins, remain relatively uncharacterized with regard to some of the mechanistic details of the reaction

The synthetically useful variant of photochemically induced [2 + 2] cycloadditions of alkenes involves reaction of an enone with an olefin, the mechanism of which is proposed to involve an excited state π-complex (exciplex) of the enone and the olefin followed by relaxation first to a biradical, and then closure to form cyclobutane (**Scheme 1**) [2,3] This mechanism is supported by the observation of exciplexes under [2 + 2] cycloaddition reaction conditions,[4] albeit recent studies draw into question exciplex involvement in enone cyclizations [5] Other studies suggest that, in some cases, the triplet π,π^* exciplex may avoid the biradical and collapse directly to products following intersystem crossing [6,7]

Although the mechanism of the general enone photocycloaddition reaction awaits elucidation, several theoretical studies provide useful perspectives on the experimental observations/interpretations A CNDO/2 study of the cycloaddition between enones and acetylenes concluded that regiocontrol results from dipole-dipole interactions in the excited state [8] CNDO/S-CI results suggest that the acceleration of the intramolecular photocycloaddition in polymethylene dicinnamates (by substitution on the aromatic rings) can be attributed to facile exciplex formation, due to favorable charge and/or spin density located on the aromatic moiety.[9] UHF/STO-3G calculations on the triplet state of 1,5-hexadien-3-one revealed that parallel ring closure should occur between C_1 and C_6 follows from examination of the high spin densities and SOMO coefficients at these atoms[10] A perturbative intermolecular orbital analysis of PPP generated orbital energies and π electronic charges of the photoaddition of a variety of chromophores to methoxyethylene predict head to tail regioselectivity[11,12,13]

$$E \xrightarrow{h\nu} {}^{1}E \longrightarrow {}^{3}E \xrightarrow{O} {}^{3}[EO] \longrightarrow {}^{3}[\bullet EO\bullet] \longrightarrow {}^{1}[\bullet EO\bullet] \longrightarrow EO$$

E = Enone, ^{1}E = Singlet Excited Enone, ^{3}E = Triplet Enone, O = Olefin, ^{3}[EO] = exciplex, ^{3}[•EO•] = Triplet Biradical Intermediate, ^{1}[•EO•] = Singlet Biradical Intermediate, EO = Cyclobutane Product

Scheme 1. Putative Mechanism for the Photoinduced Cycloaddition of Enones and Olefins

This study re-examines the enone-olefin photocycloaddition reaction using SCF-MO methods, and is divided into two parts The initial focus of this study concerns the geometry and electronic structure of the reactants (acrolein and ethylene), the putative intermediates (triplet acrolein and triplet biradical), and the product (formylcyclobutane) The remaining discussion of this study addresses the reactivity and selectivity of the acrolein-ethylene reaction, wherein the energies of the possible intermediates are discussed in the context of regioselectivity

COMPUTATIONAL METHODS

While photoinduced enone-olefin cyclizations are generally useful for only five- and six-membered ring α,β-unsaturated enones, due to competition with photochemically induced *cis-trans* isomerization in acyclic compounds and larger ring systems,[2b] the size of these systems is prohibitive at the level of theory employed Therefore acrolein has been used as a simple model enone, and ethylene as the model olefin.

Ab initio molecular orbital calculations were carried out using the *GAUSSIAN85* suite of programs[14] as implemented upon Silicon Graphics Iris 4D Workstations. All reported structures are fully optimized at either the restricted or unrestricted Hartree-Fock levels (RHF and UHF, respectively) using the 6-31G* split-valence polarization basis set.[15] All resulting extrema were characterized via normal mode analysis as true minima.

Electrostatic potentials were calculated at approximately 2000 points located on an equidensity surface enclosing ~96% of the total electron density using 6-31G* wavefunctions[16] Potential derived monopoles (atomic charges) were subsequently obtained based upon these electrostatic potentials according to the fitting method of Cox and Williams[17]

UHF wavefunctions are not eigenfunctions of the true total spin operator, and thus may be contaminated by higher spin multiplicity states.[18] Nonetheless all UHF wavefunctions reported herein exhibit expectation values of the square of the total spin angular momentum operator that indicate no contamination from higher spin states in all cases

Molecular mechanics calculations on the substituted [4 2 0] and [3 2 0] bicyclic alkanes were performed using the SYBYL 5 2 empirical force as implemented in the SPARTAN electronic structure package[19] The energies reported follow from complete energy minimization using the BFGS algorithm, and correspond to the "strain" energy of the respective molecular systems

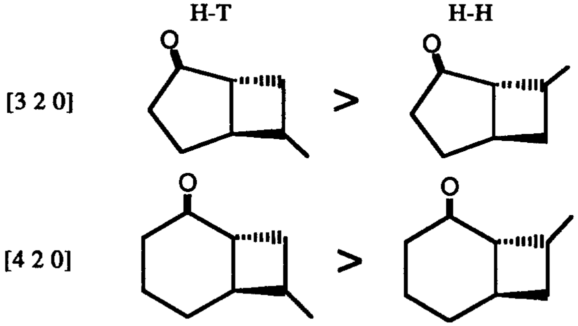
RESULTS AND DISCUSSION

I Cyclobutane Products

To begin discussion of regioselectivity of enone and olefin photoannulations, an initial consideration involves the influence of the cyclobutane moiety, and/or the fused bicyclo-alkane on the stereochemical course of the reaction in order to consider the possibility of product control. While not a proposed selectivity model, it seems important to eliminate as many sources of stereoselection (in this case stereocontrol in the second step) in light of the relative murkiness that this reaction's mechanism enjoys

Examination of the various conformers of formyl cyclobutane (**Figure 1**) suggests that there is practically no bias caused by the stability of the various products, and by extrapolation it seems unlikely that similar influences (e.g. steric interactions) to those that are present in the transition structure could contribute much to observed selectivities In analogy with acyclic aldehydes,[20] the C-O π-bond eclipses an adjacent C-H or C-C σ-bond, with a small preference to eclipse the strained C-C σ-bond of the four-membered ring in both the equatorial and axial configurations. There is also a slight favoring of equatorial over axial formyl substitution of the cyclobutane ring, which appears to be primarily steric in nature, based upon the three to four degree flattening of the cyclobutane ring in the axial forms The small equatorial preference contrasts the 1-2 kcal•mol^{-1} A-values on six-membered rings for related substituents,[21] and serves to highlight the conformational character of four-membered rings.[22]

