withdrawers lower the σ^* orbital energies.

Secondly, the direction of pyramidalization always occurs toward the bond which is most nearly eclipsed with the π orbital. In other words, the partially staggered geometry is favored over the partially eclipsed in pyramidalized species.[23] While more exotic explanations will no doubt be forthcoming, the same types of orbital arguments which have been used to explain the barrier to rotation in ethane[24] are applicable to the π pyramidalization. That is, the partially staggered pyramidalized species simultaneously maximizes the stabilizing two-electron interaction between the orbitals of the allylic CXYZ group and those of the alkene and minimizes four-electron closed-shell repulsion involving filled orbitals on these fragments. In this sense, the same effect which produces the methyl tilt,[1] causes ethane to be staggered[24] and dictates other conformational preferences,[25] also operates in pyramidal alkenes and carbonyls.[23]

Orbital distortion and alkene pyramidalization arguments generally agree as to the side of alkenes or carbonyls which is most vulnerable to attack. However, whereas orbital distortion is a purely theoretical concept, alkene pyramidalization is an observable physical property which qualitatively varies in the same direction as stereoselectivity for a series of molecules. We do not claim that the pyramidalization, in itself, dictates stereoselectivity. Pyramidalization does, however, reflect interactions in the ground states of molecules which are related to much larger energetic effects occuring in transition states. We shall report on these in due course.[26]

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(23) Computational tests indicate that this is not due merely to CH–CH bond repulsions: bending the C_1–H and C_4–H bonds upward causes an increased endo bending of the olefinic hydrogens and vice versa. Thus, the C_1–H, C_2–H eclipsing, discussed by Schleyer[14b] to account for norbornene addition stereoselectivity, is in itself insufficient to account for the endo pyramidalization.

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Origin of π-Facial Stereoselectivity in Additions to π-Bonds: Generality of the Anti-Periplanar Effect

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The understanding and control of stereoselective additions to asymmetrically substituted unsaturated molecules are subjects of intense current interest.[1] For nucleophilic attack on asymmetric carbonyl compounds, empirical generalizations (Cram's rule and its descendants)[2,3] enable qualitative predictions. Felkin,[3] and later Anh, showed that the success of these predictions arises from the strong preference for attack of nucleophiles to occur anti-periplanar with respect to the vicinal bond to the largest group.[4] "Orbital distortions", or asymmetric orbital extensions, have been proposed as the origin of stereoselective attack of various reagents on alkenes,[5] but this conclusion has been disputed.[6,7] We wish to report that the anti-periplanar, or staggering, effect proposed by Felkin et al.[3] and confirmed theoretically by Anh et al.[4] for nucleophilic additions to carbonyl groups is applicable to π systems in general and electrophilic and radical attacks as well. The effect is large and influences both stereoselectivities and reactivities of unsaturated molecules.

The top curve in Figure 1 displays the STO-3G energies obtained by rotation of the methyl of optimized propene, which has the HCCC dihedral angle equal to 0°.[8] At the STO-3G level,

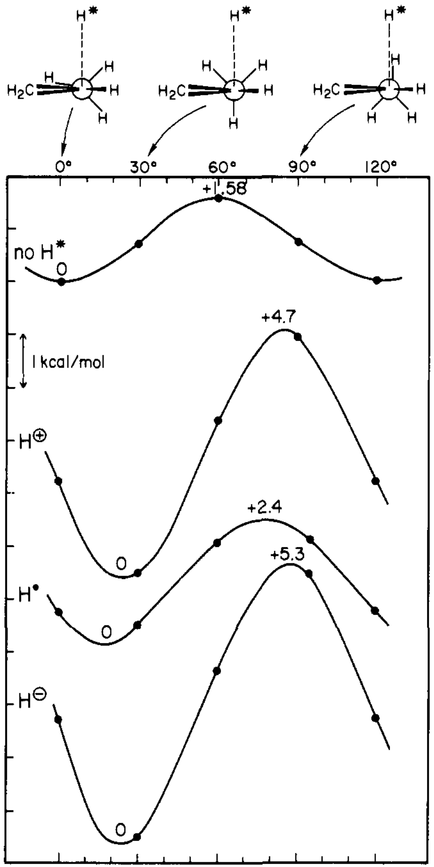

Figure 1. Energies as a function of methyl rotation.[8] Top curve: isolated propene. Second curve: propene plus H^+ placed 2 Å above C-2. Third curve: propene plus H• placed 2 Å above C-2. Bottom curve: propene plus H^- placed 2 Å above C-2.

