

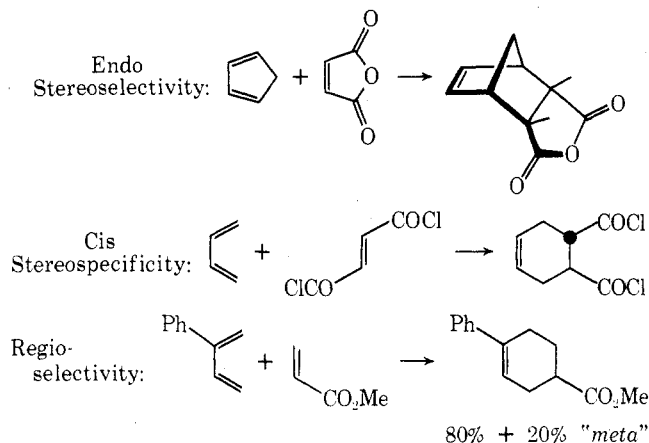
The Frontier Molecular Orbital Theory of Cycloaddition Reactions

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Cycloadditions are among the best known and most useful organic reactions. The Diels–Alder reaction, discovered nearly half a century ago, is the prototypical thermal cycloaddition. Because six-membered rings are generated with remarkable stereoselectivity and regioselectivity, the reaction is of great synthetic utility.¹



Other types of cycloadditions include 1,3-dipolar cycloadditions,² which form five-membered ring heterocycles, the [2 + 2] cycloadditions of suitably activated alkenes to form cyclobutanes,^{3,4} and the cycloadditions of allyl cations to dienes to give seven-membered rings.⁵ Clearly, a wide range of addends can be used and a variety of ring sizes may be formed by thermal cycloadditions.^{6–8} Photochemical cycloadditions provide additional possibilities.⁹

Classically, cycloaddition mechanisms have been grouped into three categories: (1) the concerted mechanism, involving simultaneous formation of both new bonds and experimentally characterized by cis stereospecificity and a lack of solvent polarity effect on rate; (2) a stepwise diradical mechanism, involving a diradical intermediate and characterized by low or nonexistent stereospecificity; and (3) a step-

wise dipolar mechanism, involving a zwitterionic intermediate and characterized by variable stereospecificity and a large effect of solvent polarity on reaction rate.^{10,11}

Several reactions fit neatly into one or another of these categories. Additions of haloalkenes to dienes are of the second type, as revealed by Bartlett's classical studies.^{4,12} Electron-rich alkenes react with electron-deficient alkenes by the dipolar-intermediate mechanism, as shown mainly by solvent effects on reaction rates.¹³ However, in spite of exhaustive studies of Diels–Alder, 1,3-dipolar, and ketene cycloadditions, the mechanisms of these reactions have been a source of some consternation: (1) the response of reaction rate to addend substitution seems compatible only with dipolar intermediates in some cases, and diradical intermediates in others; (2) their regioselectivities (selectivities in orientation of addition) seem to require dipolar or diradical intermediates;¹⁴ and

(1) H. Wollweber, "Diels–Alder Reactions", George Thieme Verlag, Stuttgart, Germany, 1972.

(2) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565, 633 (1963).

(3) J. D. Roberts and C. M. Sharts, *Org. React.*, **12**, 1 (1962); L. L. Muller and J. Hamer, "1,2-Cycloaddition Reactions", Interscience, New York, N.Y., 1967.

(4) P. D. Bartlett, *Q. Rev., Chem. Soc.*, **24**, 473 (1970); see also K. N. Houk, *Surv. Prog. Chem.*, **6**, 1 (1973).

(5) H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **12**, 819 (1973).

(6) Two classifications of cycloaddition types are in common usage. The first, due to Huisgen, uses a sum of digits, $i + j + \dots$, each of which represents the number of atoms connecting (and including) the termini of an addend.⁷ The second, due to Woodward and Hoffmann, is a sum of digits, each of which represents the number of electrons involved in bonding changes in one addend.⁸

(7) R. Huisgen, R. Grashey, and J. Sauer in S. Patai, "The Chemistry of Alkenes", Interscience, London, 1964.

(8) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(9) W. C. Herndon, *Fortschr. Chem. Forsch.*, **46**, 141 (1974), and references therein.

(10) Recent theoretical results¹¹ indicate that simple species with geometries like those classically believed to be possessed by biradical intermediates are not always energy minima.

(11) R. Hoffmann, S. Swaminathan, B. Odell, and R. Gleiter, *J. Am. Chem. Soc.*, **92**, 7091 (1970); M. J. S. Dewar and S. Kirschner, *ibid.*, **96**, 5246 (1974); T. Okada, K. Yamaguchi, and T. Fueno, *Tetrahedron*, **30**, 2293 (1974).

(12) P. D. Bartlett, L. K. Montgomery and B. Seidel, *J. Am. Chem. Soc.*, **86**, 616 (1964); L. K. Montgomery, K. Schueller, and P. D. Bartlett, *ibid.*, **86**, 622 (1964), and following papers; P. D. Bartlett, *Science*, **159**, 833 (1968).

(13) Theoretical studies also show that the distinction between biradicals and zwitterionic species is artificial, these terms applying to the two extremes of configurational composition of species with "biradicaloid" geometries; see L. Salem and C. Rowland, *Angew. Chem., Int. Ed., Engl.*, **11**, 92 (1972).

K. N. Houk was born in Nashville, Tennessee, in 1943, and grew up in Montana and Illinois. At Harvard, where he received A.B., A.M., and Ph.D. degrees, his interests were divided between chemistry and trumpet playing. Since 1968, he has been on the faculty of Louisiana State University—Baton Rouge, where he is now Professor. His research involves experimental and theoretical studies, especially of mechanisms and synthetic applications of cycloaddition reactions, photochemistry, and photoelectron spectroscopy.

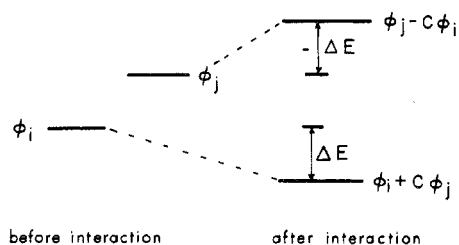


Figure 1. The interaction of two orbitals.

(3) the cis stereospecificity and small effects of solvent polarity on rates seem to require concerted mechanisms.

A general unifying principle was needed which could simultaneously explain reactivity, regioselectivity, and stereospecificity phenomena exhibited by cycloadditions and could lead to predictions of reactivity and product identities for any addend pair. This principle ultimately came from quantum mechanics, applied in an approximate manner.

Although in principle quantum mechanics can lay bare all the naked truths of chemistry, many of us are still reveling in fondly opening one button at a time and savoring each new insight. Perturbation molecular orbital (PMO) theory is an approximate quantum mechanical method to understand relative reaction rates. Its application to cycloaddition reaction mechanisms is the subject of this Account.