The relationship between the parent formyl cyclobutane and the related [n 2 0] bicyclic systems formed upon photoannulation of cyclic enones was probed with molecular mechanics calculations *Trans*-fused products of propene cycloaddition to cyclopentenone and cyclohexenone exhibited only small preferences for head-to-tail adducts The small bias for the head-to-tail adducts of 0.5-0.8 ([3 2 0] system) and 0.3-0.4 kcal•mol^{-1} ([4 2 0] system), contrast the larger stereoselectivities observed experimentally



Similarly, the analogous *cis*-fused cycloadducts have even smaller preferences (0.1 and 0.4 kcal•mol^{-1} for [3.2 0] and [4.2.0] systems, respectively) for the exo adducts, the endo *cis*-fused adducts exhibit larger head-to-tail biases of 1.8 and 2.0 kcal•mol^{-1}, respectively Notwithstanding, these model calculations contrast the experimental trends for this class of reactions

On whole, this data on the products of the cyclization reaction indicate that if the ring-forming step were reversible, rather poor stereoselectivities should be observed in all but the *cis*-fused endo cycloadducts. This result corroborated the observation (*vide supra*) that conformational effects are greatly attenuated on the four-membered ring systems studied Most importantly, such small conformational biases will be even less pronounced in the cyclization transition structures (due to longer, partially formed bonds). Thus, one can conclude that selectivity in the [2 + 2] photoinitiated cycloadditions of olefin and enone must be a consequence of an earlier intermediate along the reaction coordinate

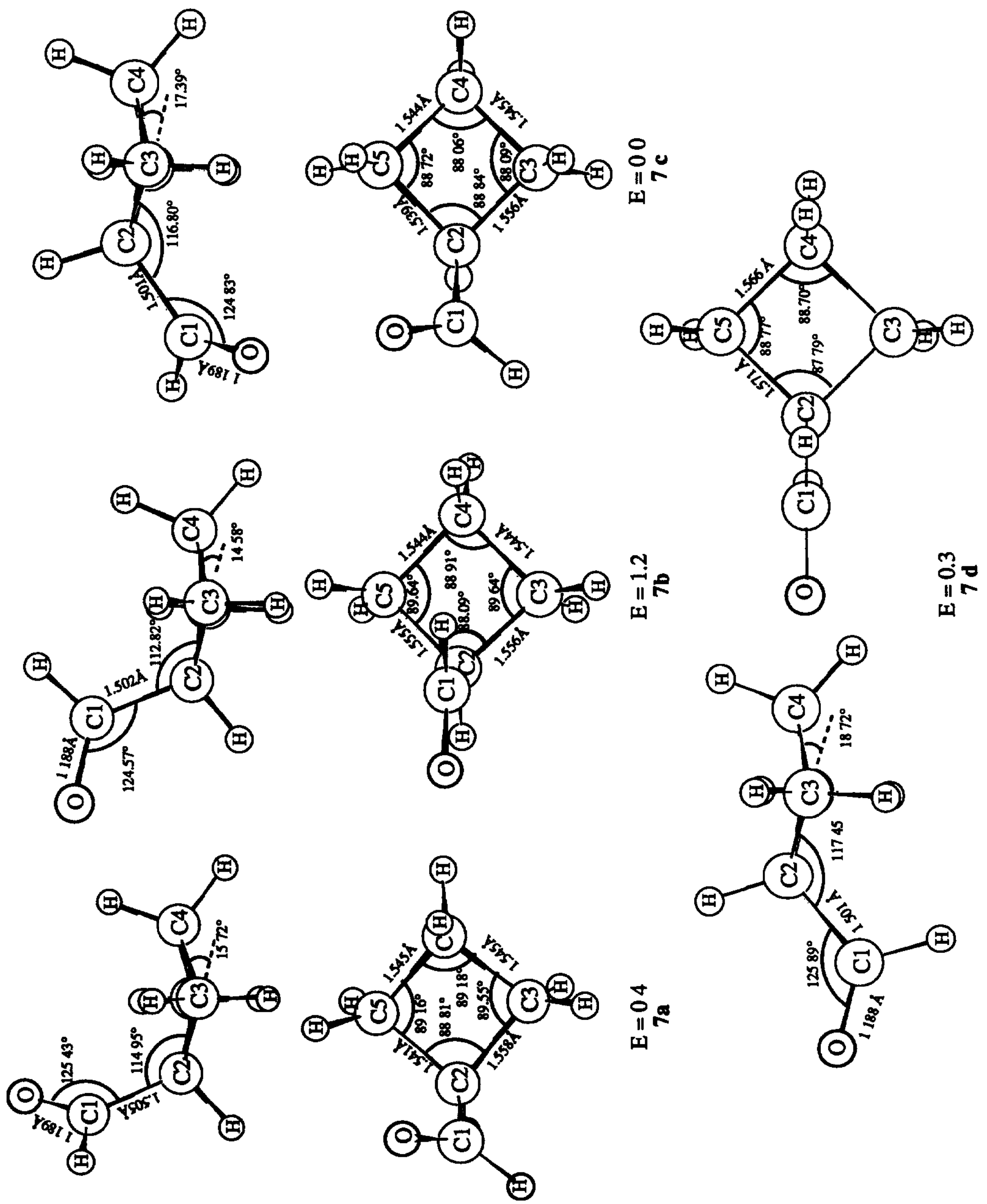
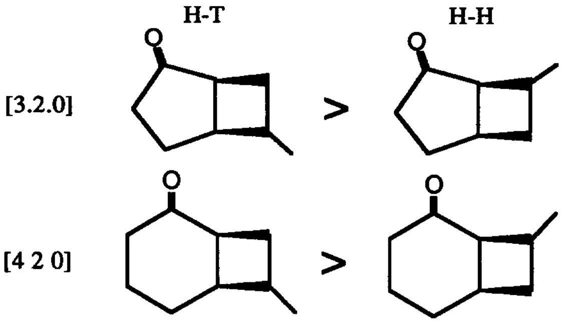


Figure 1. RHF/6-31G*//6-31G* Structures and Relative Energies of Formylcyclobutanes (Energies in kcal•mol^{-1})

