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# Photoelectron Spectra of 3-Substituted Cyclopentenes. Correlations between Ionization Potentials and Cycloaddition Regioselectivity

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**Abstract:** The photoelectron spectra of 3-X-cyclopentenes, where X = methyl, ethyl, isopropyl, cyclohexyl, hydroxy, methoxy, acetoxy, dimethylamino, and phenyl, have been measured. The trend in ionization potentials is similar to that found for 3-X-propenes, but the changes are considerably smaller in the cyclopentenes. A simple model is developed relating the HOMO and LUMO coefficients of the substituted cyclopentene to the change in ionization potential caused by the substituent. A reasonable correlation is found between the regioselectivities of benzonitrile oxide cycloadditions to these cyclopentenes and a theoretical function of ionization potentials, $(9.18 - IP)(IP - 4.5)^{-1}$, which relates orbital coefficients and energies to ionization potentials.

Recently, Caramella and Cellerino reported a study of the products of cycloadditions of benzonitrile oxide to 3-substituted cyclopentenes (X-CP).[2] As shown in Scheme I, four

**Scheme I**



X – anti-(*z*)    X – syn –(*z*)

X – anti – (*e*)    X – syn – (*e*)
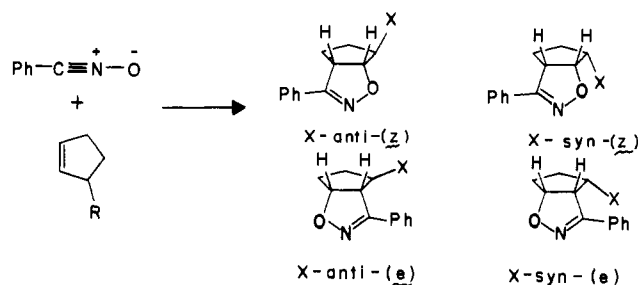
products can be obtained as a result of (1) cycloaddition to the same side of the cyclopentene ring as the substituent (syn ad-

dition) or to the opposite side (anti addition), and (2) cycloaddition with the oxygen of the nitrile oxide nearest the substituent (*z* addition) or furthest from the substituent (*e* addition).[3] The products will be discussed here in terms of the nomenclature shown in Scheme I.

Caramella and Cellerino made the reasonable assumption that the ratio of *z* and *e* anti adducts would be a reflection of the electronic effect of the substituent, X, upon the double bond. That is, X does not interact through space with benzonitrile oxide when attacking from the anti side, so that the influence of the substituent on the ratio of isomers should result from alteration of the orbital energies and coefficients of the double bond.[4] However, a plot of the ratio of isomers vs. Taft's polar substituent constant, $\sigma^*$ (Figure 1), a commonly accepted measure of electron-donor or -acceptor potency of a substituent,[5] shows some notable deviations from linearity, particularly for the phenyl, dimethylamino, and acetoxy substituents. A linear relationship might have been expected if the regiose-
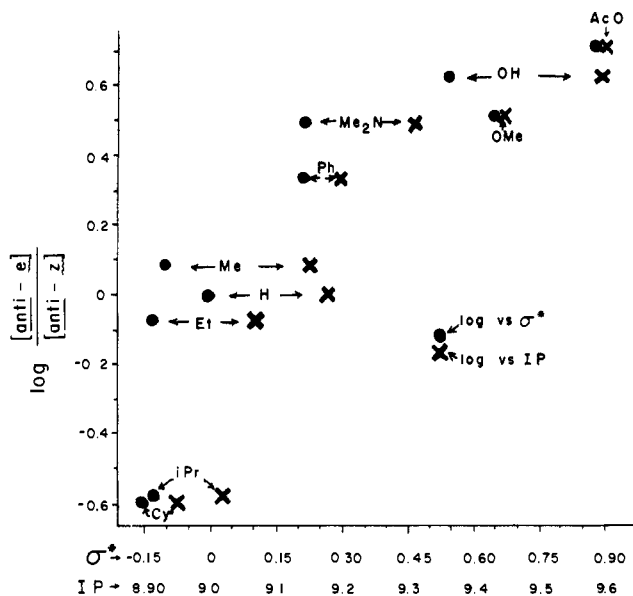
Figure 1. Plot of ratio of anti isomers (anti-*z*:anti-*e*) vs. substituent σ* for the substituents, and vs. the vertical ionization potentials of the π orbital of the cyclopentenes.

lectivity were determined by stabilization of transition states having partial charge development on the alkene moiety.