The Frontier Molecular Orbital Model of Cycloaddition Reactions

Perturbation theory has been applied to a variety of chemical phenomena,¹⁵ including explicitly cycloaddition reactions.¹⁶ Simply stated, the interaction of two orbitals gives rise to a new set of orbitals, as represented in Figure 1. If overlap is neglected, the difference in energy before and after the interaction is given by the second-order perturbation expression:

$$\Delta E = (H_{ij})^2 / (\epsilon_i - \epsilon_j) \quad (1)$$

The denominator of this expression indicates that, the closer in energy the orbitals, the more they will interact, while the numerator indicates that, if the orbitals are of the same symmetry and overlap effectively, the interaction will be large.

Paraphrasing Fukui, *those orbitals will interact most which overlap best and are closest in energy*.^{15c-e} If the two orbitals contain two or three electrons, the interaction will result in stabilization, or a net lowering of electronic energy, while if four electrons are present, destabilization or closed-shell repulsion results.¹⁶ Of the stabilizing terms, those arising from the interaction of the HOMO of one molecule with the LUMO of the second, and vice versa, will dominate energy changes, since these orbitals are closest in energy. This "frontier orbital" approxima-

(14) R. A. Firestone, *J. Org. Chem.*, **37**, 2181 (1972), and references therein.

(15) (a) E. Heilbronner and H. Bock, "Das HOMO-Modell und Seine Anwendung", Verlag Chemie, GmbH, Weinheim/Bergstr., 1970; (b) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969; (c) K. Fukui, *Fortschr. Chem. Forsch.*, **15**, 1 (1970); (d) "Chemical Reactivity and Reaction Paths", J. Klopman, Ed., Wiley-Interscience, New York, N.Y., 1974; (e) K. Fukui, *Acc. Chem. Res.*, **4**, 57 (1971).

(16) L. Salem, *J. Am. Chem. Soc.*, **90**, 543, 553 (1968); A. Devaquet and L. Salem, *ibid.*, **91**, 3793 (1969); R. Sustmann and G. Binsch, *Mol. Phys.*, **20**, 9 (1971).

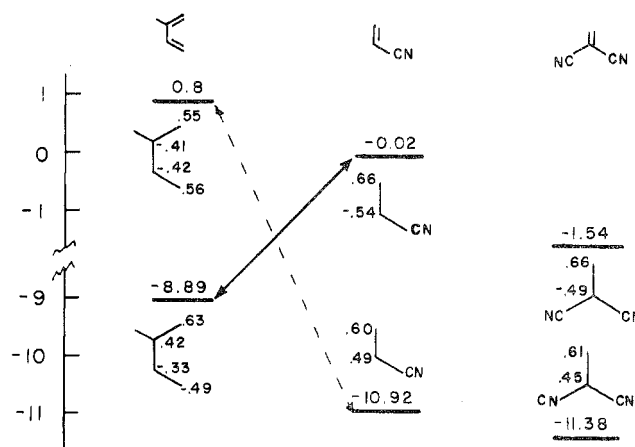


Figure 2. Frontier molecular orbitals of isoprene, acrylonitrile, and vinylidene cyanide.

tion, advocated first by Fukui, is remarkably successful in rationalizing reactivity and regioselectivity phenomena, in spite of the fact that interactions of extrafrontier orbitals, closed-shell repulsions, and coulombic terms contribute to energy changes, also.^{16,17}

An alternative, but essentially equivalent, derivation of frontier MO theory can be constructed along the lines of Mulliken charge-transfer theory.^{18a} Fukui,^{15c,d} and more recently Epiotis,^{18b} have discussed this alternative formalism. In charge-transfer or configuration-interaction (CI) language, the ground-state complex is stabilized by admixture with some of the charge-transfer configuration in which an electron is transferred from the donor HOMO to the acceptor LUMO. The extent of stabilization is evaluated in the same manner as in the frontier molecular orbital theory, except that ionization potentials (IP) and electron affinities (EA), rather than orbital energies, enter the denominator of eq 1 (see below).

Since an attempt to justify theoretically the validity of the frontier MO theory is probably less convincing to practitioners of the synthetic art than a demonstration of its utility, an example of the practical application of frontier MO theory is given here. In order to explain the reactivities and regioselectivities of a pair of addends, one starts with the frontier MO's of each molecule, as shown for isoprene, acrylonitrile, and vinylidene cyanide in Figure 2. The assigned occupied orbital energies are the negatives of the experimentally determined vertical IP's, the vacant orbital energies are the negatives of the EA's (estimated for isoprene), and the orbital coefficients are calculated by the CNDO/2 method.¹⁹ Since EA's and IP's are used, a CI, or charge-transfer, model is implicitly assumed here. In order to carry out a calculation for the transition state itself, one would need to know coefficients, IP's, and EA's for the addends in that geometry. Since addend geometries are probably rather undistorted in cycloaddition transition states, a reasonable approximation involves using iso-

(17) G. Klopman and R. F. Hudson, *Theor. Chim. Acta*, **8**, 165 (1967); G. Klopman, *J. Am. Chem. Soc.*, **90**, 223 (1968).

(18) (a) R. S. Mulliken and W. B. Person, "Molecular Complexes", Wiley-Interscience, New York, N.Y., 1969; (b) N. D. Epiotis, *Angew. Chem., Int. Ed. Engl.*, **13**, 751 (1974), discusses the CI treatment of pericyclic reactions.

(19) (a) K. N. Houk, L. L. Munchausen, and Y.-M. Chang, submitted for publication; (b) K. N. Houk in "Pericyclic Reactions", R. E. Lehr and A. P. Marchand, Ed., Academic Press, New York, N.Y., in press.

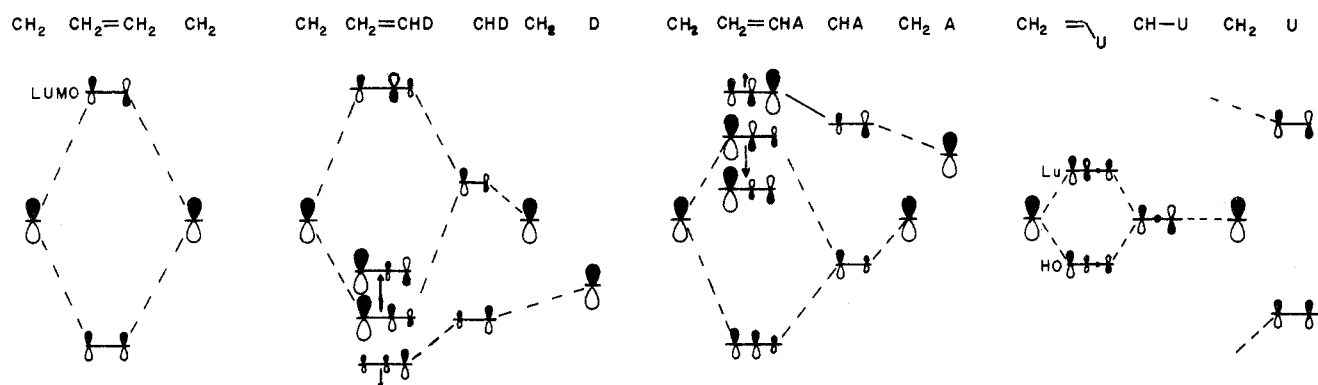


Figure 3. Qualitative derivation of the frontier molecular orbitals of the three classes of alkenes.

lated addend quantities, but $IP - EA - Q$ for the denominator of eq 1, where Q is 3–5 eV.^{19b}

Figure 2 shows that the isoprene HOMO–acrylonitrile LUMO interaction produces the greatest stabilization, because these frontier orbitals are closest in energy. The stabilization of the “para” transition state is greater than that for the “meta”, because the overlap is better (numerator larger in eq 1) when the larger terminal coefficients are united. Experimentally, the “para” isomer predominates (70% at 20°).²⁰

Vinylidene cyanide has a larger EA (lower LUMO energy)¹⁹ than acrylonitrile, resulting in a greater interaction with the diene HOMO and a faster reaction rate. Although the isoprene data have not been measured, cyclopentadiene reacts 100 times faster with vinylidene cyanide than with acrylonitrile.²¹ The regioselectivity of the vinylidene cyanide–isoprene is greater (91% “para”),²⁰ because the difference between the vinylidene cyanide LUMO coefficients is greater and the interaction is stronger.

