state.[36] In view of the selectivity relationships in bromination which make it possible to interpret small ρ variations, one can obtain precise information about the shifts of the transition-state position induced by structural changes. The utility of the FER coefficients for describing the energy profile of a reaction has been severely criticized in the last few years.[4,36,37] By using selectivity relationships or IFER for MSE, the factors affecting the reactivity can be more accurately quantified by the constants a and q. In particular, our results provide a new criteria for the application of the RSP, the limits of which have been discussed at great length: for the same log k, two different selectivities are observed depending on whether resonance effects occur or not, since there are two selectivity relationships for the same reaction (Figure 1). It was already known that the RSP cannot be applied to reactions where several bonds are modified;[12,37] it appears now that the reactivity-determining factors must be of the same type.

The present methods for interpreting reactivity are based on mathematical formulations of earlier qualitative concepts such as BEP modelisations of potential energy surfaces,[38] the Hammond postulate,[39] Thornton's rules,[37] etc.... Several authors[4a,40] currently question the validity of these concepts because there are few extensive data bases for testing them and their theoretical applications. There are several reasons for thinking that bromination may be helpful in this respect: (i) abundant kinetic data under standardized conditions and over a large reactivity range are available and (ii) despite the high endergonicity of its rate-determining step, the intrinsic kinetic contribution is not small with respect to the thermodynamic one. In this paper we have emphasized that the selectivity differences between the formation of benzylic bromocations bearing resonant or nonresonant substituents R arise from differences in thermodynamic contributions. This interpretation does not exclude the probability that resonance also modifies the kinetic contribution by decreasing the intrinsic barrier. Unfortunately, a Marcus model,[41] developed for electron-transfer reactions and successfully applied to proton[42] and methyl[27b] transfer reactions, is not strictly applicable to the kinetic contribution in bromination: α is probably close to 1, identity reactions of bromination do not exist, and thermodynamic data for the rate-determining step are not at present available. Further work in progress will enable the evaluation of more general models[27a,30,43] in bromination.

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Trajectory Analysis. 1.[1] Theoretical Model for Nucleophilic Attack at π-Systems. The Stabilizing and Destabilizing Orbital Terms

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Abstract: A simple model is proposed for qualitatively describing the trajectory along the reaction coordinate of an attacking nucleophile at a π-electrophilic center. Two sets of first-order interactions are considered: (1) the *stabilizing* (charge transfer) interactions of the nucleophile HOMO with the lowest unoccupied π^* and σ^* molecular orbitals of the electrophile and (2) the *destabilizing* (repulsive) interactions of the nucleophile HOMO with the highest occupied π and σ molecular orbitals of the electrophile. A more complete analysis involving all unoccupied and occupied molecular orbitals on the π-electrophile is also presented.

In a classic series of papers, Burgi, Dunitz, et al.[2-5] were able to map portions of the reaction coordinate for the addition of oxygen- and nitrogen-centered nucleophiles to carbonyl groups by correlating structural regularities found in a large number of solid-state structures. From this elegant analysis, the trajectory followed by such nucleophiles in the course of addition to a carbonyl group was described by an angle θ with respect to the C-O bond axis (Figure 1). Values of θ ranging from 70° to 80° were observed at nucleophile-substrate distances of 2.5-3.5 Å. An ab initio SCF calculation of the trajectory of hydride ion attacking formaldehyde gave similar results.[2] More recently, trajectory calculations of hydride attacking acetylene and ethylene[6,7] likewise characterized a transition state described by an acute angle θ. In these cases θ values of 54° and 56° were reported for acetylene and ethylene, respectively. The authors of these studies suggest that the calculated trajectories are de-

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(1) In the context of this research, the word "trajectory" means the minimum-energy path through the multidimensional geometrical space characterizing the approach of two reacting species in the immediate vicinity of the "transition state" geometry. In the sense used here, the word has a meaning substantially different from that used in classical mechanics where it represents the dynamic path through classical phase space of a system characterized by well-defined initial conditions or the usage in statistical analysis of reactions that follow paths across a well-defined potential surface from initial reactants in precisely defined states to final products in similarly well-defined states.