Since σ* constants were determined for conformationally free systems, and represent the average of a substituent influence on a remote position over various attainable conformations, we undertook a study of the photoelectron spectra of the 3-substituted cyclopentenes studied by Caramella and Cellerino. Our first goal was to determine whether the substituent held in a relatively rigid conformation with respect to the double bond would exhibit a similar effect on the ionization potential of the double bond as it does in a conformationally less rigid system. Our second goal was to determine whether the regioisomer ratios correlated with some function of the cyclopentene ionization potential, as would be expected according to the model developed below.

**Photoelectron Spectra.** The photoelectron spectra were measured on a Perkin-Elmer PS-18 photoelectron spectrometer equipped with an He(I) source. Resolution was approximately 20 meV. Xenon and argon were used as calibration standards. The low-energy regions of these spectra are shown in Figure 2, and the values of ionization potentials obtained from these spectra are given in Table I.

The first band in the spectrum of 3-methylcyclopentene shows rich vibrational structure of about ~1350 cm$^{-1}$, and weaker progressions which have not been analyzed. This vibrational spacing is essentially identical with that observed in propene[5] and cyclopentene.[6] As the size of the alkyl group increases, the resolution of vibrational structure is lost, and only a broad band is obtained for 3-cyclohexylcyclopentene. The change in cyclopentene ionization potential upon alkylation is somewhat smaller than the change caused by alkylation of propene, as can be seen from a comparison of the 3-alkylcyclopentene IPs with those of Masclet et al.[7] This comparison holds also for the electron-withdrawing groups—hydroxy, methoxy, and amino—whose influences on the propene IP are much larger than on the cyclopentene IP. This result must be due, in part, to the greater delocalization of the cyclopentene π orbital than the propene π orbital. Thus, substituents, regardless of their mechanisms of electron donation or withdrawal, affect the cyclopentene IP less than the propene IP. Conformational differences in the two types of molecules may also play a role in the different magnitudes of substitutent effects, but data on the structures of these molecules are unfor-
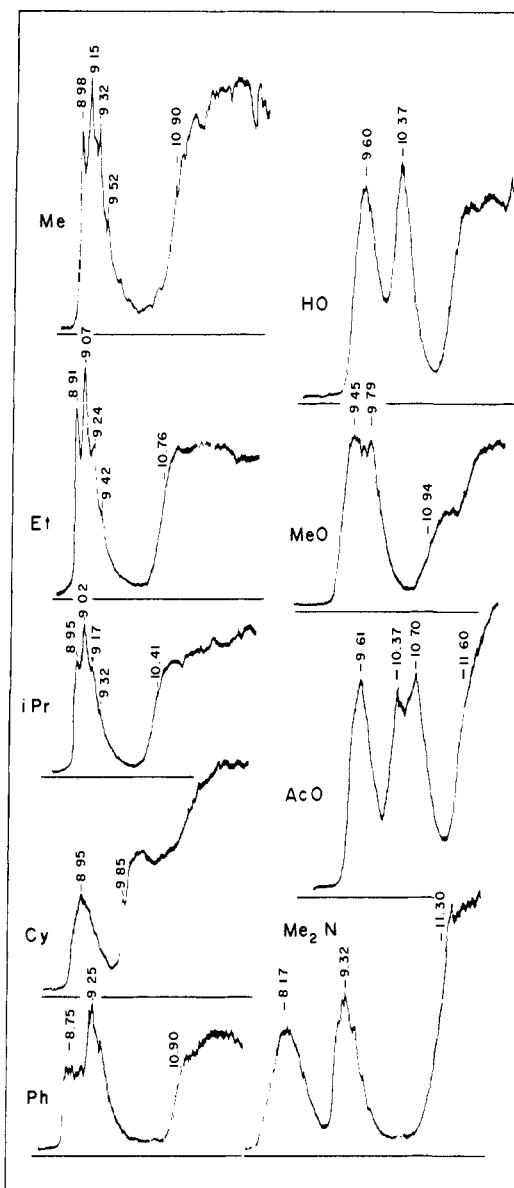


Figure 2. Photoelectron spectra of 3-substituted cyclopentenes. The 3 substituent is listed next to each spectrum.

tunately not available, nor are any of the ionization potentials sufficiently unusual to allow deductions about conformations.

The spectrum of 3-phenylcyclopentene is particularly difficult to decipher because of the lack of resolution of the three low IP bands. The appearance of the first band suggests the presence of a broad ionization centered at 8.75 eV due to removal of an electron from the orbital corresponding to the b$_1$ orbital of toluene. In allylbenzene, this band is relatively broad, with a vertical IP of 8.85 eV.[8] The a$_2$ phenyl orbital and the cyclopentene π orbital give rise to the sharper band centered at 9.19 eV. In allylbenzene, the phenyl a$_2$ ionization is sharp and occurs at 9.27 eV. We estimate that the cyclopentene π ionization is at ~9.2 eV, while that of the phenyl a$_2$ orbital is at ~9.3 eV.