This comparison is one example of a phenomenon often observed in cycloaddition chemistry: increasing reactivity is accompanied by increasing selectivity. Another example is found in the ratios of rates of reaction of isoprene and butadiene with acrylonitrile (1.5), vinylidene cyanide (9.9), and tetracyanoethylene (30).²⁰ For a relatively large diene HOMO–dienophile LUMO separation, a 0.14-eV decrease of diene IP (isoprene, 8.89 eV; butadiene, 9.03 eV)²² results in slight acceleration. As the butadiene HOMO–dienophile LUMO gap decreases, then a 0.14-eV additional decrease has a larger effect on reactivity.

Properties of Molecular Orbitals of Cycloaddends

To apply the theory to all cases, one must know the properties of reactant frontier MO's. Calculations on specific addends of all types by a variety of methods have been reported,^{23,24} but simple generalizations often suffice for predictive purposes. We have generally relied on pictorial representations of MO properties, since “a graphic representation is worth 1K bytes (W. T. Wipke, 1974)”, and have emphasized

the perturbation approach to explain substituent effects, since the raw results of a MO calculation on one system do not directly indicate the origin of the results.²⁵ Several alternative derivations of substituent effects on alkene coefficients and energies have been proposed,^{25,26} but that shown in Figure 3 seems to be the most general.

The ethylene HOMO and LUMO are formed by uniting two 2p orbitals of isolated methylene groups while the frontier π MO's of a substituted alkene, CH₂CHS, are formed by uniting a methylene 2p orbital and a CHS π orbital (S is the substituent). This approach is shown in Figure 3 for the case of ethylene, electron-rich alkenes (D = donor group such as alkyl or amino characterized by a high-lying filled MO), electron-deficient alkenes (A = acceptor group such as cyano, carbonyl, or nitro, characterized by a low-lying vacant orbital), and a conjugated alkene (U = unsaturated group such as vinyl or phenyl characterized by a moderately high energy HOMO and a low energy LUMO).

The evolution of the electron-rich alkene frontier MO's from the parent atomic orbitals may be traced as follows: starting with an isolated 2p orbital on a methylene group and a filled donor orbital below that in energy on the far right of the diagram, a perturbed methylene orbital (CH–D) is obtained by mixing the orbitals in the usual way. For a weak donor (e.g., the “ π CH₂” orbital of a methyl group) the only orbital of much import will be the upper, antibonding combination, whose energy will be somewhat above that of the CH₂ group. This orbital and the unsubstituted methylene orbital mix to generate a lower energy orbital, polarized away from the substituent, and a higher energy orbital, polarized toward the substituent. Further interaction with the lower CHD orbital will further raise the HOMO energy (arrows in Figure 3).

For an acceptor substituent, A, a similar analysis yields the shapes of the MO's as well as the energies relative to the MO's of ethylene. For an unsaturated conjugating group, U, the CHU orbitals are the familiar allyl orbitals. To a first approximation, the middle MO of allyl is at the same energy as that of the CH₂ orbital, and the mixing proceeds as with the union of two CH₂ orbitals. However, the terminal coefficient

(20) T. Kojima and T. Inukai, *J. Org. Chem.*, **35**, 1342 (1970).

(21) J. Sauer, H. Wiest, and A. Meilert, *Chem. Ber.*, **97**, 3183 (1964).

(22) M. Beez, G. Bieri, H. Bock, and E. Heilbronner, *Helv. Chim. Acta*, **56**, 1028 (1973).

(23) (a) K. N. Houk, *J. Am. Chem. Soc.*, **95**, 4092 (1973); (b) see also O. Eisenstein, J. M. LeFour, and N. T. Anh, *Tetrahedron Lett.*, 969 (1971).

(24) K. N. Houk, J. Sims, R. E. Duke, Jr., R. W. Strozier, and J. K. George, *J. Am. Chem. Soc.*, **95**, 7287 (1973); K. N. Houk, *ibid.*, **94**, 8953 (1972).

(25) L. Libit and R. Hoffmann, *J. Am. Chem. Soc.*, **96**, 1370 (1974).

(26) For the application of this idea to substituent effects on cycloadditions and leading references, see W. C. Herndon, J. Feuer, W. B. Giles, D. Otteson, and E. Silber in ref 15d, p 275.

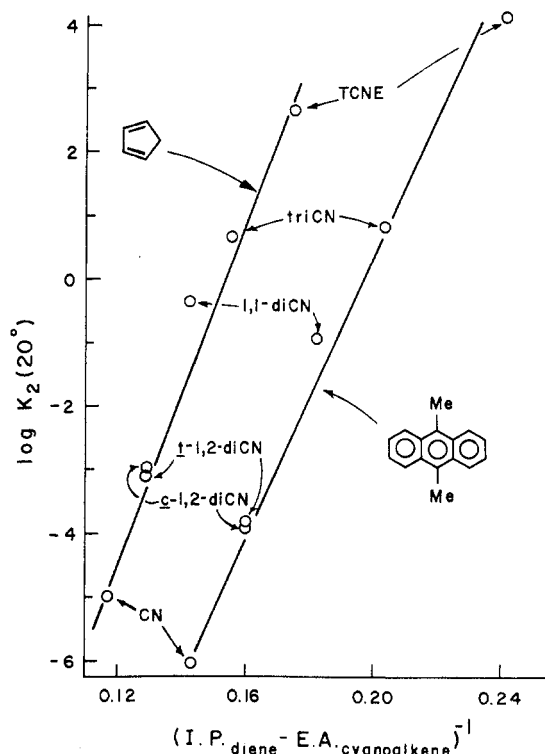


Figure 4. Plot of rates of cycloadditions of dienes with cycloalkenes vs. the inverse of the diene HOMO-dienophile LUMO energy gap.

at allyl is $1/(2^{1/2})$ versus unity for an isolated p orbital, so the HOMO-LUMO splitting in butadiene is less than that in ethylene. Further interactions with the lowest and highest allyl orbitals (not shown) would produce the familiar antisymmetric and symmetric butadiene HOMO and LUMO.

The shapes and energies of the frontier orbitals of alkenes can be generalized as follows. **Electron-rich alkenes:** $\epsilon(\text{HOMO})$ and $\epsilon(\text{LUMO})$ increase as donor strength increases, the former more than the latter, and the unsubstituted HOMO coefficient is larger than the substituted HOMO coefficient. The LUMO coefficients are opposite in magnitude, but the difference in coefficient magnitudes is smaller.