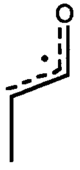


II Geometry and Electronic Structure of Open Shell Intermediates

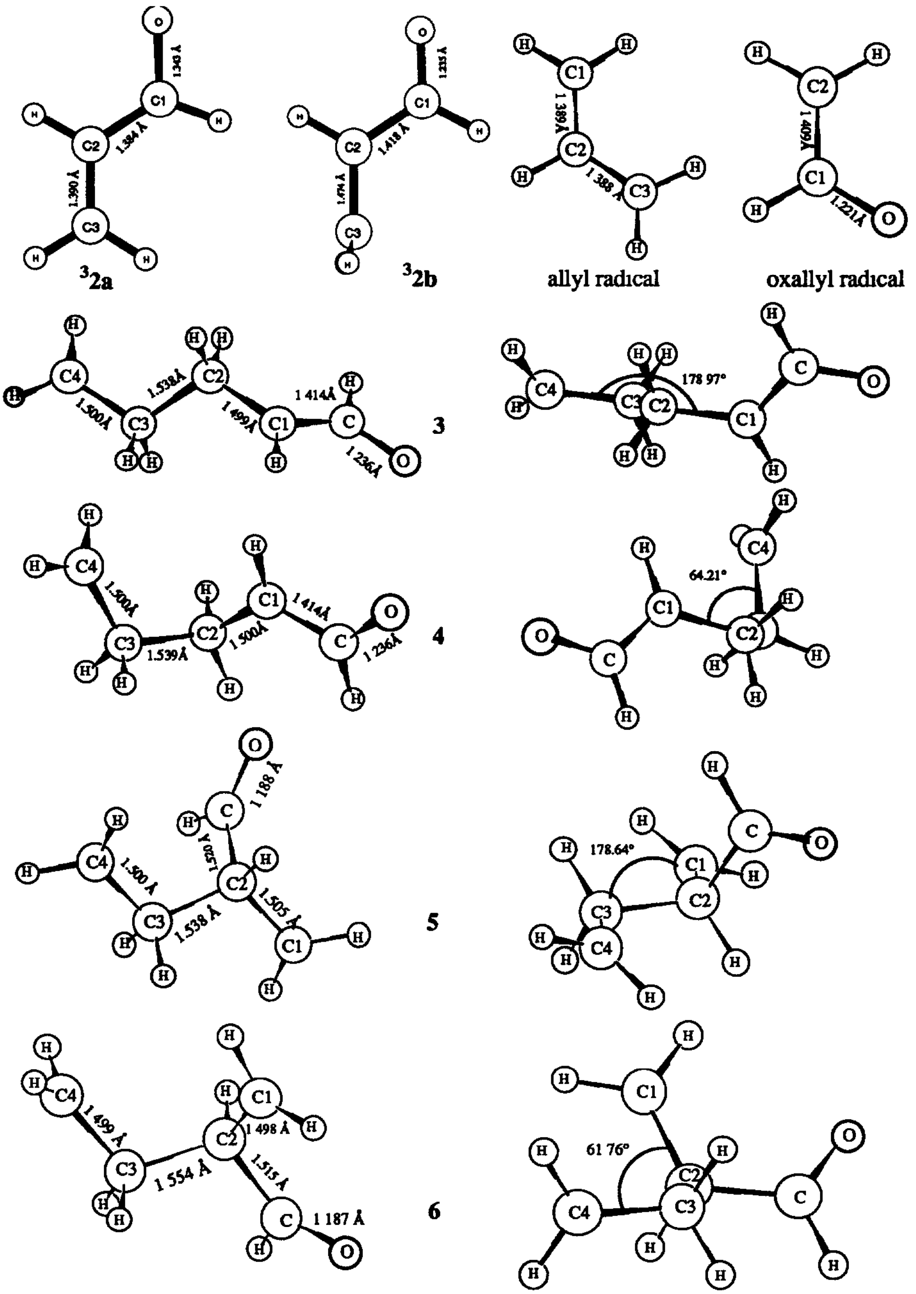
The excitation of acrolein results in the formation of the excited state singlet that rapidly intersystem crosses to the triplet state,[2,3] and it is the triplet state that is primarily responsible for the formation of cyclobutanes.[3,7] During the electronic reorganization to the triplet state, several significant geometric alterations occur that bear comment. In this regard, the structures of both the planar n-π^* state and the twisted, π-π^* state forms have been calculated, and are displayed in **Figure 2**, the twisted π-π^* excited state is proposed to be involved in the [2 + 2] cycloaddition reaction.[2]

The C_α-C_β and C_α-$C_{C=O}$ carbon-carbon bond lengths in the planar form of triplet acrolein are 1.39Å and 1.38Å, respectively, which are both slightly longer than typical C-C double bonds and indeed are reminiscent of a delocalized allyl system.

This classification is also reflected in a carbon-oxygen bond length (1.34Å) indicative of a C-O single bond to an sp^2 center.[23] On the other hand, the twisted form of acrolein assumes a significantly different structure. Here the C_α-C_β bond length of 1.47Å is in line with a typical single bond length between two sp^2 centers,[23] whereas the C_α-$C_{C=O}$ (1.42Å) and the C-O bond length (1.24Å), are both intermediate between single and double bond lengths. Thus, the twisted form of triplet acrolein is structurally similar to an oxallyl radical wherein one of the unpaired electrons is delocalized into the formyl group, and with the other electron residing primarily on the terminal β-carbon.



Consideration of the π spin density on the two triplet moieties provides another informative perspective. Examination of the π spin densities of the n-π^* state of triplet acrolein (**Figure 3**) indicate that there is considerable unpaired electron density on the carbonyl carbon and C_β, which is of similar size and alteration to that of allyl radical. Very little spin density is located on the oxygen in the plane containing the "allylic π-system", but rather a large amount (0.885 electrons) lies in an orthogonal orbital. In contrast, the π-π^* state of triplet acrolein resembles an oxallyl radical, with significant amounts of unpaired π spin density on both the



^{3}**2a** ^{3}**2b** allyl radical oxallyl radical

3

4

5

6

Figure 2. Geometries of Radical and Triplet Biradical Species (UHF/6-31G*//6-31G*)