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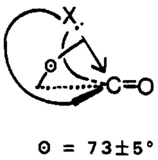

Figure 1. θ trajectory for nucleophilic attack at π-electrophilic center.

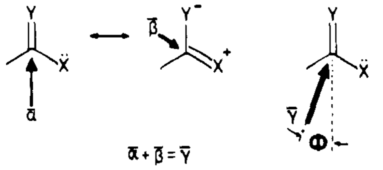

Figure 2. Contributions of Lewis (resonance) structures to ϕ trajectory.

termined by the contour of the π^* orbital and changes in the nature of the nucleophile and the substituent on the electrophilic substrate might be expected to cause changes in the preferred approach direction. Baldwin,[8-11] in a series of papers, has described rules for approximating preferred nucleophilic approach trajectories at π-systems. These qualitative rules, termed "approach vector analysis", are summarized as follows: (a) the angle θ is assumed to be 70° for all cases where the approaching nucleophile is derived from a first-row element, (b) the angle ϕ is determined by the resultant of the vector addition of the trajectories for the two leading Lewis structures ($-\ddot{X}-C{=}Y \leftrightarrow -X{=}C-\ddot{Y}$) associated with the functional group $-\ddot{X}-X{=}Y$. The magnitude of each vector is dependent upon the relative contribution of that Lewis (resonance) structure as shown in Figure 2. Thus, the angle ϕ becomes greater in the series X = CR_3, NR_2, OR, O^-. With this model, Baldwin was able to rationalize the stereochemistry of the products formed from a large number of cyclization, hydride reduction, and alkylation reactions. It was also noted that, in contrast to first-row nucleophiles, second-row nucleophiles were able to achieve reaction trajectories with larger θ values. This was partially ascribed to the ability of these nucleophiles to participate in 3d back-bonding. This latter interaction, of course, would be maximized at $\theta > 90°$. Thus, the experimental and theoretical observations at this juncture indicate that (1) first-row nucleophiles approach reactive π-systems with $\theta < 90°$ and that this may be a result of the π^*-orbital contour, (2) with respect to a reference π-electrophile, θ appears to vary from one nucleophile to another, and (3) ϕ is determined by the magnitude of the π-electron donating ability of the atoms bonded directly to the π-system. Consideration of these points raises the following questions: How does the angle θ vary with the nature (or more precisely, the eigenfunctions and eigenvalues) of the π-electrophile and the nucleophile? Is the predicted trajectory a summation of independent terms each representing the nucleophile and the π-electrophile or are the two systems interrelated? Finally, can a simple (and necessarily qualitative) model be derived that will answer these questions with a minimum of molecular orbital parametric input so as to be of value in predicting the reactivity window of organic and biochemical reactions without recourse to extensive SCF-MO computations? We now wish to report such a model.

Theoretical Model

Frontier molecular orbital analysis requires that the first leading stabilizing (two-electron) term for nucleophilic attack upon π-systems is that associated with the highest occupied molecular orbital (HOMO) of the nucleophile, E_N, and the lowest unoccupied π^* orbital of the π-electrophile. While this approximation has been highly successful, it is important to recognize that stabilizing two-electron (charge transfer) interactions with unoccupied σ^* molecular orbitals and destabilizing four-electron (repulsive) interaction with occupied π and σ molecular orbitals also make important energetic contributions. *The model proposed in this manuscript includes the stabilizing two-electron (charge transfer) interactions of the nucleophile HOMO with all the unoccupied π^* and σ^* molecular orbitals on the π-electrophile, as well as the net destabilizing four-electron (repulsive) interactions of the nucleophile HOMO with all the occupied π and σ molecular orbitals* (Figure 3). A qualitative estimate of the angle θ for this reacting system near the transition state is derived from simultaneous maximization of the two-electron stabilizing interactions and minimization of the four-electron destabilizing interactions. For the sake of simplicity and understanding, it will be initially assumed that the π-electrophile has associated with it only the following molecular orbitals: one unfilled π^*, one unfilled σ^*, one filled π, and one filled σ. In essence, the derivation will be performed at the π,σ-frontier levels. The resulting equations will subsequently be elaborated to include all unfilled and filled molecular orbitals.