The ionization potentials of the heterosubstituted cyclopentenes have been assigned using the ionization potentials of simple model compounds for reference. Thus, the 10.37 eV IP of HO-CP is close to the lone pair IP of methanol (10.96 eV). The similar band at 9.79 eV in MeO-CP is at a value close to that of dimethyl ether (10.04 eV), and the nitrogen lone pair in Me$_2$N-CP appears at 8.17 eV, close to the 8.56 eV IP of trimethylamine. The IPs of AcO-CP at 10.37 and 10.70 eV

**Table I.** Ionization Potentials of 3-Substituted Cyclopentenes[a] and Acyclic Models

| Substituent | 3-X-Cyclopentenes | | | 3-X-Propenes | | |
| | $\pi$ IP | Substituent IPs | $\sigma$ onset | $\pi$ IP[b] | Substituent IPs | Ref |
| --- | --- | --- | --- | --- | --- | --- |
| None[c] | 9.01, **9 18**, 9.35, 9.52 | | 10.9 | 9.72, **9.88**, 10.05, 11.22 | | 5 |
| Methyl | 8.98, **9.15**, 9.32, 9.50 | | 10.76 | 9.63 (**9.80**) | | 7 |
| Ethyl | 8.91, **9.07**, 9.24, 9.42 | | 10.53 | 9.52 (**9.69**) | | 7 |
| Isopropyl | 8.85, **9.02**, 9.17, 9.32 | | 10.41 | 9.45 (**9.62**) | | 7 |
| Cyclohexyl | **8.95** | | 9.85 | | | |
| Phenyl | ~**9.2** | ~8.75 ($b_1$), 9.3 ($a_2$) | 10.90 | **9.71** | 8.85 ($b_1$), 9.27 ($a_2$) | 8 |
| Hydroxy | **9.60** | 10.37 ($n_O$) | 11.25 | **10.16** | 10.93 ($n_O$) | 5 |
| Methoxy | **9.45** | 9.79 ($n_O$) | 10.94 | **9.84** | 10.34 ($n_O$) | This work |
| Acetoxy | **9.61** | 10.37 ($n_{CO}$), 10.70($n_O$) | 11.60 | | | |
| Dimethyl-amino | **9.32** | 8.17 ($n_N$) | 11.30 | ($NH_2$) **10.84** | 9.44 ($n_N$) | 5 |

[a] Values listed are positions of peak maxima. The most intense vibrational bands are given in boldface type. All values are ±0.05 eV. [b] Numbers in parentheses are estimated assuming the usual 0.17 eV 0-0, 0-1 separation. [c] Reference 6.

**Table II.** Ratios of Regioisomers Observed in Cycloadditions of Benzonitrile Oxide (Ether, 0 °C) to 3-Substituted Cyclopentenes

| Substituent | Anti-$e$/anti-$z$ | Log anti-$e$/anti-$z$ | $\sigma^{*c}$ | IP ($\pi$) | $(9.18 - IP)/(IP - 4.50) \times 10^3$ |
| --- | --- | --- | --- | --- | --- |
| None | 1.00 | 0.000 | 0.00 | 9.18 | 0.00 |
| Methyl[a] | 1.21 | +0.083 | −0.10 | 9.15 | 6.452 |
| Ethyl[a] | 0.840 | −0.076 | −0.12 | 9.07 | 24.07 |
| Isopropyl | 0.264 | −0.578 | −0.13 | 9.02 | 35.40 |
| Cyclohexyl[b] | 0.238 | −0.623 | −0.15[d] | 8.95 | 51.69 |
| Phenyl | 2.28 | +0.358 | +0.22 | 9.2 | −4.255 |
| Hydroxy | 4.42 | +0.645 | +0.55 | 9.60 | −82.35 |
| Methoxy | 3.23 | +0.509 | +0.66 | 9.45 | −54.55 |
| Acetoxy | 5.13 | +0.710 | +0.89 | 9.61 | −84.15 |
| Dimethylamino | 3.04 | +0.483 | +0.22 | 9.32 | −29.05 |

[a] These values have been corrected from those in ref 2 by careful VPC analysis. [b] Values obtained since publication of ref 2. [c] R. P. Wells, "Linear Free Energy Relationships", Academic Press, New York, N.Y., 1968, p 38. Values of $\sigma^*$ are for R in $RCH_2$. [d] Estimated.

correspond rather closely to those of methyl acetate at 10.59 and 11.21 eV. The latter are due to the carbonyl lone pair orbital ($n_{CO}$) and the lone pair on the ether oxygen ($n_O$), which is mixed with the carbonyl $\pi$ orbital.