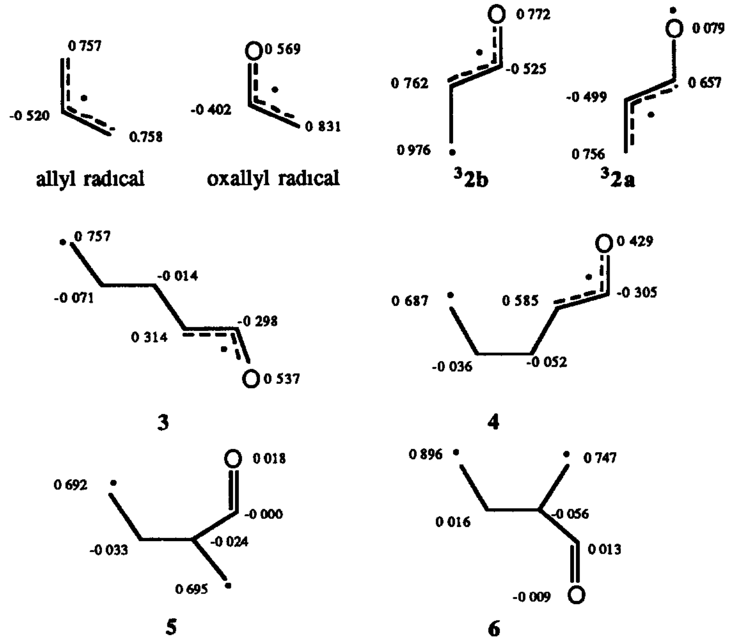


Figure 3. π Spin Densities of Radical and Triplet Biradical Species (UHF/6-31G*//6-31G*)

oxygen and C_α. Additionally, a large amount of spin density (0.976 electrons) is located on the terminal carbon, in an orbital orthogonal to the C_α-$C_{C=O}$-O plane. While in both the planar and twisted triplets the two unpaired electrons of like spin avoid interaction, the differences in the electronic states are striking.

The mechanism outlined in **Scheme 1** indicates that two distinct triplet biradicaloid species may be formed depending on which carbon-carbon bond is formed first. The formation of a carbon-carbon bond between the β-carbon of acrolein and the olefin results in a 1-formyl biradical (the 1,4-biradicals are **3** and **4** in **Figure 2**), whereas initial C-C bond formation at the α-carbon of acrolein yields a 2-formyl biradical (the 2,3-biradicals are **5** and **6** in **Figure 2**). Both isomeric triplet biradical species are flexible and sufficiently unconstrained to sample a variety of conformations, only the low energy *gauche* and *trans* conformations of the 1,4 and the 2,3-biradicals are discussed.

The geometries of the triplet 2,3-biradicals (**5** and **6** in **Figure 2**) are structurally and electronically similar exclusive of the $C_1C_2C_3C_4$ dihedral angle. All carbon-carbon bonds are within the expected range of unexceptional single bonds, and the carbonyl bond of the formyl group exhibits a normal bond length of 1.19Å. Not surprisingly, the π spin densities are localized on the radical centers (**Figure 3**) with little leakage onto the aliphatic backbone. The conformers of the 1,4 biradicals are also quite similar (**3** and **4** in **Figure 2**), nevertheless they are quite distinct from the isomeric 2,3 biradicals. The geometries (**Figure 2**) of the 1,4 biradical intermediates are controlled by the formyl group, which in each case affords a significant degree of delocalization of an adjacent radical center. As before the $C_{C=O}$-C_α bond length of 1.41Å, and the C-O bond length of 1.24Å are in a range intermediate between normal single and double bond lengths, and are analogous to the geometry calculated for oxallyl radical (**Figure 2**). This characterization is corroborated by the π spin densities of the 1,4-biradicals (**Figure 3**) in which the greatest unpaired spin density resides on the carbonyl oxygen and C_α.[24]

III. Reactivity and Selectivity

1. Energy Pathways

The energies of the geometry optimized acrolein-ethylene photocycloaddition reactants, triplet intermediates and product are collected in **Table 1**; they are summarized graphically in **Figure 4**.

Table 1. Hartree-Fock Energies for the Putative Olefins, Aliphatic Biradicals and Cyclobutane Involved in [2+2] Cycloaddition of Acrolein and Ethylene.^{a}

	Energies		**Zero Point Energies**	
Compound	**Ground State**	**Triplet**	**Ground State**	**Triplet**
(**1**) ethylene	-78.031718		0.054782	
(**2a**) acrolein (planar)	-190.762426	-190.701511	0.066490	0.061561
(**2b**) acrolein (twisted)		-190.706902		0.060420
(**3**) *trans*-1-formyl-biradical		-268.778687		0.121330
(**4**) *gauche*-1-formyl-biradical		-268.778172		0.121200
(**5**) *trans*-2-formyl-biradical		-268.756658		0.119500
(**6**) *gauche*-2-formyl-biradical		-268.755963		0.118855
(**7**) formylcyclobutane	-268.822523		0.129344	

(a) Energies in Hartrees

It warrants notice that the inclusion of zero point energies has only a negligible effect on calculated energetics in all cases. The initial increase in energy corresponds to the excitation of acrolein to the triplet state (which is formed upon intersystem crossing from the excited singlet state) and is underestimated at 31.0 kcal•mol^{-1}.[25] Within the context of the putative mechanism (**Scheme 1**), triplet acrolein forms an exciplex with the ground-state olefin prior to the bond forming step, however, the significance of the exciplex in issues of reactivity are beyond the scope of this work.[26] The formation of a bond (with ethylene) at the α-carbon of acrolein results in a 2-formyl substituted biradical (2,3-biradical) that lies 8.5 kcal•mol^{-1} below (**1**) + (^{3}**2b**), with a slight preference for the *trans* conformer, **5**. On the other hand, the formation of a bond at C$_\beta$ results in a 1,4-biradical (**3** or **4**) that is favored energetically over the 2,3-biradicals by 12.6 kcal•mol^{-1}.[27] This additional stability (of the 1,4-biradicals) is a consequence of radical delocalization onto the adjacent formyl group. Intersystem crossing to the singlet and subsequent collapse of the biradical results in the formation of formylcyclobutane, the overall reaction thermodynamics calculated reveal an exothermicity of 12.7 kcal•mol^{-1}. Thus, it is reasonably concluded that the formation of the first carbon-carbon bond at C$_\beta$ of the enone is favored thermodynamically, and lacking a large steric bias (i.e., caused by substitution on the enone) this same bond should be preferred kinetically as well. In other words, factors that stabilize the biradical intermediates seem likely to also stabilize the corresponding transition states.