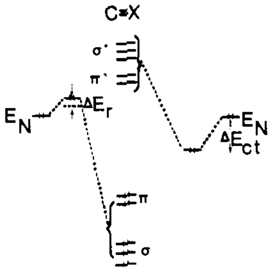

Figure 3. Energy considerations in trajectory model.

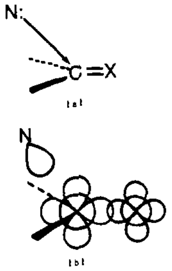

Figure 4. Orbital considerations in trajectory model.

Stabilizing Two-Electron (Charge Transfer) Terms. In order to evaluate the contributions of the stabilizing two-electron (charge transfer) interactions, let us consider the system in Figure 4a in which the C=A functionality is arranged such that the π-orbital array is oriented along the z axis, the σ-orbital array associated with the C—A bond axis is oriented along the x axis, and the nucleophile orbital is approaching the carbon atom in the x,y plane. The corresponding orbital representation is illustrated in Figure 4b. The π^* and σ^* molecular orbitals have energies E_{π^*} and E_{σ^*}, respectively, and the filled orbital on the nucleophile has an energy E_N. The wave functions associated with E_{π^*}, E_{σ^*}, and E_N are represented by the following equations:

$$\Psi_{\pi^*} = (c_{p_z^*} p_z)_C + (c_{p_z^*} p_z)_A$$

$$\Psi_{\sigma^*} = (c_{s^*} p_s + c_{p_x^*} p_x)_C + (c_{s^*} p_s + c_{p_x^*} p_x)_A$$

$$\Psi_N = c_{p_N} p_N$$

where the subscripts C and A designate the atomic centers on the C=A electrophile, $c_{p_z^*}$, $c_{p_x^*}$, and c_{s^*} are the coefficients associated with the p_z, p_x, and s atomic orbitals, respectively, at each of these centers, and c_{p_N} is the coefficient associated with the nucleophile atomic orbital p_N. In order to simplify the model, only the atomic orbital components associated with the π-reaction center (center at carbon) will be considered. Approximating the wave function of the total system as a linear combination of Ψ_{π^*}, Ψ_{σ^*}, and Ψ_N and minimizing the energy, E, of the system with respect to each

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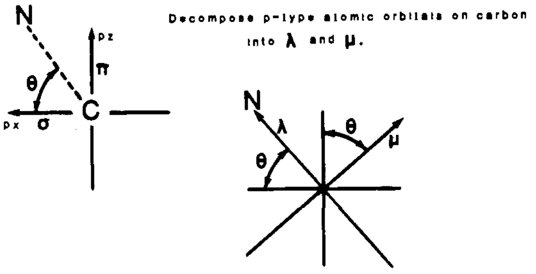

Figure 5. Origin of λ,μ-coordinate system.

of the contributing components results in the following secular determinant:

$$\begin{vmatrix} (E_{\sigma^*} - E) & H_{\sigma^*\pi^*} & H_{\sigma^*\mathrm{N}} \\ H_{\sigma^*\pi^*} & (E_{\pi^*} - E) & H_{\pi^*\mathrm{N}} \\ H_{\sigma^*\mathrm{N}} & H_{\pi^*\mathrm{N}} & (E_\mathrm{N} - E) \end{vmatrix} = 0$$

where all $H_{\mathrm{ii}} = E_\mathrm{i}$, $S_{\mathrm{ii}} = 1$, and $S_{\mathrm{ij}} = 0$. Defining