Electron-deficient alkenes: $\epsilon(\text{HOMO})$ and $\epsilon(\text{LUMO})$ decrease as acceptor strength increases, the latter more than the former. The unsubstituted coefficient is larger than the substituted coefficient in both HOMO and LUMO, with the difference in coefficient magnitudes much larger in the LUMO.

Conjugated alkenes: $\epsilon(\text{HOMO})$ is higher and $\epsilon(\text{LUMO})$ is lower than in ethylene, and the unsubstituted coefficients are larger in both MO's.

The molecular orbitals of several other species of interest can be understood in a similar fashion. For example, 1- and 2-substituted dienes are vinyllogs of the alkenes in Figure 3.²⁴ Cumulenes such as ketene have both a typical acceptor LUMO (the in-plane π^*_{CO} orbital where O replaces CHA) and a donor HOMO (the out-of plane enol ether type orbital).²⁷ 1,3-Dipoles (Figure 5) have frontier MO's resembling those of perturbed allyl anions,^{24,28,29} and a qualita-

(27) K. N. Houk, R. W. Strozler, and J. A. Hall, *Tetrahedron Lett.*, 897 (1974), and references therein.

(28) K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *J. Am. Chem. Soc.*, 95, 7301 (1973).

(29) K. N. Houk, Y.-M. Chang, J. Sims, D. C. Kaufman, L. L. Munchausen, and A. Battaglia, submitted for publication.

tive derivation of coefficient magnitudes can be achieved by uniting the MO's of a species $X \equiv Y$ with those of Z.

With this brief summary of the characteristics of frontier orbitals, we turn to applications of these results.

Regioselectivity and Reactivity in Diels-Alder Reactions

Both perturbation and frontier MO theory have been applied to the Diels-Alder reaction.^{23,30} Pioneering advances in this field include Fukui's recognition of the importance of HOMO-LUMO interactions,³¹ Hoffmann and Woodward's explanation of endo stereoselectivity in Diels-Alder reactions,³² and Herndon's PMO calculations on regioselectivity.³³ However, "quantitative" numerical applications often failed to give even qualitative agreement with experiment,³⁴ or failed to elucidate the origin of the phenomenon when a correct prediction was made. Sustmann showed how the frontier orbital approach could account for reactivity phenomena,³⁵ and we utilized a similar approach to show the origin of regioselectivity phenomena.²³

Normal "Alder rule" Diels-Alder transition states have highly stabilizing diene-HOMO-dienophile-LUMO interactions. Electron-rich alkenes are unreactive with simple dienes, due to the absence of a strongly stabilizing interaction. Diels-Alder reactions with "inverse electron demand" arise when the diene-LUMO-dienophile-HOMO interaction is greatest, so that electron release on the dienophile accelerates the reaction rate.

More quantitative correlations have been found. Sustmann noted a correlation between IP (diene) - EA (dienophile) and the rate of Diels-Alder reactions in a series including two dienophiles and an extensive series of dienes,³⁶ and we have shown that there is an excellent linear correlation between the reciprocal of the difference between the diene IP and the dienophile EA and the log of the reaction rate for a series of cyanoalkenes with two dienes, cyclopentadiene and 9,10-dimethylanthracene, as shown in Figure 4.¹⁹ These excellent linear correlations are unusual, but demonstrate that frontier MO theory can be quantitative when factors other than frontier interactions are constant, or are linearly related to frontier orbital energies.

Regioselectivity is also subject to explanation in frontier orbital terms. In dienes or polyenes, the terminus β to an alkyl or conjugating substituent has the larger HOMO coefficient.²³ In reactions with conjugated or electron-deficient dienophiles, the diene-HOMO-dienophile-LUMO interaction is strongest and favors the "para" or "ortho" isomer, as in the ex-

(30) W. C. Herndon, *Chem. Rev.*, 72, 157 (1972).

(31) K. Fukui in "Molecular Orbitals in Chemistry, Physics, and Biology", P.-O. Lowdin and B. Pullman, Ed., Academic Press, New York, N.Y., 1964, pp 513ff.

(32) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, 87, 4388 (1965); see also K. N. Houk, *Tetrahedron Lett.*, 2621 (1970); K. N. Houk and L. J. Luskus, *J. Am. Chem. Soc.*, 93, 4606 (1971).

(33) J. Feuer, W. C. Herndon, and L. H. Hall, *Tetrahedron*, 24, 2575 (1968).

(34) See introduction of ref 23a.

(35) R. Sustmann, *Tetrahedron Lett.*, 2721 (1971).

(36) R. Sustmann and H. Trill, *Angew. Chem., Int. Ed. Engl.*, 11, 838 (1972).

ample discussed earlier. There are some less straightforward cases, when both addends are substituted with donor groups, or both with acceptor groups. For the most part, the former combination does not react, but several reactions of the latter type are known. The HOMO's of electron-deficient alkenes have the larger coefficient on the unsubstituted terminus,^{23,24} but there is little difference in coefficient size. Thus, ortho-para regioselectivity is smaller, but is still observed. Secondary orbital interactions will also favor the "ortho" and "para" isomers.³⁷

Epiotis, who considers that the HOMO of an electron-deficient alkene has the larger coefficient at the substituted carbon, concludes that Diels-Alder reactions between two electron-deficient addends must be nonconcerted processes.³⁸ While we have also concluded that Diels-Alder reactions of addends of similar polarity are often stepwise, regioselectivity predictions are the same, regardless of mechanism.

Catalysis of Diels-Alder reactions can be discussed in a similar fashion.³⁹ Protonation or Lewis-acid complexation of the carbonyl group of an α,β -unsaturated carbonyl compound results, to a first approximation, in a large increase in the effective electro-negativity of the substituent, with a resulting lowering of the MO energies. Furthermore, the orbital energies are changed in such a way as to enlarge the terminal coefficient. Qualitatively, the LUMO of the protonated species resembles that of an allyl cation, with large terminal coefficients, and a node at the central atom. For the reaction illustrating regioselectivity, the AlCl_3 catalysis produces an acceleration of 10^5 at 20° , and the regioselectivity is increased from 80:20 "para:meta" in the uncatalyzed reaction to 97:3 with AlCl_3 catalyzed.⁴⁰ While cis stereospecificity is retained in the catalyzed reactions, the endo stereoselectivity is increased, as exemplified by the increase in percent of endo adduct from 80% in the uncatalyzed reaction of cyclopentadiene and methyl acrylate to 95% in the AlCl_3 -catalyzed reaction.⁴¹ The explanation for all of these phenomena is contained in frontier MO changes.³⁹ There is no need to invoke a change in mechanism, and experimental evidence for such a change exists in only a few cases.