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(1) (a) Morrison, J. D.; Mosher, H. S. "Asymmetric Organic Reactions"; Prentice-Hall, Englewood Cliffs, NJ, 1971. ApSimon, J. W.; Seguin, R. P. *Tetrahedron* **1979**, *35*, 2797. Bartlett, P. A. *Tetrahedron* **1980**, *36*, 1. (b) For a recent spectacular exploitation of stereoselective attack on alkenes, see: Nagaoka, H.; Rutsch, W.; Schmid, G.; Iio, H.; Johnson, M. R.; Kishi, Y. *J. Am. Chem. Soc.* **1980**, *102*, 7962.

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(7) Footnotes 24 and 25 in ref 17.

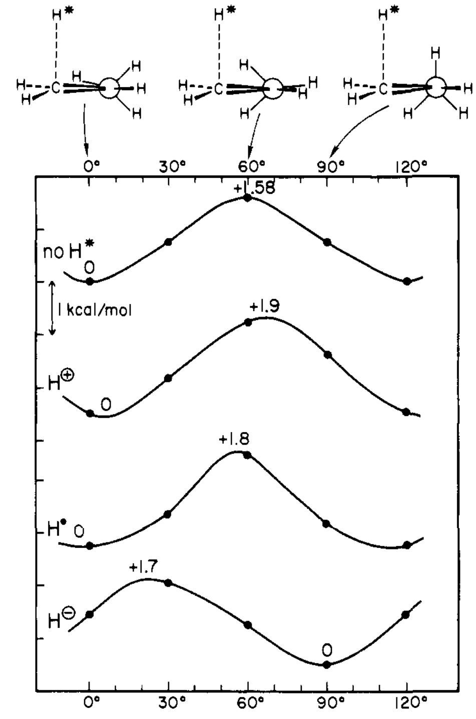

Figure 2. Same as Figure 1, except H*'s attacking C-1.

the calculated barrier (1.58 kcal/mol) is somewhat lower than the experimental barrier (2.00 kcal/mol).[8b] Upon interaction with H* (* = +, ·, or −) situated at 2 Å along a line perpendicular to the CCC plane and passing through C-2 of propene, this curve changes dramatically. For H$^+$ or H$^-$ attack, rotation of methyl from ∠HCCC = 0° to ∠HCCC = 30° lowers the energy by $\sim$2 kcal/mol.[8c] In this geometry, one allylic CH bond is anti-periplanar to the forming C···H* bond. Staggered attack is favored by $\sim$5 kcal/mol over eclipsed attack (∠HCCC = 90°). For hydrogen atom attack, these effects are much smaller but in the same direction.

These surprisingly large effects persist in higher level calculations. Anti-periplanar attack of H$^+$ is energetically preferred over syn-periplanar attack by 3.3, 3.5, and 3.2 kcal/mol, according to STO-3G, 4-31G, and MP2/4-31G[9] calculations, by using STO-3G optimized[8b] propene with the methyl group rigidly rotated by 90°. The MP2 calculation includes a significant correlation energy correction.[9] For H$^-$ attack, these three theoretical levels imply a 3.7, 1.5, and 1.5 kcal/mol preference for staggered attack. As expected, the minimal basis set calculations are seriously deficient in the treatment of anionic species, but the substantial preference for staggered attack remains in higher level calculations.

The influence of methyl rotation is greatly attenuated upon attack at C-1 of propene, as shown in Figure 2. For H$^+$ and H· attack, the preferred eclipsed conformation of propene is maintained during attack. For H$^-$, homo-syn-periplanar attack is favored by $\sim$1.5 kcal/mol over homo-anti-periplanar.