$$E = E_\mathrm{N} + \Delta E_{\mathrm{ct}}$$

and assuming

$$\Delta E_{\mathrm{ct}} << (E_{\sigma^*} - E_\mathrm{N})$$

$$\Delta E_{\mathrm{ct}} << (E_{\pi^*} - E_\mathrm{N})$$

and

$$H_{\pi^*\sigma^*} = 0,$$

the expression related to the change in energy (ΔE_{ct} in Figure 2) accompanying the attack of the nucleophile at the carbon π-center (eq 1) may be derived:

$$\Delta E_{\mathrm{ct}} = \frac{-2H_{\pi^*\mathrm{N}}^{2}}{E_\mathrm{N} - E_{\pi^*}} - \frac{2H_{\sigma^*\mathrm{N}}^{2}}{E_\mathrm{N} - E_{\sigma^*}} \tag{1}$$

where

$$H_{\pi^*\mathrm{N}} = c_{\mathrm{p}_z^*}c_{\mathrm{p_N}}\langle \mathrm{p}_z|H|\mathrm{p_N}\rangle$$

and

$$H_{\sigma^*\mathrm{N}} = c_{\mathrm{s}^*}c_{\mathrm{p_N}}\langle \mathrm{s}|H|\mathrm{p_N}\rangle + c_{\mathrm{p}_x^*}c_{\mathrm{p_N}}\langle \mathrm{p}_x|H|\mathrm{p_N}\rangle$$

$H_{\pi^*\mathrm{N}}$ and $H_{\sigma^*\mathrm{N}}$ are the resonance integrals describing the interaction of the nucleophile orbital with π* and σ*, respectively. In order to introduce the trajectory angle θ into this analysis, it is convenient to describe the p atomic orbitals (p_z and p_x) on carbon in terms of a new coordinate system (λ, μ) in which one of the axes (λ) is pointed directly at the incoming nucleophile at an angle θ with respect to the x axis (Figure 5). In terms of the λ,μ-coordinate system, is can be shown that

$$\mathrm{p}_z = \lambda \sin\theta + \mu \cos\theta$$

and

$$\mathrm{p}_x = \lambda \cos\theta - \mu \sin\theta$$

where

$$\mathrm{H}_{\pi^*\mathrm{N}} = c_{\mathrm{p}_z^*}c_{\mathrm{p_N}}\,(\sin\theta)\langle\lambda|H|\mathrm{p_N}\rangle + c_{\mathrm{p}_z^*}c_{\mathrm{p_N}}(\cos\theta)\langle\mu|H|\mathrm{p_N}\rangle$$

and

$$H_{\sigma^*\mathrm{N}} = c_{\mathrm{s}^*}c_{\mathrm{p_N}}\langle \mathrm{s}|H|\mathrm{p_N}\rangle + c_{\mathrm{p}_x^*}c_{\mathrm{p}N}(\cos\theta)\langle\lambda|H|\mathrm{p_N}\rangle - c_{\mathrm{p}_x^*}c_{\mathrm{p_N}}(\sin\theta)\langle\mu|H|\mathrm{p_N}\rangle$$

Since the p orbital on the nucleophile is orthogonal to the μ-component,

$$\langle\mu|H|\mathrm{p_N}\rangle = 0$$

By definition

$$\langle\lambda|H|\mathrm{p_N}\rangle = \beta_\mathrm{p}$$

and

$$\langle \mathrm{s}|H|\mathrm{p_N}\rangle = \beta_\mathrm{s}$$

The former term represents the σ-interaction of two p orbitals while the latter represents the σ-interaction between a p orbital and an s orbital. The resonance integrals ($H_{\pi^*\mathrm{N}}$ and $H_{\sigma^*\mathrm{N}}$) may now be described by the following trigonometric functions:

$$\mathrm{H}_{\pi^*\mathrm{N}} = c_{\mathrm{p}_z^*}c_{\mathrm{p_N}}\beta_\mathrm{p} \sin\theta$$

$$\mathrm{H}_{\sigma^*\mathrm{N}} = c_{\mathrm{s}^*}c_{\mathrm{p_N}}\beta_\mathrm{s} + c_{\mathrm{p}_x^*}c_{\mathrm{p_N}}\beta_\mathrm{p} \cos\theta$$