**A Model for Substituent Effects on Ionization Potentials and Regioselectivity.** Caramella and Cellerino proposed a simple qualitative model to account for the fact that electron-donating 3 substituents caused a preponderance of anti-$z$ adducts to be formed, while electron-withdrawing 3 substituents caused mainly the anti-$e$ regioisomer to be formed. The reasoning is represented schematically in Figure 3. On the left side of the figure, the frontier MOs of a typical nitrile oxide are shown.[9-11] Interaction of the LUMO of the nitrile oxide with the HOMO of the alkene, and, to a lesser extent, the HOMO of the nitrile oxide and the LUMO of the alkene, will occur in such a fashion as to maximize overlap in the cycloaddition transition state.[9,10]

Donor substitution on ethylene will result in polarization of the alkene HOMO away from the substituent, and of the LUMO in the opposite direction.[10,12] The transition state that leads to the 5-substituted isoxazoline (the $z$ regioisomer) will be most stabilized. Acceptor substitution will polarize the HOMO and LUMO in opposite directions to those produced by a donor,[13] and the 4-substituted isoxazoline ($e$ regioisomer) will be favored.

This qualitative model nicely accounts for the fact that 3-donor substituted cyclopentenes give a preponderance of the $z$ product and 3-acceptor cyclopentenes give mainly the $e$ product as shown in Table II. Methyl is a curious exception to this generalization for reasons as yet unknown to us.[14] Figure 1 shows a plot of anti regioisomer ratios vs. the vertical $\pi$ ionization potentials of the cyclopentenes. There is a qualitative correlation of the data, but the same type of deviations from linearity are observed as for the $\sigma^*$ plot. The model only
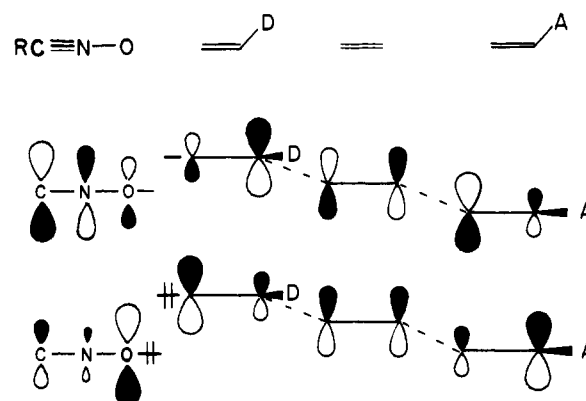


**Figure 3.** Schematic representation of influence of donor (D) and acceptor (A) substituents on alkene HOMO and LUMO energies and coefficients. The HOMO and LUMO of a nitrile oxide are shown on the left.

qualitatively rationalizes the regioselectivity trends. That is, donors lower IPs and give mainly $z$ products, while acceptors raise IPs and give $e$ products.

It is possible to make this model more quantitative, using perturbation theory to relate the change in IP upon substitution to the variation in coefficients arising from substituent induced HOMO-LUMO mixing in cyclopentene.

According to the perturbation treatment of cycloaddition reactivity and regioselectivity,[10] the stabilization of a concerted transition state arising from interaction of the HOMO of one molecule (e.g., benzonitrile oxide, BN) with the LUMO of the other (e.g., cyclopentene, CP) can be expressed in terms of the coefficients at the sites of interaction and energy differences between the various orbitals involved. Figure 4 shows the frontier orbital energies of fulminic acid (whose IP has been
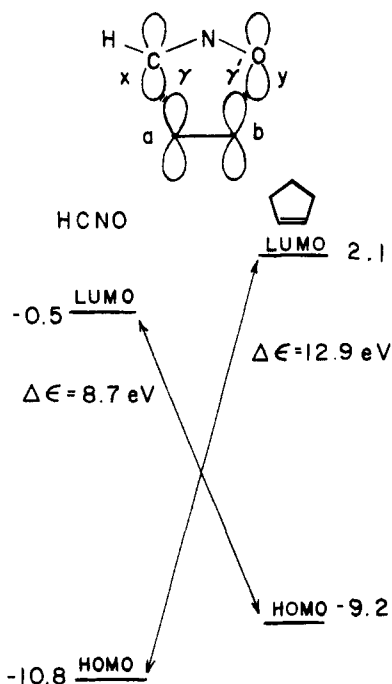
**Figure 4.** Frontier molecular orbital energies (−IPs and −EAs) of fulminic acid and cyclopentene.