1,3-Dipolar Cycloadditions

Sustmann first applied the frontier orbital concept to reactivity in 1,3-dipolar cycloadditions. He explained why phenyl azide reacts rapidly with both electron-rich alkenes (dipole-LUMO-dipolarophile-HOMO gap smallest) and electron-deficient alkenes (dipole-HOMO-dipolarophile-LUMO gap smallest), but reacts slowly with alkenes of intermediate polarity (no small frontier orbital gap).⁴²

The regioselectivity of 1,3-dipolar cycloadditions had perplexed many workers in the field for some time,^{42,43} and, in order to apply PMO theory to this puzzle, we undertook a theoretical study of 1,3-dipole MO's.^{24,28} The results of this study satisfactorily ex-

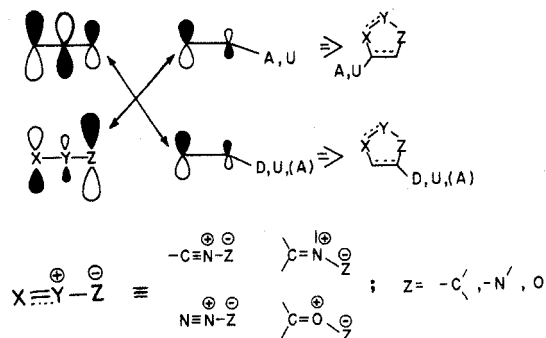


Figure 5. Frontier orbital interactions in 1,3-dipolar cycloadditions.

plain regioselectivity and reactivity phenomena amassed over the last 20 years by Huisgen² and others. As our work was in progress, Bastide and coworkers independently treated 1,3-dipolar reactivity and regioselectivity by perturbation methods and arrived at conclusions similar in most respects to ours.⁴⁴

The explanation of 1,3-dipolar cycloaddition reactivity regioselectivity may be summarized briefly as follows: the various ylides are all electron-rich species, characterized by high-lying HOMO's and LUMO's. These species react preferentially with electron-deficient alkenes; such a pair of addends has a narrow dipole-HOMO-dipolarophile-LUMO gap. The nitrile and azomethine imines and oxides react rapidly with both electron-rich and electron-deficient species, while nitrous oxide and ozone are electrophilic species due to their low-lying HOMO's and LUMO's.

From these generalizations and the coefficient magnitudes discussed earlier, the regioselectivity of most 1,3-dipolar cycloadditions can be rationalized by reference to Figure 5. One frontier orbital interaction generally favors one regioisomer while the other favors the opposite regioisomer. This is because the larger HOMO coefficient is on "Z", while the larger LUMO coefficient is on "X".⁴⁵ For alkenes, the important frontier orbitals have larger coefficients at unsubstituted terminus on both the HOMO and LUMO. If one interaction clearly predominates, then predictions are straightforward. The situation is complicated somewhat by the fact that the HOMO-LUMO gap for 1,3 dipoles is relatively small, so that both interactions may be important. However, if one frontier orbital gap is 1 eV or so less than the other, clear-cut predictions are made. We have rationalized the regioselectivity of all 1,3-dipolar cycloadditions based on this model. Recently, a thorough numerical perturbation treatment of the diazomethane-ethylene reaction has been carried out by Fukui and coworkers,⁴⁶ and the results of these calculations are in complete accord with the qualitative deductions.

In a number of cases, regioselectivity can be rationalized by the classical concepts of nucleophilicity and electrophilicity, but the power of frontier molecular orbital theory lies in its power to rationalize intermediate cases. For example, nitrile oxides and nitrones

(37) P. V. Alston, R. M. Ottenbrite, and D. D. Shillady, *J. Org. Chem.*, **38**, 475 (1973).

(38) N. D. Epiotis, *J. Am. Chem. Soc.*, **95**, 5624 (1973).

(39) K. N. Houk and R. W. Strozier, *J. Am. Chem. Soc.*, **95**, 4094 (1973).

(40) T. Inukai and T. Kojima, *J. Org. Chem.*, **31**, 1121 (1966).

(41) J. Sauer and J. Kredel, *Tetrahedron Lett.*, 731 (1966).

(42) R. Sustmann, *Tetrahedron Lett.*, 2717 (1971).

(43) See last paragraph of ref 8.

(44) J. Bastide, N. El Ghandour, and O. Henri-Rousseau, *Tetrahedron Lett.*, **41**, 4225 (1972); *Bull. Soc. Chim. Fr.*, 2290 (1973); J. Bastide and O. Henri-Rousseau, *ibid.*, 2294 (1973); O. Henri-Rousseau, Thèse, Perpignan, 1974.

(45) The nitrile ylides are apparent exceptions.^{24,28}

(46) T. Minato, S. Yamabe, S. Inagaki, H. Fujimoto, and K. Fukui, *Bull. Soc. Chem. Jpn.*, **47**, 1619 (1974).

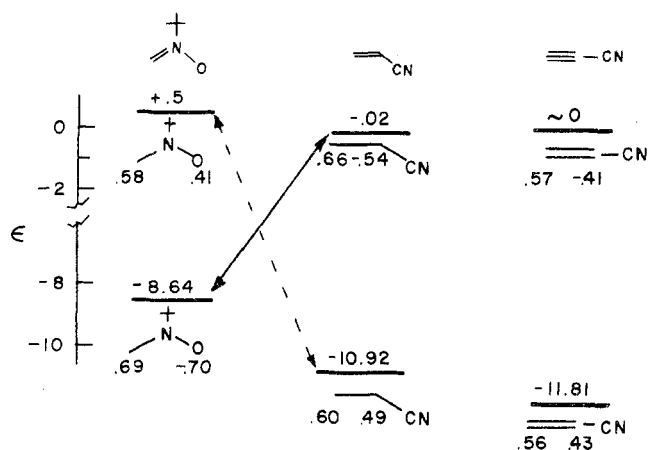


Figure 6. Frontier molecular orbitals of *N-tert*-butylnitron, acrylonitrile, and cyanoacetylene.

were long thought to add to all monosubstituted alkenes to form 5-substituted adducts, regardless of the donor or acceptor character of the substituent. Frontier molecular orbital theory provided an explanation of this phenomenon, and provided predictions of reversal of regioselectivity with highly electron-deficient alkenes.²⁸ Because this is a particularly demanding test of the theory, one example is discussed here.

For *N-tert*-butylnitron and acrylonitrile, the dipole-HOMO-dipolarophile-LUMO interaction is clearly largest (Figure 6), and further electron withdrawal on the dipolarophile increases the reaction rate. However, the coefficients are nearly the same at both termini of the dipole HOMO, so both regioisomers are equally favored by this interaction. The 5 isomer is preferred because the dipole-LUMO-dipolarophile-HOMO interaction favors the transition state leading to the 5 isomer even though this interaction contributes less to the total transition-state stabilization.

Cyanoacetylene has a higher IP than acrylonitrile, but the EA's of the molecules are probably nearly the same. The decrease in nitron-LUMO-dipolarophile-HOMO interaction decreases the preference for the 5-substituted adduct. Experimentally, acrylonitrile gives only the 5-cyano adduct with *N-tert*-butylnitron, while cyanoacetylene gives a 50:50 mixture of the 4- and 5-substituted adducts.⁴⁷

The reversal of regioselectivity of cycloadditions of nitrones and nitrile oxides to very electron-deficient alkenes was the first new prediction of the frontier MO treatment of 1,3-dipolar cycloaddition regioselectivity to be confirmed experimentally in our laboratories. As the IP of the nitrile oxide or nitron decreases, or as the IP of the dipolarophile increases, the extent of reversal tends to increase.⁴⁷⁻⁴⁹ These conclusions are derived from studies with the 1,3-dipoles *N-tert*-butylnitron, *C*-phenyl-*N*-methylnitron, *C*-mesityl-*N*-methylnitron, dihydroisoquinoline *N*-oxide, and mesitylnitrile oxide and the alkenes cyanoacetylene, trifluoropropyne, vinyl sulfones, nitroethylene, and vinylidene cyanide, among others.