Substitution into eq 1, differentiating ΔE_{ct} with respect to θ, and setting the resulting expression equal to zero gives eq 2, which

$$\cos\theta_{\mathrm{ct}} = \frac{\dfrac{c_{\mathrm{s}^*}c_{\mathrm{p}_x^*}}{E_\mathrm{N} - E_{\sigma^*}}}{\dfrac{c_{\mathrm{p}_z^*}^{2}}{E_\mathrm{N} - E_{\pi^*}} - \dfrac{c_{\mathrm{p}_x^*}^{2}}{E_\mathrm{N} - E_{\sigma^*}}}\,(\beta_\mathrm{s}/\beta_\mathrm{p}) \tag{2}$$

describes the contribution of the stabilizing two-electron (charge transfer) interactions toward the nucleophile trajectory. The value of $\beta_\mathrm{s}/\beta_\mathrm{p}$ for a carbon nucleophile located 2.0 Å away from the electrophilic center is 1.58. If the overlap is included in the derivation of the stabilizing two-electron (charge transfer) equation, then the factor $\beta_\mathrm{s}/\beta_\mathrm{p}$ is replaced by

$$\frac{\beta_\mathrm{s}\beta_\mathrm{p} - E_\mathrm{N}\beta_\mathrm{s}S_{\mathrm{pp}} - E_\mathrm{N}\beta_\mathrm{p}S_{\mathrm{sp}}}{\beta_{\mathrm{p}}^{2} - 2\mathrm{E_N}\beta_\mathrm{p}\mathrm{S_{pp}}}$$

Destabilizing Four-Electron (Repulsive) Terms. In evaluating the contribution of the destabilizing four-electron (repulsive) interactions (Figure 3), overlap must be explicitly included since only the *net* destabilization of the sytem will be considered. The orbital array described in Figure 4 will be adopted and the wave functions associated with E_π and E_σ of the π-electrophile are represented by the following equations:

$$\Psi_\pi = (c_{\mathrm{p}_z}\mathrm{p}_z)_\mathrm{C} + (c_{\mathrm{p}_z}\mathrm{p}_z)_\mathrm{A}$$

$$\Psi_\sigma = (c_\mathrm{s}\mathrm{s} + c_{\mathrm{p}_x}\mathrm{p}_x)_\mathrm{C} + (c_\mathrm{s}\mathrm{s} + c_{\mathrm{p}_x}\mathrm{p}_x)_\mathrm{A}$$

As in the case of ΔE_{ct}, only the atomic orbital components associated with the reaction center will be considered. The interactions of the nucleophile HOMO with π and σ are assumed to be pairwise additive. The energies for each interactive pair are determined and the sum of the initial (unperturbed) energies are substracted from the resultant (perturbed) energies to obtain the net destabilizing energy. The net change in energy (ΔE_r) for the system is given by eq 3

$$\Delta E_\mathrm{r} = -4H_{\pi\mathrm{N}}S_{\pi\mathrm{N}} - 4H_{\sigma\mathrm{N}}S_{\sigma\mathrm{N}} \tag{3}$$

where

$$H_{\pi\mathrm{N}} = c_{\mathrm{p}_z}c_{\mathrm{p_N}}\langle \mathrm{p}_z|H|\mathrm{p_N}\rangle$$

$$S_{\pi_\mathrm{N}} = c_{\mathrm{p}_z}c_{\mathrm{p_N}}\langle \mathrm{p}_z|\mathrm{p_N}\rangle$$