These results are in line with the trapping experiments of Weedon et. al.[28] In their work, H_2Se was introduced into the photoannulation of cyclopentenone and various substituted alkenes (for example, ethyl vinyl ether). This reaction resulted in reduction and disproportionation products rather than cycloadduct formation. Of the four reduction and disproportionation products possible, only the two arising from biradicals (one head-to-head and the other head-to-tail) which have no primary radical centers were formed and in ~ 1:1 ratio. These results along with the calculations presented here on the unsubstituted enone-olefin reaction, suggest that only stabilized biradicals (secondary or delocalized) are formed in the photoannulation. Regioselection probably arises from the relative rates at which each of these biradicals revert back to starting materials. This speculation is based upon Weedon's results and our calculations which suggest that the ring closure step it is an unlikely place for regioselection.

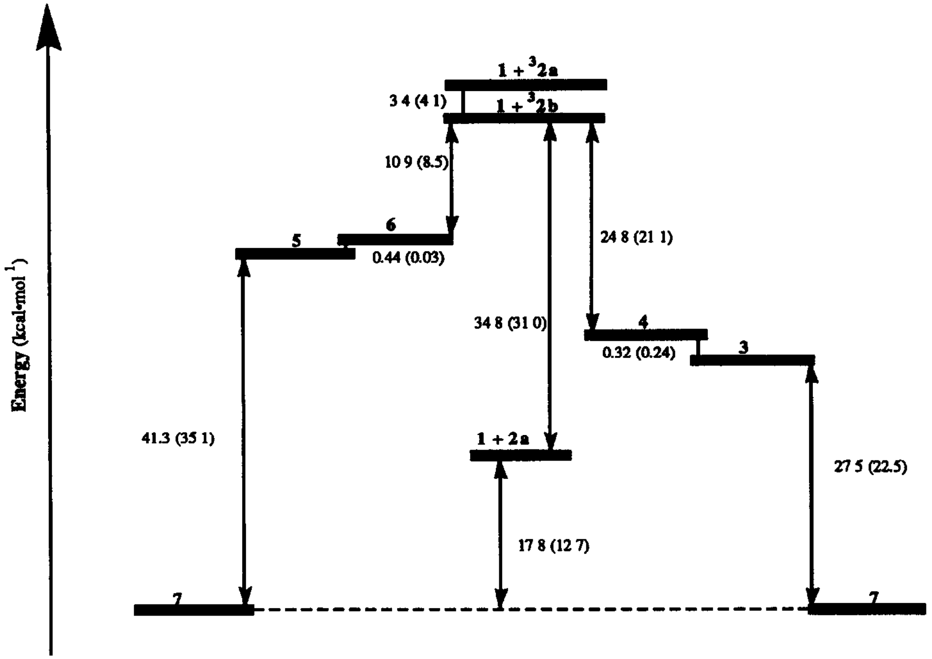
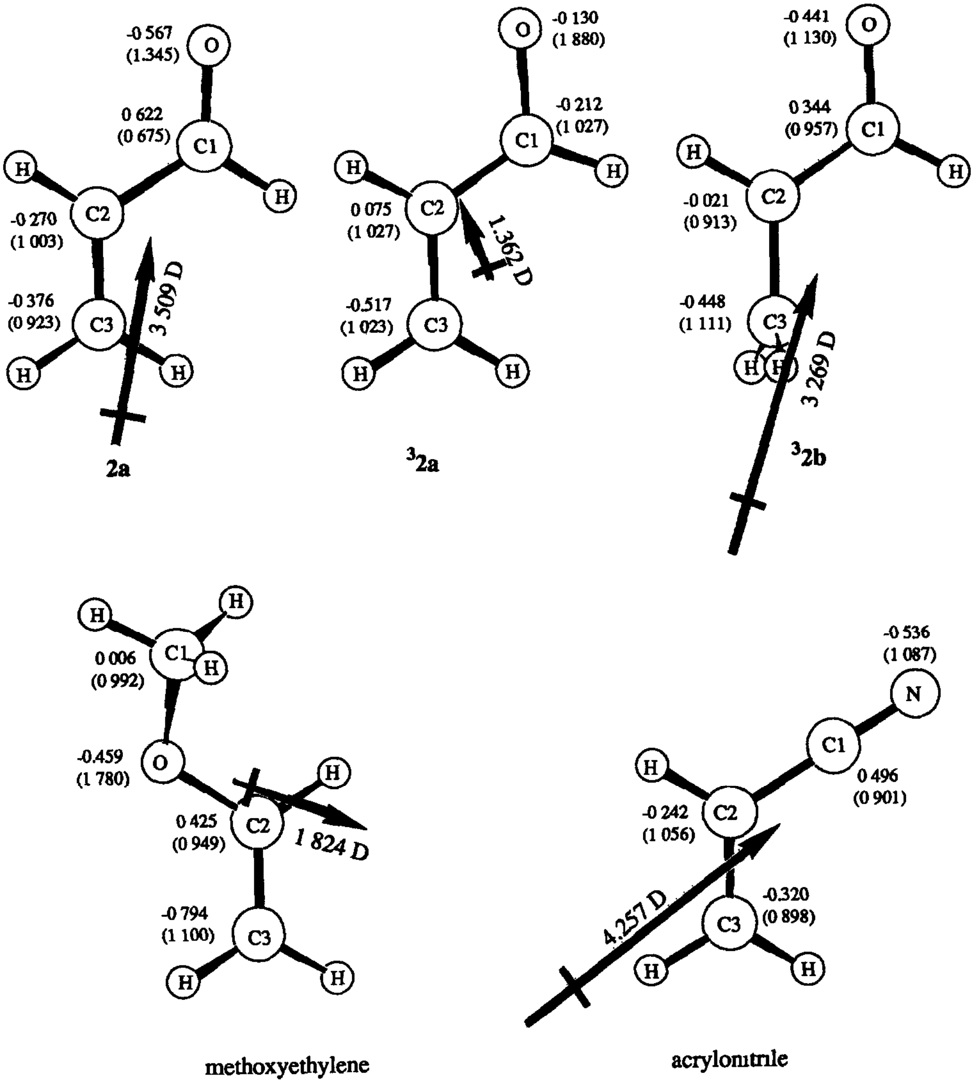