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(48) J. Sims, Dissertation, Louisiana State University, Baton Rouge, 1973.

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With very electron-deficient alkenes and very electron-rich dipoles, a change in mechanism to one involving a zwitterionic intermediate might be anticipated. To test for the intermediacy of dipolar species of this type, solvent effects on rates of these cycloadditions were studied. If significant charge development were to occur in the transition state, then the reaction should be accelerated by polar solvents. The opposite is true. The reaction of *C*-phenyl-*N*-methylnitron with ethyl acrylate to give the 5-carboethoxy adduct⁵⁰ shows exactly the same sensitivity to solvent polarity as the reaction of this nitron with cyanoacetylene, which gives only the 4-cyano adduct.⁴⁸ Both reactions are accelerated slightly by decreasing solvent polarity. The rates of reaction of more polar reactants, such as mesitylnitrile oxide and tetracyanoethylene, are slowed more by increasing solvent polarity.⁴⁹ The stereoselectivity and solvent effects on nitrile oxide-bis(trifluoromethyl)fumaronitrile reactions also indicate a concerted mechanism.

It is noteworthy that the 1,3-dipolar cycloaddition appears to always follow a concerted pathway, even when addends which could stabilize an intermediate zwitterionic species very effectively are used. By contrast, Stewart found that TCNE reacts with 4-methyl-1,3-pentadiene by both a concerted [4 + 2] and a stepwise [2 + 2] path involving a zwitterionic intermediate.⁵¹ That is, in nitromethane, a very fast reaction to form only the [2 + 2] adduct occurs, whereas in cyclohexane, a slower reaction giving 30% of the [4 + 2] adduct occurs. The difference apparently arises because the diene can be prevented from readily attaining the cisoid conformation required for the concerted reaction. We are still attempting to find a stepwise 1,3-dipolar cycloaddition.⁵²

Periselectivity

Our first studies in the field of cycloadditions involved the study of reactions between trienes and dienes in a search for a [6 + 4] cycloaddition.⁵³ While this search was successful, we became intrigued with the factors which determined which of the thermally allowed cycloadducts would be formed when many were possible. The word "periselective" was coined for reactions in which the distribution of thermally allowed adducts is very different from the statistical ratio.⁵⁴

Periselectivity and regioselectivity phenomena are treated by frontier orbital theory in the same manner. The class of compounds investigated most thoroughly by this method is the fulvenes.⁵⁵ The frontier MO's of fulvene are shown in Figure 7. Initial consternation over the seeming inconsistency between the [6 + 4] cycloadditions of troponone⁵⁴ and diazomethane⁵⁶ to fulvenes and the [4 + 2] cycloaddition

(50) R. Huisgen, H. Seidl, and I. Bruning, *Chem. Ber.*, **102**, 1102 (1969).

(51) C. A. Stewart, Jr., *J. Am. Chem. Soc.*, **84**, 117 (1962).

(52) L. C. Dunn, D. E. McElwee, A. Russo, and K. N. Houk, unpublished results.

(53) K. N. Houk and R. B. Woodward, *J. Am. Chem. Soc.*, **92**, 4143, 4145 (1970).

(54) K. N. Houk, L. J. Luskus, and N. S. Bhacca, *J. Am. Chem. Soc.*, **92**, 6392 (1970); N. S. Bhacca, L. J. Luskus, and K. N. Houk, *Chem. Commun.*, 109 (1971); K. N. Houk, L. J. Luskus, and N. S. Bhacca, *Tetrahedron Lett.*, 2297 (1972).

(55) K. N. Houk, J. K. George, and R. E. Duke, Jr., *Tetrahedron*, **30**, 523 (1974).

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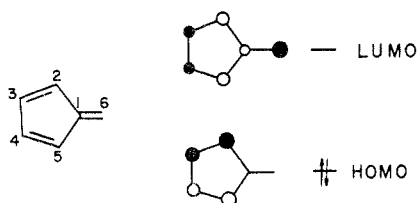


Figure 7. Frontier MO's of fulvene.

of most other 1,3 dipoles and dienes to fulvenes^{57,58} was turned into gratification upon inspection of the frontier MO's of fulvene. Reaction of an electron-rich species with fulvene will take place preferentially at C-6 (and, in the case of a 4π -electron species, simultaneously at C-2). Diazomethane, an electron-rich species, adds across these positions,⁵⁶ while other 1,3 dipoles, which are less electron rich, interact most strongly with the fulvene HOMO, and only [4 + 2] cycloadditions occur. This generalization suggests many experimental tests, which are under way.⁵²

Mechanisms of [2 + 2] Cycloadditions

The reaction of two alkenes to form a cyclobutane is apparently one of the simplest cycloadditions, but the reactions of a fantastic variety of addend pairs have been discovered, and a nearly as impressive number of mechanisms have been proposed. Many related intermolecular reactions which are formally pericyclic [2 + 2] processes are known, such as carbene cycloadditions, hydroborations of alkenes, and electrophilic additions to alkenes. Frontier molecular orbital theory provides a unified treatment of all these reaction mechanisms. What follows is an elaboration of Woodward and Hoffmann's pioneering discussions of [2 + 2] cycloadditions,⁸ extended so as to explicitly take into account frontier orbital properties of substituted alkenes, and all mechanistic types.

Six limiting geometries of addend approach are shown in Figure 8. The geometries are named according to the number of orbitals on each addend involved in bonding and the suprafacial (s) or antarafacial (a) nature⁸ of the bonding stereochemistry.

As pointed out by Woodward and Hoffmann, the $[2_s + 2_s]$ and $[2_a + 2_a]$ geometries are forbidden. They are not stabilized by frontier orbital interactions. In the C_2 $[2_s + 2_a]$ approach, there is a symmetry-allowed interaction only between the LUMO of the suprafacial addend and the HOMO of the antarafacial addend—thus the D (donor) and A (acceptor) superscripts to indicate the type of substitution required to stabilize this geometry. In a distorted $[2_s + 2_a]$ approach of C_2 or lesser symmetry, some stabilization by the opposite frontier interaction is possible, but substantial stabilization is only possible when the donor addend is the antarafacial component. This conclusion is opposite to that of Epiotis, who argued that the acceptor double bond would be more weakened by adding an electron to its LUMO than the donor double bond would be weakened by giving up an electron from its HOMO, so that the acceptor would preferably be the antarafacial component.⁵⁹

The $[1_s + 1_s]$ geometry or its syn version is that commonly proposed for the transition state of a reac-

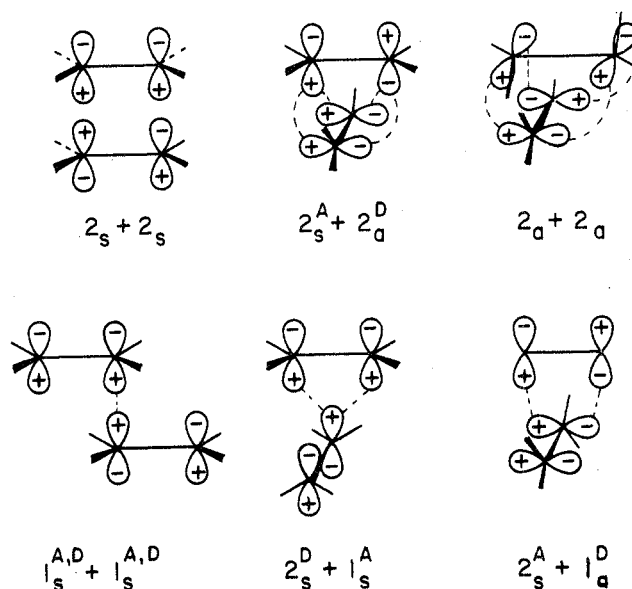


Figure 8. Some geometries of addend approach in [2 + 2] cycloadditions.

tion leading to dipolar or diradical intermediates.⁴ For the $[1_s + 1_s]$ geometry, increased stabilization will occur as donation on one addend and acceptance on the other are increased, but both pairs of frontier orbital interactions are simultaneously stabilizing.