$$H_{\sigma_\mathrm{N}} = c_\mathrm{s}c_{\mathrm{p_N}}\langle \mathrm{s}|H|\mathrm{p_N}\rangle + c_{\mathrm{p}_x}c_{\mathrm{p_N}}\langle \mathrm{p}_x|H|\mathrm{p_N}\rangle$$

$$S_{\sigma_\mathrm{N}} = c_\mathrm{s}c_{\mathrm{p_N}}\langle \mathrm{s}|\mathrm{p_N}\rangle + c_{\mathrm{p}_x}c_{\mathrm{p_N}}\langle \mathrm{p}_x|\mathrm{p_N}\rangle$$

Describing the atomic p orbitals at the electrophilic π-center in terms of the λ,μ-coordinate system (Figure 5), substitution into equation 3, differentiating ΔE_r with respect to θ, and setting the resulting expression equal to zero gives eq 4. In contrast to the

$$\sin\theta_\mathrm{r} = \frac{c_\mathrm{s}c_{\mathrm{p}_x}}{c_{\mathrm{p}_z}^{2} - c_{\mathrm{p}_x}^{2}}\,0.5[(\beta_\mathrm{s}/\beta_\mathrm{p}) - (S_{\mathrm{sp}}/S_{\mathrm{pp}})] \tag{4}$$

two-electron stabilizing terms, the minimum destabilization associated with an approaching nucleophile is described by the μ-component (Figure 5). The p orbital on the nucleophile is

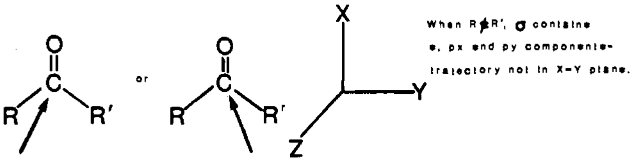

Figure 6. ϕ trajectories of nucleophiles at unsymmetrical π-electrophilic centers.

orthogonal to the λ-component.

Three-Dimensional Trajectory Terms. If the π-center undergoing nucleophilic attack (Figure 6) is located in a molecular environment having a symmetrical distribution of nuclei with respect to the x,z plane (ethylene, formaldehyde, acetylene), the θ's as defined by eq 2 and 4 are sufficient to describe the trajectory since the pertinent frontier σ^* and σ molecular orbitals contains only s and p_x components. Thus, the trajectory will be in the x,z plane. If, however, the π-center is located in a molecular environment having an asymmetric distribution of nuclei with respect to the x,z plane (propylene, acetaldehyde), the pertinent frontier σ^* and σ molecular orbitals will contain contributions from p_y as well as from p_x. Thus, the resulting nucleophile trajectory will contain x, y, and z vector components. The in-plane p-component of σ^* and σ are now described by the functions ($c_{p_x^*} \cos\phi + c_{p_y^*} \sin\phi$) and ($c_{p_x} \cos\phi + c_{p_y} \sin\phi$) in place of the $c_{p_x^*}$ and c_{p_x} terms, respectively, in eq 2 and 4. The resulting equations represent the expression required to complete the three-dimensional analysis of the θ trajectory on the frontier molecular orbital levels. The resulting trajectory angles θ and ϕ may be estimated by combining the differential equations describing the stabilizing two-electron and destabilizing four-electron terms ($\mathrm{d}\Delta E_{\mathrm{ct}}/\mathrm{d}\theta$, $\mathrm{d}\Delta E_{\mathrm{ct}}/\mathrm{d}\phi$, $\mathrm{d}\Delta E_{\mathrm{r}}/\mathrm{d}\theta$, and $\mathrm{d}\Delta E_{\mathrm{r}}/\mathrm{d}\phi$) and solving by an iterative procedure. Values of c_{s^*}, $c_{p_x^*}$, $c_{p_y^*}$, $c_{p_z^*}$, c_s, c_{p_x}, c_{p_y}, c_{p_z}, E_{π^*}, E_π, E_{σ^*}, and E_σ may be obtained from semiempirical molecular orbital calculations performed on a given π-electrophile. E_N can be determined from a similar calculation performed on a given nucleophile. The resonance integrals, β_s and β_p, may be easily estimated by the procedures suggested by Mulliken[12] and Hoffmann[13] using the ionization potentials of a carbon 2s electron (−21.85 ev), a carbon 2p electron (−12.05 ev), and an electron in the highest occupied molecular orbital of the nucleophile (α_N), and the σ-overlap integrals $(S_{i,j})_\sigma$ describing the interaction of a p orbital on the nucleophile with 2p $(S_{2p,2p})\sigma$ and 2s $(S_{2p,2s})\sigma$ orbitals on carbon. The values for the overlaps ($S_{i,j}$) may be easily determined from the tables listed in a publication by Mulliken, Rieke, Orloff, and Orloff.[14]