measured[15] and EA has been estimated[11]) and cyclopentene (EA is that of cyclohexene[16]). For a four-center interaction, the transition state stabilization, calculated by second-order perturbation theory,[12] arising from the interaction of the BN LUMO and the CP HOMO is

$$\Delta E = \frac{(xa\gamma + yb\gamma')^2}{\epsilon_{CP} - \epsilon_{BN}}$$

where the $\epsilon$'s are the orbital energies of the CP HOMO and BN LUMO, $x$, $y$, $a$, and $b$ are coefficients at interacting centers defined in Figure 4, and $\gamma$ and $\gamma'$ are resonance integrals for interaction of orbitals on the terminal atoms at a particular distance. There will be a similar term for the BN HOMO interaction with CP LUMO.

For the opposite regioisomer, the stabilization energy is

$$\Delta E' = \frac{(xb\gamma + ya\gamma')^2}{\epsilon_{CP} - \epsilon_{BN}}$$

The difference in stabilization energy for formation of the two regioisomers is

$$\Delta\Delta E = \Delta E - \Delta E' = \frac{(x^2\gamma^2 - y^2\gamma'^2)\,(a^2 - b^2)}{\epsilon_{CP} - \epsilon_{BN}}$$

If we assume that the transition states for all of these reactions are essentially identical—that is, that the geometrical distortions of the nitrile oxide and alkene, and the extent of CC and CO bond formation, are identical in the transition states of all these reactions—then the term $x^2\gamma^2 - y^2\gamma'^2$ will be a constant, and the last equation becomes

$$\Delta\Delta E = \frac{k(a^2 - b^2)}{\epsilon_{CP} - \epsilon_{BN}}$$

The diradical mechanism ($\gamma' = 0$), which is rarely, but persistently, proposed for these reactions,[18] will conform to this equation, although the magnitude of $b^2$ will be irrelevant.

A direct relationship between regioselectivity and IP can be expected, since the changes in coefficients upon substituent perturbation of an alkene $\pi$ bond can be related to the change in IP by perturbation theory.[12] We will adopt the simplest possible form of perturbation theoretical treatment, neglecting overlap and assuming an unspecified form of perturbation

(hyperconjugative, inductive, or electrostatic, or some combination).

We will further assume that substituents are changing the $\pi$ orbitals of cyclopentenes much more than they change the $\pi^*$ orbital energies, and we will, therefore, neglect changes in the $\pi^*$ orbital of cyclopentene caused by substituents. This assumption can be justified in ways: (1) the BN LUMO-CP HOMO interaction is strongest and should dominate reactivity and regioselectivity[1,9-11] (Figure 4); (2) allyl substituents will likely modify the hyperconjugative ability of the methylene groups flanking the cyclopentene $\pi$ bond, and alkyl group hyperconjugation influences mainly the occupied orbital energies of alkenes;[12] and (3) if $\pi^*$ changes are of much effect, the changes in $\pi^*$ energies and coefficients are very probably linearly related to the corresponding $\pi$(HOMO) changes.

The change in $\pi$ orbital energy caused by a donor substituent (D) is, to second order,[12]

$$\Delta\epsilon = \frac{H_{D\pi}{}^2}{\epsilon_\pi - \epsilon_D}$$

where $H_{D\pi}$ is the resonance integral for interaction of the donor and the $\pi$ orbital, and $\epsilon_\pi$ and $\epsilon_D$ are the energies of the cyclopentene $\pi$ and the donor orbitals, respectively. While the energy of the $\pi$ orbital is changed by a substituent, D, the substituent also causes mixing of the $\pi$ and $\pi^*$ orbitals. The coefficient of mixing of the cyclopentene $\pi^*$ into $\pi$, $C_{\pi^*,\pi}$, caused by the donor is[12]

$$C_{\pi^*,\pi} = \frac{1}{\epsilon_\pi - \epsilon_{\pi^*}} \frac{H_{D\pi^*} H_{D\pi}}{\epsilon_\pi - \epsilon_D}$$

If we assume that $H_{D\pi^*}$ equals, or is proportional to, $H_{D\pi}$, a reasonable assumption if $H$ is assumed proportional to overlap, then the second term in the equation for $C_{\pi^*,\pi}$ becomes identical with $\Delta\epsilon$, that is

$$C_{\pi^*,\pi} = \frac{1}{\epsilon_\pi - \epsilon_{\pi^*}} \Delta\epsilon$$

Rather than evaluating $1/(\epsilon_\pi - \epsilon_{\pi^*})$, we will set it equal to yet another constant, $k'$.