The $[2_s + 1_s]$ geometry is that of a π complex, and the role of such a geometry has been proposed in discussions of the reactions of alkenes with benzyne,⁶⁰ singlet oxygen,⁶¹ carbonyl compounds, and nitroso⁵⁰ compounds.⁶² This complex will be stabilized as donor groups are substituted on the 2_s component and acceptor groups are substituted on the 1_s component. Substitution in the opposite sense will destabilize this complex. Finally, the $[2_s + 1_a]$ geometry is stabilized by donor groups on the 1_a component and acceptor groups on the 2_s component.

Different mechanistic possibilities will be preferred depending on the electronic nature of the two addends. We will consider, for the most part, only those transition states for which stabilization by the usual types of frontier orbital interactions are possible. However, Epiotis has suggested that the $[2_s + 2_a]$ transition state can be stabilized if one alkene is very electron rich and the other is very electron deficient. This will arise if a charge-transfer state, involving a donor-HOMO-acceptor-LUMO electron transfer, is of lower energy than the "ground-state" complex.^{18a,59,63} There is, however, some doubt that reactants differing sufficiently in polarity will react in a $[2_s + 2_a]$ fashion by a concerted mechanism. For example, tetrakis(dimethylamino)ethylene and tetracyanoethylene give a salt involving formation of a dication and a dianion, but do not give any cyclobutane.⁶⁴ Less extreme donor-acceptor pairs are known to form radical cations and anions,⁶⁵ although these

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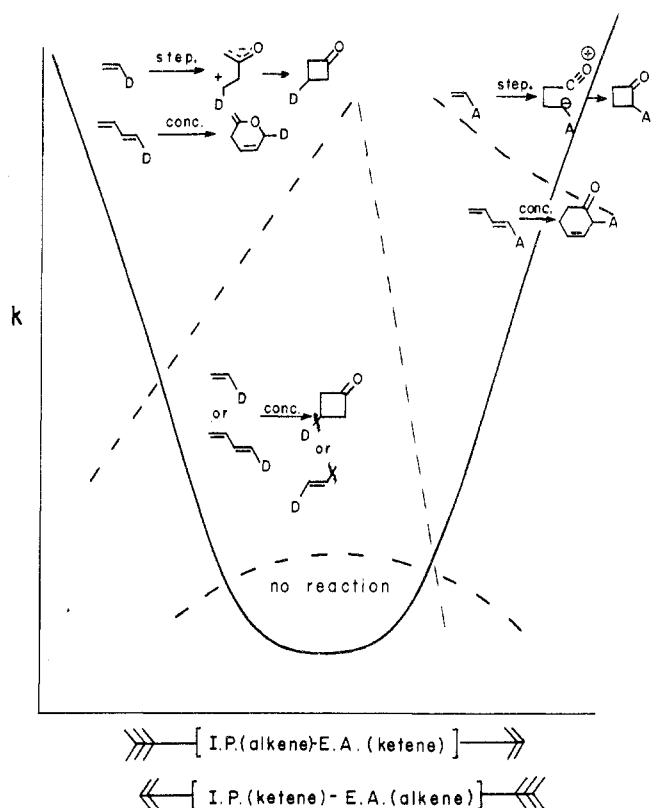


Figure 9. Schematic representation of the relative reactivity and mechanisms expected for ketene reactions with alkenes and dienes of varying donor and acceptor character (D = donor group; A = acceptor group).

are, for the most part, not compounds expected to undergo cycloadditions. Although electron transfer can be followed by a concerted $[2_s + 2_s]$ reaction, extreme donor-acceptor character will probably accelerate certain allowed pathways to an even larger extent.

For reactions of two alkenes, I and II, of similar polarity, only the $[1_s + 1_s]$ geometry can be stabilized simultaneously by both $\text{HOMO}^I\text{-LUMO}^{II}$ and $\text{LUMO}^I\text{-HOMO}^{II}$ interactions. Thus, haloalkenes, alkylethylenes, and conjugated alkenes are expected to undergo reactions from initial $[1_s + 1_s]$ geometries. Experimental evidence seems in accord with this argument.^{3,4} Calculations indicate that the $[1_s + 1_s]$ geometry collapses to a biradical-like species (biradicaloid) which may or may not be an intermediate.¹¹ A $[1_s + 1_s]$ transition state may be comparable in energy to the $[4_s + 2_s]$ transition state in cases of reaction of dienes and dienophiles of similar polarity due to the fact that both diene-NHO and -HOMO-dienophile-LUMO, and diene-NLUMO and -LUMO-dienophile-HOMO interactions can stabilize the former, while only HOMO-LUMO interactions can stabilize the latter.^{66,67}

As alkene I becomes a better donor and II a better acceptor, the stabilization of the $[2_s^I + 1_s^{II}]$ geometry

will increase rapidly (increased $\text{HOMO}^I \rightarrow \text{LUMO}^{II}$ interaction, decreased $\text{HOMO}^{II} \rightarrow \text{LUMO}^I$ interaction). For unsymmetrical substitution of the donor, the difference in terminal coefficient magnitudes as well as any charge separation will favor asymmetry in the direction of the $[1_s + 1_s]$ geometry. For substituted ethylenes, there are three limiting cases: the $[1_s + 1_s]$ geometry is favored for (1) nonpolar reactants and (2) good donor-acceptor pairs where the donor is very unsymmetrical; (3) the $[2_s + 1_s]$ geometry is favored for good donor-acceptor pairs when the donor is not highly unsymmetrical.

While the preferred geometry of approach cannot be exactly determined by these arguments, the trend toward the $[2_s + 1_s]$ geometry with a better donor-acceptor pair is unequivocal, and from this geometry collapse to cyclobutane may occur stereospecifically, or, if polar solvents provide sufficient stabilization, a long-lived intermediate may be formed.⁴ If this $[2_s + 1_s]$ geometry is an actual intermediate, only acceptor rotation can occur, so this geometry, rather than the $[2_s + 2_a]$ proposed by Epiotis, can account for preferred acceptor rotation in polar $[2 + 2]$ cycloadditions. In other cases, the $[2_s + 1_s]$ geometry may be a charge-transfer complex which collapses to cyclobutane with rate-determining activation.