In a similar fashion eq 5 and 6 may be derived. These represent

$$\cos\theta_{\mathrm{ct}} = \frac{\sum \dfrac{c_{s^*} c_{p_x^*}}{E_N - E_{\sigma^*}}}{\sum \dfrac{{c_{p_z^*}}^2}{E_N - E_{\pi^*}} - \sum \dfrac{{c_{p_x}}^2}{E_N - E_{\sigma^*}}} (\beta_s/\beta_p) \qquad (5)$$

$$\sin\theta_{\mathrm{r}} = \frac{\sum c_s c_{p_x}}{\sum {c_{p_z}}^2 - \sum {c_{p_x}}^2} 0.5[(\beta_s/\beta_p) - (S_{sp}/S_{pp})] \qquad (6)$$

a more complete view of the two-electron and four-electron components in this trajectory analysis since *all* unoccupied and occupied molecular orbitals are included.

Conclusions

The following generalizations may be deduced from the proposed model: (1) Both the stabilizing two-electron and destabilizing four-electron minimum-energy trajectory angles, θ_{ct} and θ_{r}, respectively, are independent of the magnitude of the orbital coefficient associated with the nucleophile. (2) θ_{r} is independent of both the energy level of the nucleophile HOMO and the energy levels of the occupied molecular orbitals of the π-electrophile. (3) For a given π-electrophile, as the energy of the frontier molecular orbital of the nucleophile (HOMO) becomes less negative, θ approaches 90°. Thus, hard nucleophiles (nucleophiles with low-lying HOMO's) would be expected to approach the reaction center of a given substrate at a smaller angle than corresponding soft nucleophiles (nucleophiles with higher lying HOMO's).

In conclusion, a simple model based upon the analysis of the first-order interactions between the highest filled molecular orbital on a nucleophile and all unoccupied and occupied molecular orbitals on the π-electrophile has been proposed for qualitatively predicting the trajectory of an attacking nucleophilic reagent with respect to a particular π-electrophilic center.

Acknowledgment. We thank the National Science Foundation, Department of Energy, and the National Institutes of Health for grants that supported this investigation.

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Quinones of Azulene. 3. Generation and Trapping of the Reactive 1,4- and 1,6-Quinones[1]

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Abstract: The 1,4-quinone of azulene (**1**) and the 1,6-quinone of azulene (**2**) have been synthesized for the first time. Oxidation of bicyclic trienone **3** followed by acetylation provides the two azulene diacetates **7** and **8** which serve as ideal precursors for the quinones. Neither quinone could be isolated in monomeric form, but both could be efficiently trapped by cyclopentadiene to give stable Diels–Alder adducts (**13** and **15**). The high chemical reactivity of azuloquinones **1** and **2** was anticipated on the basis of earlier theoretical calculations.

Nearly 50 years have elapsed since the first synthesis of azulene,[2] and the roots of quinone chemistry can be traced back to antiquity.[3] Why, then, is so little known about the quinones of azulene which lie at the intersection of these two venerable avenues

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