When overlap is neglected, the coefficients of ethylene are $1/\sqrt{2}$ for both p orbitals in the $\pi$ orbital, and $1/\sqrt{2}$ and $-1/\sqrt{2}$ for the two p orbitals in the $\pi^*$ orbital. Although these will vary somewhat in substituted cases, the essential features of the following arguments will be retained. Similarly, the same form of the solution will be obtained if normalization is included. Mixing of an amount, $C_{\pi^*,\pi}$, of the $\pi^*$ orbital into $\pi$ will result in $\pi$ orbital coefficients of $1/\sqrt{2}\,(1 + C_{\pi^*,\pi})$ and $1/\sqrt{2}\,(1 - C_{\pi^*,\pi})$. Substituting these for $a$ and $b$, the regioselectivity term, $a^2 - b^2$, is

$$\left[\left(\frac{1}{\sqrt{2}}\right)^2(1 + C_{\pi^*,\pi})^2 - \left(\frac{1}{\sqrt{2}}\right)^2(1 - C_{\pi^*,\pi})^2\right] = 2C_{\pi^*,\pi}$$

Since $C_{\pi^*,\pi}$ has been shown to be equal to $k'\Delta\epsilon$,

$$a^2 - b^2 = 2k'\Delta\epsilon$$

Substituting this into the regioselectivity equation gives

$$\Delta\Delta E = \frac{k(2k'\Delta\epsilon)}{\epsilon_{CP} - \epsilon_{BN}} = \frac{K\Delta\epsilon}{\epsilon_{CP} - \epsilon_{BN}}$$

where $K$ collects all constants together. Equating orbital energies to negatives of IPs (occupied orbitals) or EAs (vacant orbitals), we obtain

$$\Delta\Delta E =$$

$$K\frac{IP(\text{cyclopentene}) - IP(\text{substituted cyclopentene})}{IP(\text{substituted cyclopentene}) - EA(\text{benzonitrile oxide})}$$

One difficulty with the use of this equation directly has to do with the fact that the IP and EA used in the denominator

should actually be those of the molecules in the transition state.[4,10] That is, the molecular distortions present in the transition state[17,19] will alter the IP and EA (or HOMO and LUMO energies) to a small extent, but more importantly, the IP of the donor will be lowered in the presence of the acceptor, and the EA of the acceptor will be raised in the presence of the donor. Put another way, the energy required to transfer an electron from a donor molecule, D, to an acceptor molecule, A, when the molecules are infinitely separated is $IP_D - EA_A$. However, the amount of energy required for this electron transfer drops drastically as the molecules are brought into close proximity, owing to the Coulombic attraction of $D^+$ for $A^-$. For separations like those in the transition states of 1,3-dipolar cycloadditions,[17,19] this Coulombic attraction amounts to 3.5–5 eV.[4,10] We have used a correction factor of −4 eV in the denominator, and arrive at

$$\log \frac{(\text{anti-}e)}{(\text{anti-}z)} = \Delta\Delta E = K \frac{9.18 - IP(X\text{-}CP)}{IP(X\text{-}CP) - 4.5 \text{ eV}}$$

Figure 5 is a plot of the log of the regioisomer ratios vs. the last quantity (listed in Table II). There is a moderately good correlation, which, by least squares, gives a line (solid line in Figure 5), fitting the equation

$$\log \frac{[\text{anti-}e]}{[\text{anti-}z]} = -9.30 \left[ \frac{9.18 - IP}{IP - 4.50} \right] + 0.0239$$

which has a correlation coefficient, $r$, of 0.928. There appears to be some curvature in the plot, the points due to H, Me, Et, $i$-Pr, and Cy describing a line (dotted in Figure 5),

$$(\text{alkyl}) \quad \log \frac{[e]}{[z]} = -14.5 \left[ \frac{9.18 - IP}{IP - 4.50} \right] + 0.1032$$

with $r$ = 0.915, while the electron-withdrawing groups, OAc, OH, OMe, NMe₂, and Ph define a different line (dashed in Figure 5),

$$(\text{acceptor}) \quad \log \frac{[e]}{[z]} = -3.90 \left[ \frac{9.18 - IP}{IP - 4.50} \right] + 0.3425$$

with $r$ = 0.969. This is not unreasonable, since the proposed model is rather crude, in that it does not take into account the fact that hyperconjugation at both termini will be altered by substitution. That is, the donor groups (Me through Cy) will increase the hyperconjugative ability of the substituted moiety relative to that of the unsubstituted, while the acceptor groups will decrease the hyperconjugative ability of the substituted moiety relative to that of the unsubstituted. Thus, the mechanisms of polarization are similar, but the same constant, $K$, should probably not be assumed for both donors and acceptors. In light of inaccuracies in experimental measurements of adduct ratios and vertical ionization potentials (±0.05 eV, at best), the correlations obtained here are reasonable, and in relatively good accord with the frontier orbital model regioselectivity.