Figure 4. Energy Differences of the Putative Intermediates of the Acrolein-Ethylene Photocycloaddition Reaction (Energy differences with zero point corrections are in parenthesis)

2 Selectivity

(a) Coulombic Models. Enone photocycloadditions are known to exhibit head-to-tail and head-to-head regioselectivity when olefins containing electron donating groups and electron withdrawing groups, respectively, are employed.[2b,3] This selectivity has been attributed to orientational effects in the putative triplet exciplex, wherein it is believed that the triplet state has a reversed polarization of C_α and C_β (i.e C_β is negative relative to C_α) relative to the ground state [2b,3] The alignment of dipoles in the exciplex would thus provide a rationalization for the noted product distributions

A test of the proposal that regioselectivity arises from favorable "dipolar alignment" of the two reactants followed from molecular electrostatic potentials calculated from HF/6-31G* wavefunctions Fitted monopoles[17] and calculated dipole moments were also employed in the characterization (see **Figure 5**) For the additions of triplet acrolein (twisted form) to electron-poor olefins, the Corey-DeMayo[2,3] model for regioselectivity is inconsistent with calculated results Specifically, the proposed[2,3] polarization of the electron-deficient double bond is incorrectly assigned based upon these calculations, i.e the β-carbon is negatively charged relative to the α-carbon in acrylonitrile and acrolein. Applying Corey's regioselectivity model using the atomic charges (in **Figure 5**) for acrylonitrile and triplet acrolein would assign a head-to-tail orientation, contrary to the experimental observations [3] Notwithstanding, Corey's assignment of polarization in electron-rich double bonds is consistent with these calculations, i e C_β is more negative than C_α. Here Corey's model correctly assigns observed regiochemistries As an example, the dipolar interaction between methoxyethylene and triplet acrolein would lead to a head-to-tail cyclization which is in accord with experiment [3] Thus, consideration of both electron-rich and electron-deficient cyclo-addends speaks against Corey's polarization model



2a

^{3}**2a**

^{3}**2b**

methoxyethylene

acrylonitrile

Figure 5 Fitted Atomic Charges, Dipole Moments and Mulliken π Electron Densities (in parentheses) of Substituted Olefins (HF/6-31G*//6-31G*)

Extension of the polarization to consider the alignment of the molecular dipoles of the cyclo-addends does not improve its ability to make assignments of regiochemistry. For example, the most favorable alignment of the dipoles of triplet acrolein (twisted) and acrylonitrile situates the two double bonds in a head-to-tail orientation, opposite to the experimentally preferred regiochemistry. Moreover, this type of analysis is even more problematic in the electron-rich olefin case where the alignment of the dipoles of methoxyethylene and triplet acrolein places the two double bonds in a perpendicular orientation in which no regiochemical preference can be assigned.

It is interesting to note that while the overall coulombic quantities like electrostatic potential derived atomic charges and molecular dipole moments fail to provide insight into the origin of regiochemical preferences, consideration of only the π orbital contribution in the coulombic interactions proposed does yield a successful model for regiochemical assignments. π-only electron densities[29] (**Figure 5**) derived using a Mulliken population analysis[30] correctly assigns head-to-head and head-to-tail cycloaddition regiochemistries of triplet acrolein adding to acrylonitrile and methoxyethylene, respectively. Nevertheless, it is important to note that population methods and in particular Mulliken methods partition electron density in a well defined yet arbitrary fashion, and thus can give only gross approximations for charge distributions.[18] While the noted trend is strictly empirical, it does lead to regiochemical assignments that agree with experimental results.

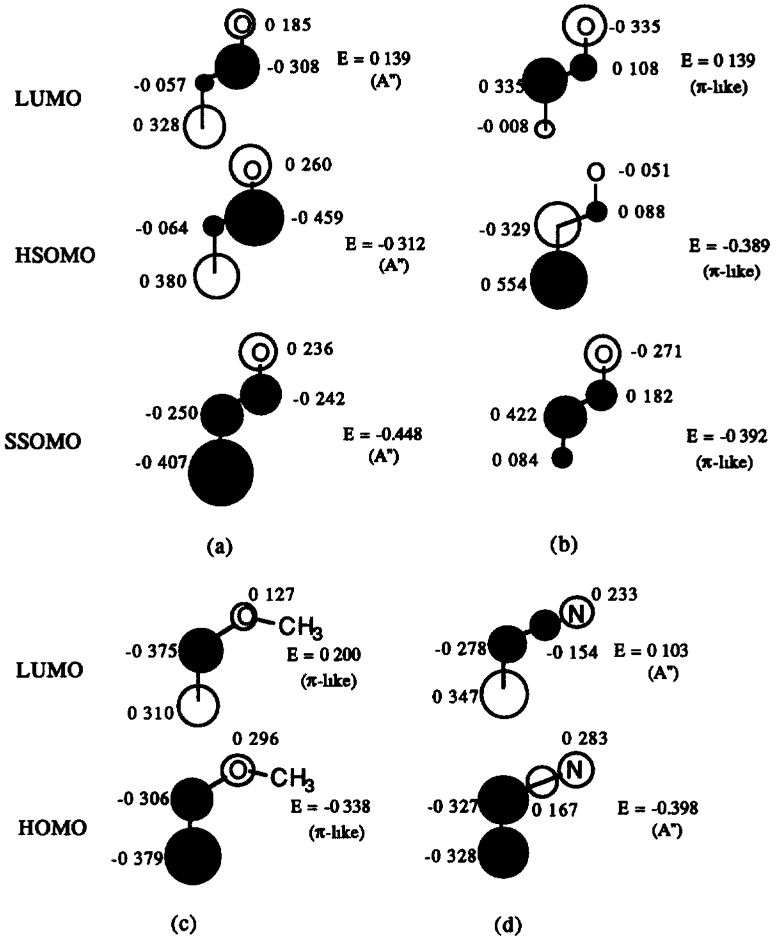
(b) Orbital Overlap Models. An alternative perspective from which regioselectivity may be discussed is the interaction between the frontier molecular orbitals (FMO) of the triplet enone and substituted olefins. Here, as in all FMO approaches, a balance must be struck between the square of the orbital overlap and the energy separation of the interacting orbitals, $\Delta\varepsilon$.[31] A similar analysis addressing the regioselectivity of the addition of methyl radical to substituted olefins, involving the SOMO-HOMO interaction, was reported as successful.[32]

The frontier orbitals of triplet acrolein and ethylene are displayed in **Figure 6**. Both of the two singly occupied molecular orbitals (SOMO) and the lowest unoccupied molecular orbital (LUMO) of triplet acrolein are included, as are the highest occupied molecular orbital (HOMO) and the LUMO of the olefins considered. Within this manifold of frontier orbitals, the subjacent SOMO-HOMO and the highest SOMO-HOMO interactions have significantly smaller orbital energy separations ($\Delta\varepsilon$) and hence should dominate in the frontier orbital expression. This analysis provides a characterization of initial bond formation in the [2 + 2] photocycloaddition as a radical attack (triplet acrolein acting as the radical) on substituted olefins.