The $[2_s^A + 1_a^D]$ or $[2_a^D]$ interactions are likely to be important only when at least one end of the acceptor is sterically unhindered. In all cases where this interaction has been invoked, except one,⁶⁸ both $[2_s^{D(I)} + 1_s^{A(II)}]$ and $[2_s^{A(I)} + 2_a^{D(II)}]$ or $[1_a^{D(II)}]$ interactions are simultaneously possible. A probable reaction of this type is the formation of perepoxides ("collapsed $[2_s + 1_s]$ geometries") from reactions of singlet oxygen,⁶¹ and the calculated shallow $[2_s + 1_s]$ minima along the reaction coordinate calculated for benzyne⁶⁰ or carbonyl⁶² reactions are stabilized by both of these types of interactions. Similar interactions may assist in stabilization of the related geometries for reaction of carbenes and boranes with alkenes.

Rather than discuss the general validity of this approach, we again cite its utility in the area of ketene cycloadditions. In the Woodward-Hoffmann model for ketene cycloadditions,⁶⁹ a $[2_s^0 + 1_s^K]$ interaction, involving the alkene (0) HOMO and ketene (K) in-plane LUMO, respectively, and a simultaneous $[2_s^0 + 2_a^K]$ (or $[2_s^0 + 1_a^K]$ depending on the exact geometry) interaction involving the alkene LUMO and ketene HOMO, stabilize the transition state. The $[2_s^0 + 1_s^K]$ interaction is facilitated by donation on the alkene and withdrawal on the ketene, while the $[2_s^0 + 2_a^K]$ is favored by withdrawal on the alkene and donation on the ketene. The $[2_s^0 + 1_s^K]$ interaction is strengthened at the expense of the $[2_s^0 + 2_a^K]$ by donation on the alkene, until with enamines a stepwise reaction occurs,⁷⁰ most likely through a $[1_s + 1_s]$ interaction,

(66) Thus, Dewar, Griffin, and Kirschner's distinctly biradicaloid geometry for the butadiene-ethylene Diels-Alder transition state⁶⁷ is probably the result of relatively large frontier orbital gaps. For more usual Diels-Alder addends involving a good donor-acceptor pair, frontier orbital interactions are likely to give a much more symmetrical transition state, and to lead to a larger energetic advantage of the concerted $[4 + 2]$ cycloaddition over the stepwise $[2 + 2]$ cycloaddition: K. N. Houk and S. E. Reiter, submitted for publication.

(67) M. J. S. Dewar, A. C. Griffin, and S. Kirschner, *J. Am. Chem. Soc.*, **96**, 6225 (1974).

(68) The "classic" $[\pi_2^s + \pi_2^s]$ dimerization of a strained *trans*-cyclooctene (K. Kraft and G. Koltzenburg, *Tetrahedron Lett.*, 4357, 4723 (1967)) may be a stepwise process since more thoroughly studied cases of the same type appear to involve biradicaloid species: A. Padwa and S. Clough, *J. Am. Chem. Soc.*, **92**, 5308 (1970); J. Leitich, *Angew. Chem., Int. Ed. Engl.*, **8**, 909 (1969).

(69) Perturbation calculations using an SCF method have verified the essential features of the Woodward-Hoffmann mechanism: R. Sustmann, A. Ansmann, and F. Vahrenholt, *J. Am. Chem. Soc.*, **94**, 8099 (1972). See also ref 27.

(70) R. Huisgen and P. Otto, *J. Am. Chem. Soc.*, **91**, 5922 (1969).

which is just the unsymmetrical limit of the $[2_s + 1_s]$ interaction. With moderate donor dienes (D), cyclobutanones are formed, but with a strongly donating diene, the $[2_s^D + 2_a^K]$ interaction is too feeble to compete with a $[4_s^D + 2_s^K]$ interaction leading to a Diels-Alder reaction at the carbonyl group.⁷¹

If a diene were sufficiently electron-deficient relative to a ketene, then the out-of-plane ketene HOMO should prompt behavior like that of a typical, slightly electron-rich, dienophile; that is, a concerted Diels-Alder reaction with "inverse electron demand" should occur at the CC bond of ketene. While this behavior is observed with α,β -unsaturated ketones,⁷² extensive tests of this prediction have not been carried out. Finally, with very electron-deficient alkenes, the $[1_s + 1_s]$ interaction involving the ketene HOMO and ketenophile LUMO will determine control of the initial bonding interaction, and formation of a cyclobutanone *via* a dipolar intermediate is predicted.²⁷ Figure 9 shows this rich mixture of rationalization and prediction. We have applied similar arguments to other cumulene reactions.²⁷

Conclusions

Through an understanding of the properties of the frontier molecular orbitals of unsaturated species, it has become possible to rationalize or predict the fa-

cility of a reaction between two addends, the favored geometry of approach, and the products of the reaction. **Violations**—there are some! But the theory is capable of refinement through inclusion of extrafrontier interactions and steric and coulombic effects, as well as through the input of quantitative experimental data about unsaturated systems. These refinements, as well as the applications of these principles to the design of new reactions and the synthesis of old molecules by new tricks, are the directions in which our research is progressing.

The impetus to develop this theoretical approach arose from the significant experimental discoveries by my coworkers, who are named in the references. Financial support of various aspects of our research has been generously provided by the Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, the National Institutes of Health, the Camille and Henry Dreyfus Foundation, and the Alfred P. Sloan Foundation. I must also acknowledge the assistance and encouragement that Professor W. C. Herndon has given to my research endeavors in this area, stimulating charge transfers with Professor W. A. Pryor, and the hospitality afforded me during a semester at Princeton University, where most of this Account was written.

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Theoretical Approaches to the Structure of Carbocations

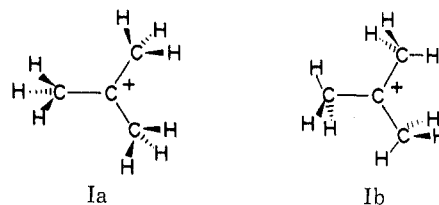
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Among the most impressive accomplishments in organic chemistry during the last decade has been the development of a variety of experimental tactics for the direct observation of reactive carbocation intermediates in solution.² The pioneering systematic efforts of Olah and his coworkers have resulted in a multitude of NMR, vibrational ir, and Raman and ESCA spectroscopic data on literally hundreds of carbon-containing ions under stable long-lived conditions in superacid media. Despite this flourish of activity, however, the detailed geometrical structure of not a single such ion is known to date. Consider the case of the *tert*-butyl cation. Here the ¹H and ¹³C NMR spectra^{3,4} depict the obvious structure, one with two different kinds of carbon atom, but—on the time scale of the experiment—with all hydrogens equivalent. The ESCA measurements,⁵ of the carbon inner-shell shieldings, concur fully. Interpretation of

the ir and Raman data⁶ suggests parallels with the corresponding spectra of isoelectronic trimethylborane, leading to the assignment of a planar (or nearly planar) carbon skeleton for the *tert*-butyl cation. In addition, evidence based on vibrational selection rules seems to favor an ion of C_{3v} symmetry (Ia) rather than a propeller-shaped, C_{3h} symmetry, form (Ib). Other methyl group arrangements, leading to lower overall symmetry, are certainly possible but were not considered in the analysis.



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