It is particularly interesting that constant values of $\gamma$ and $\gamma'$ are assumed, implying more or less constant values of the lengths of the bonds forming in the transition state. Recent calculations on the 1,3-dipolar cycloaddition also indicate only slight changes in transition state structure with substituent changes.[17]

The classical alternatives to the use of perturbation theory to treat cycloaddition regioselectivity would be to consider substituent effects upon transition states (or intermediates) with partial charges (1), or diradical character (2).[18] As shown in Figure 1, the $\sigma^*$ plot shows pronounced curvature, so that differential stabilization of positive charge by substituents in the transition does not seem to adequately account for the experimental changes. Although there is no obvious connection between stabilization of potential diradical intermediates, or
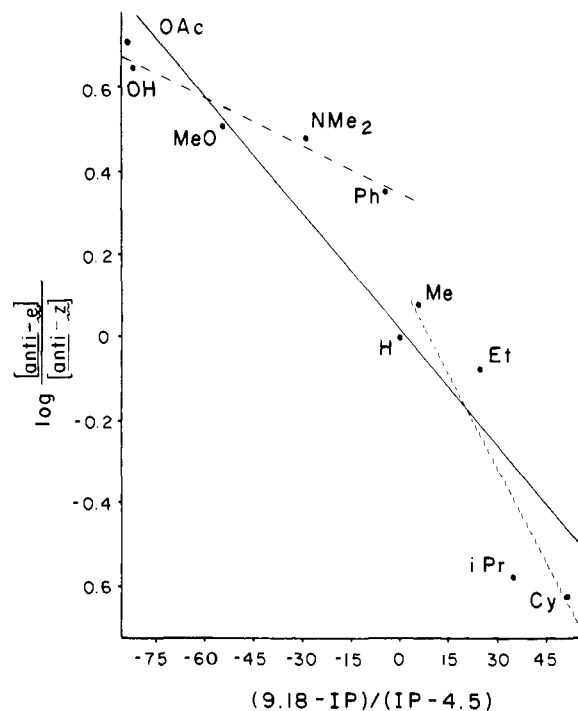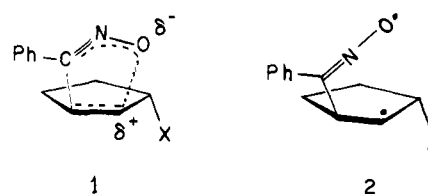


**Figure 5.** Plot of log (ratio anti adducts) vs. the quantity $(9.18 - IP)/(IP - 4.5)$ for the substituted cyclopentene.



transition states, **2**, and experimentally observed isomer ratios, "polarized diradicals"[18] might be invoked to correct this problem using the diradical theory.

**Generalized Relationships between Orbital Coefficients and Ionization Potentials.** Although the treatment here is quite successful in relating regioselectivity to ionization potentials, this is not expected to be so simple in general. In the case of substituents attached directly to a $\pi$ bond, inductive and conjugative effects may influence coefficients in opposite directions, and several high-lying filled and low-lying vacant orbitals might need to be included in the treatment in cases of strongly conjugating substituents. Nevertheless, the treatment reported here should be capable of elaboration in other cases, so that a truly quantitative correlation between physical properties (IPs and EAs) and regioselectivity might be obtained.