Bond formation at C_β and $C\alpha$ of triplet acrolein is predicted by HSOMO-HOMO and the SSOMO-HOMO interactions, respectively, between triplet acrolein and ethylene. In the case of the reaction of excited enones with electron deficient olefins, the best orbital interaction in the acrylonitrile-triplet acrolein frontier orbital analysis is the SSOMO-HOMO interaction, wherein there is no preference for the site of first bond formation. In contrast to the regiochemical ambiguities assigned for electron-deficient olefins, electron-rich olefins exhibit marked regioselectivity using an identical FMO analysis. In these later cases, the best orbital interaction involves the HSOMO of triplet acrolein and the HOMO of the electron-rich olefin, methoxyethylene, and this interaction clearly favors initial bond formation between C_β of triplet acrolein and C_β of methoxyethylene, this leads to an incorrect assignment of a (i.e. head-to-head) of adduct stereoselectivity.

CONCLUSION

In summary, several conclusions follow from the previous discussion regarding reactivity and selectivity in [2 + 2] photocycloadditions. Conformational analysis of substituted cyclobutane products and extrapolation of these analyses to the related transition structures makes it clear that observed selectivities cannot occur in the ring closure step, but rather selectivity must be a consequence of an earlier step in the reaction. The geometry and electronic structure of triplet acrolein, and the thermodynamic data of the two putative triplet biradicals suggest C_β of triplet acrolein as the most reactive site for initial bond formation This initial bond formation must be the source of observed stereoselectivity.



(a) (b)

(c) (d)

Figure 6. Inner π Orbital Coefficients and Orbital Energies for the Frontier Orbitals of (a) planar triplet acrolein (b) twisted triplet acrolein (c) methoxyethylene (d) acrylonitrile (Energies in Hartrees)

Two possible causes for the noted regioselectivity of the photoinduced enone [2 + 2] cycloaddition have been probed in this study The first possibility is regiocontrol arising from the initial reaction of the two isolated species involving an early transition state This was examined using perturbation theory, FMO analyses have had success in explaining regiochemical preferences in the addition of radicals to olefins[32] Notwithstanding, treatment of the initial bond formation using an FMO approach was unsuccessful in the assignment of regiochemistry consistent with experiment This speaks against the possibility of regioselectivities arising from the addition of a radical moiety to a substituted olefin

The second possibility, following a proposal in the literature,[3,9] is the assignment of regioselectivities based upon simple coulombic interactions between the triplet enone and substituted olefins This proposed model was tested via calculated electrostatic potentials and dipole moments. It was discovered that simple coulombic interactions do not correlate with observed regiochemistries. This result casts doubt on the coulombic interaction of the isolated reactants as the source for regioselection. An interesting correlation, however, involves Mulliken π electron densities and experimental regiochemical observations. These densities can be used as a model, albeit a strictly empirical one due to known deficiencies with population analyses, to explain observed regiochemical outcomes in enone-olefin photocycloadditions.

The major significance of this study lies in the following two conclusions: 1) regio- and stereoselectivity arise from the first bond formation and 2) the regioselectivity model involving simple coulombic interactions (which has been used for almost 30 years) is not consistent with the calculated electrostatic properties of the species involved! Although the possibility of exciplex controlled regioselectivity remains, the results discussed here in conjunction with the work of Weedon et. al.[28] point to the relative back reaction rates, i.e. reversion to starting materials, of the head-to-head and head-to-tail biradicals formed in the enone-olefin photoannulation reaction as the source of regioselection.

Acknowledgment.

We thank Dr. David Hartsough for an implementation of the electrostatic potential fitting procedure.

REFERENCES AND NOTES

1. (a) Roberts, J. D.; Sharts, C. M. *Org. React.* **1962**, *12*, 1-56. (b) Bartlett, P. D. *Quart. Rev. J. Chem. Soc.* **1970**, *24*, 473-497. (c) Hoffman, R.; Swaminathan, S.; Odell, B. G.; Gleiter, R. *J. Am. Chem. Soc.* **1970**, *92*, 7091-7097. (d) Maier, W. F.; Lau, G. C.; McEwen, A. B. *J. Am. Chem. Soc.* **1985**, *107*, 4724-4731. (e) Duran, R.; Bertran, J. *J. Mol. Struct.(THEOCHEM)* **1984**, *107*, 239-244. (f) Segal, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 7892-7898. (g) Burke, L. A.; Leroy, G. *Bull. Soc. Chim. Belg.* **1979**, *88*, 379-393. (h) Bernardi, F.; Bottini, A.; Robb, M. A.; Schlegel, H. B.; Tonachini, G. *J. Am. Chem. Soc.* **1985**, *107*, 2260-2264. (i) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 117-124. (j) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 199-206. (k) Okado, T.; Yamaguchi, K.; Fueno, T. *Tetrahedron* **1974**, *30*, 2293-2300. (l) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1975**, *97*, 6108-6116. (m) Wright, J. S.; Salem, L. *J. Am. Chem. Soc.* **1972**, *94*, 322-329. (n) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.*, **1980**, *102*, 5409-5410. (o) Doubleday, C.; McIver, J. W.; Page, M. J.; *J. Am. Chem. Soc.*, **1982**, *104*, 3768-3770. (p) Doubleday, C.; Camp, R. N.; King, H. F.; McIver, J. W.; Mullally, D.; Page, M. *J. Am. Chem. Soc.*, **1984**, *106*, 447-448.
2. (a) DeMayo, P. *Acc. Chem. Res.* **1971**, *4*, 41-47. (b) Baldwin, S. W. *Organic Photochemistry* **1981**, *5*, 123-225 (c) Sano, T.; Horiguchi, Y.; Tsuda, Y. *Chem. Pharm. Bull.* **1987**, *35*, 23-34. (d) Loutfy, R. O.; DeMayo, P. *Can. J. Chem.* **1972**, *50*, 3465-3471. (e) Loutfy, R. O.; DeMayo, P. *J. Am. Chem. Soc.* **1979**, *99*, 3559-3565.
3. Corey, E. J.; Bass, J. D.; LeMahieu, R.; Mitra, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 5570-5583.
4. Caldwell, R. A.; Creed, D. *Acc. Chem. Res.* **1980**, *13*, 45-50.
5. (a) Schuster, D. I.; Heibel, G. E.; Brown, P. B.; Turro, N. J.; Kumar, C. V. *J. Am. Chem. Soc.* **1988**, *110*, 8261-8623. (b) Lange, G. L.; Organ, M. G; Lee, M. *Tett. Lett.* **1990**, *31*, 4689-4692.
6. Epiotis, N. D. *Theory of Organic Reactions*; Springer-Verlag: Berlin, **1978**, 51-100.
7. Lenz, G. R. *Rev.Chem. Intermediates* **1981**, *4*, 369-405.
8. Burnstein, K. Y.; Serebryakov, E. P. *Tetrahedron* **1978**, *34*, 3233-3238.
9. Kuzuya, M.; Yokota, N.; Akihiro, N.; Okuda, T. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1379-1385.
10. Ohsaku, M. *J. Mol. Struct.(THEOCHEM)* **1988**, *179*, 95-105.
11. Chadha, R; Ray, N. K. *Proc. Ind. Acad. Sci.* **1980**, *89*, 539-547.
12. Chadha, R; Ray, N. K. *Ind. J. Chem.* **1986**, *25A*, 111-115.