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(13) Electron acceptors which are also conjugated with the alkene π system will polarize the HOMO in the same directions as, but to a smaller extent than, inductive acceptors.[9]

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# Transits across a Cyclopentadienyl: Organic and Organometallic Haptotropic Shifts

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**Abstract:** Organic and organometallic haptotropic shifts in cyclopentadienyl compounds CpX are analyzed by studying the motion of an $X^+$ across the face of a $C_5H_5^-$ ring. The ligand in transit, $X^+$, may be $H^+$, $CH_3^+$, $XH_3^+$ (X = Si, Ge, Sn), $Mn(CO)_3^+$, $Li^+$, $CuR^+$, and $CH_2^{2+}$ and $CH_2$, the latter serving as models for $BR_2^+$, $AlR_2^+$ and $NR_2^+$, $PR_2^+$ as well. The $Cp^-$ offers donor orbitals of a + e symmetry. The interactions of the ligand may be dominated by an acceptor orbital of symmetry type a ($H^+$, $CH_3^+$) in which case $\eta^1$ and $\eta^2$ geometries are favored, or a set of acceptor orbitals of a + e symmetry ($Mn(CO)_3^+$, $Li^+$, $CuR^+$), the e component of which greatly stabilizes the most symmetrical $\eta^5$ coordination. The lower the energy of the e acceptor set and the better the overlap with its Cp counterpart, the more are $\eta^2$ and $\eta^5$ stabilized relative to $\eta^1$. In the case of $XH_3^+$ (X = C, Si, Ge, Sn) an e acceptor orbital moves to lower energy as one proceeds down the group, and this is responsible for the decreasing barrier for sigmatropic shifts in $CpXH_3$. The $XH_2$ case, which yields a number of interesting collapse structures, is analyzed in detail for X, a main group center.

Contrast the interaction of a cyclopentadienide anion and a proton with the interaction of the same anion and a $Mn(CO)_3^+$ fragment. Both result in stable molecules: cyclopentadiene (**1**) and $\eta^5$-$CpMn(CO)_3$ (**2**). But what a difference
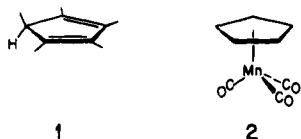


in the equilibrium geometries of these end products of the interaction! If we focus our attention on the cyclopentadienide site where the interacting partner settles down, then the proton chooses a position near to one carbon of the ring, but the $Mn(CO)_3^+$ fragment sits directly over the center of the ring. The ramifications of this differential are the concern of this paper. We will examine the interaction of a cyclopentadienide ($C_5H_5^-$, Cp) ion with an interacting group X, $X = H^+, CH_3^+$, $SiR_3^+, Mn(CO)_3^+, CH_2^{2+}, CH_2$. The result will consist of some conclusions concerning the equilibrium geometry of CpX as well as the relative energetics of the various haptotropic reactions of this species.[1,2]

Consider the passage of the interacting group X across the face of a Cp molecule, moving as indicated in **3** in a plane
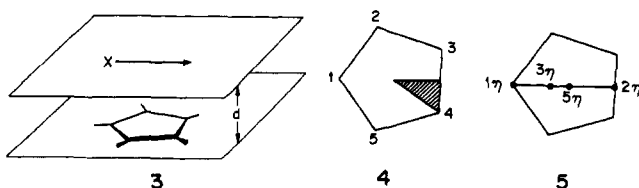


parallel to the Cp ring. Let the distance $d$ be a separation at which there is sizable interaction between the frontier orbitals of X and the Cp π system. For a surface so constrained the asymmetric unit that need be calculated consists of the shaded area in **4**, and two of the three boundaries of that area are contained in a transit along a line shown in projection in **5**. Mirror symmetry is maintained at all points. The numbers $n\eta$ shown along that line are convenient labels invoking a connection to the inorganic $\eta^n$ notation[2] for denoting an approximate coordination geometry. In order to avoid confusion with structure numbers and ring carbon numbers, we have labeled the various sites along the transit line as $1\eta, 2\eta, \ldots, 5\eta$. The site labeled $1\eta$, or some geometry near it, corresponds to $\eta^1$ or simple σ interaction, such as we have in the collapse product cyclopentadiene. The $\eta^5$ site $5\eta$ is where one better come up with maximum stabilization for $X = Mn(CO)_3^+$. The site labeled $2\eta$ positions X over the center of a bond, and obviously will describe the important transition state region for a sigmatropic shift of a system like cyclopentadiene. $3\eta$ and $4\eta$ are not so easily defined. Experimentally, slippage of Cp rings from $\eta^5$ coordination is often observed and $\eta^3$ or $\eta^4$ coordination may or may not be invoked. Somewhat arbitrarily we define $3\eta$ at the intersection of the transit line with the line joining C-2 and C-5 projected on the transit plane. The tetrahapto coordination site is most ambiguous (it could be near $3\eta$ or near $5\eta$), and so we will not label any position as such.

The analysis will consist of an inspection of interaction diagrams for the orbitals of Cp and X, as the ligand X and its position along the transit are varied. The qualitative arguments based on symmetry and overlap are supported by extended Hückel calculations whose details are given in the Appendix. The reader should be aware that this is an approximate method