13 Kim, J H.; Oh, S. W., Lee, Y. S.; Shim, S. C. *Bull Korean Chem Soc*. **1987**, *8*, 298-301.

14 *GAUSSIAN85* : Hout, R. F , Jr.; Francl, M. M.; Kahn, S D.; Dobbs, K. D.; Blurock, E. S.; Pietro, W. J ; McGrath, M P., Steckler, R ; Hehre, W. J. University of Illinois (Urbana-Champaign) and University of California (Irvine), **1988**.

15. (a) Hariharan, P. C ; Pople, J. A. *Chem Phys. Lett* **1972**, *16*, 217-219 (b) Hariharan, P C ; Pople, J A. *Theor Chim Acta* **1973**, *28*, 213-22 (c) Hariharan, P. C., Pople, J. A. *Mol Phys* **1974**, *27*, 209-214.

16. (a) Kahn, S D , Pau, C. F.; Hehre, W. J. *Int J Quantum Chem Sympos*. **1988**, *22*, 575-591 (b) Francl, M. M., Hout, R F , Jr.; Hehre, W J *J Am Chem. Soc* **1984**, *106*, 563-570. (c) See appendix in Kahn, S D., Pau, C. F., Overman, L E ; Hehre. W. J. *J Am Chem Soc* **1986**, *108*, 7381-7396.

17 Cox, S R.; Williams, D E. *J Comput Chem* **1981**, *2*, 304-323.

18 Hehre, W. J.; Radom, L., Schleyer, P v. R., Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley· New York, **1986**, 22-24.

19 Calculations employed the SYBYL 5 2 force field as implemented in *SPARTAN*. *SPARTAN* 1.0. Wavefunction, Inc., Irvine CA, **1991**. SYBYL 5.2 force field· Clark, M ; Cramer, R. D ; van Opdenbosch, N. *J Comp Chem* **1989**, *10*, 982-1012.

20 (a) Kilb, R. W , Lin, C C.; Wilson, E. B Jr *J Chem Phys* , **1957**, *26*, 1695-1703. (b) Wiberg, K. B. *J Am Chem. Soc* , **1986**, *108*, 5817-5822.

21. A-values for -CH=CH_2 and for -CO_2H, are 1.7 and 1.36 respectively. see: March, J.; *Advanced Organic Chemistry*, Wiley New York; **1985**, 126.

22 The closest contacts between the formyl group and the 3-axial hydrogen are approximately 0.5Å longer compared to cyclohexanes. The computed rotational barrier of 1.5-2 0 kcal•mol^{-1} for a formyl group on a cyclobutane ring is in line with work on more conventional groups adjacent to carbonyl functionality

23 see reference 21, p. 19.

24 Wiberg, K. B.; Breneman, C M ; Laidig, K E.; Rosenburg. R E. *Pure Appl Chem* **1989**, *61*, 635-642.

25 The experimental triplet energy of acrolein is 69 kcal•mol^{-1} see· Birge, R R ; Leermakers, P A. *J Am Chem. Soc* , **1972**, *94*, 8105-8117.

26 To properly describe intermolecular interactions requires inclusion of electron correlation and significantly increases the number of degrees of freedom; both of which increase the computational expense of the system considerably. This problem is compounded by the fact that one of the participants is in the excited state Unfortunately, no method has been developed that allows exciplexes of the type represented by these systems to be addressed.

27 The value estimated for allyl delocalization is 14.0 kcal•mol^{-1} from ESR derived kinetic data. see. Korth, H G., Trill, H ; Sustmann, R , *J Am Chem Soc* **1981**, *103*, 4483-4489

28 Andrew, D , Hastings, D J , Oldroyd, D L., Rudolph, A., Weedon, A C , Wong, D F., Zhang, B *Pure & Appl Chem* , **1992**, *64*, 1327-1334, and references therein

29 The charge distributions reported herein are consistent with previous reports (a) Zimmerman, H. E ; Binkley, R W., McCullough, J J ; Zimmerman, G A *J Am Chem Soc* **1967**, *89*, 6589-6595 (b) Jungen, M.; Labhart, H *Theoretica Chim Acta* **1968**, *9*, 345-365

30 Mulliken, R. S *J Chem Phys* , **1955**, *23*, 1833, 1941, 2338, and 2343.

31 Fleming, I , *Frontier Orbitals and Organic Chemical Reactions*, Wiley: New York; **1976**, 27-29.

32 Canadell, E ; Eisenstein, O , Ohanessian, G , Poblet, J. M *J Phys Chem* **1985**, *89*, 4856-4861