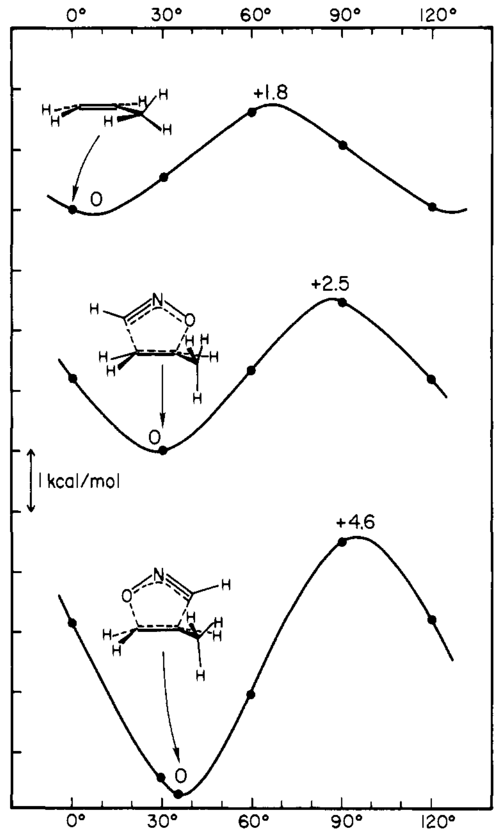

Figure 3. Top curve: conformational energies of propene distorted into the fulminic acid cycloaddition transition-state geometry.[10] Second curve: energies of fulminic acid, propene model cycloaddition transition state[10] as a function of methyl rotation. Bottom curve: same as above for the "reversed" regioisomer.

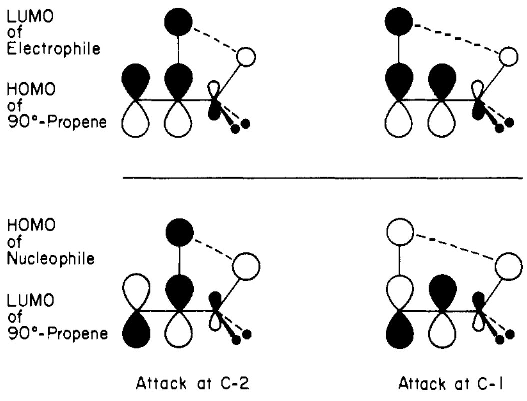

Figure 4. Interaction of the LUMO of an electrophile with the HOMO of 90° propene at C-2 and C-1. Bottom: Interaction of the HOMO of a nucleophile with the LUMO of 90° propene. Solid lines represent primary bonding interactions; dashed lines represent secondary orbital interactions.

These results are not an artifact of the use of charged species in these model calculations. Figure 3 shows the influence of methyl rotation upon the energy of model transition states[10] for attack of fulminic acid on propene leading to the 5- or 4-substituted isoxazoline products, which correspond to the major and minor products of such reactions, respectively. At the top Figure 3, the rigid-rotor energies for isolated, but distorted, propene are shown for comparison. For this mildly electrophilic cycloaddition, the conformation with one allylic CH bond approximately anti-periplanar to the forming CO or CC bond is highly favored. Similar studies with 1-butene show that the conformation having the C–CH$_3$ bond anti-periplanar to the forming bonds is preferred over those with anti-periplanar CH bonds.

These large conformational preferences in transition states can be rationalized tentatively on the basis of secondary orbital interaction arguments made earlier by Anh et al. for nucleophilic attack on carbonyls[4] and by us to account for anomalous re-

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(8) (a) Calculations were performed with the GAUSSIAN 70 program: Hehre, W. J.; Lathan, W. A.; Ditchfield, R.; Newton, M. D.; Pople, J. A. *QCPE* 236. (b) STO-3G optimized propene: Radom, L.; Lathan, W. A.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 5339. (c) For H* attack, the geometry of propene is that determined by Radom et al.[8b] in conformers labeled 0, 60, and 120° (the latter two obtained by rigid rotation of the 0° conformer) and that optimized by us for ∠HCCC = 90°[17] in conformers labeled 30 and 90°.

(9) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem.* **1976**, *S10*, 1.

(10) The transition-state model was constructed starting from the recently computed 4-31G transition state for the HCNO + HC≡CH reaction: Komornicki, A.; Goddard, J. D.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1980**, *102*, 1763.

gioselectivities observed in some cycloadditions.[11,12] We propose that these arguments may be extended to form a powerful, general rule of stereoselectivity: *attack of a reagent at an unsaturated site occurs such as to minimize antibonding secondary orbital interactions between the critical frontier molecular orbital of* the *reagent and those of the vicinal bonds.*[13]

A pictorial representation of this is given in Figure 4. The top drawings represent attack of an electrophile syn-periplanar to an allylic bond. Secondary orbital interactions diminish HOMO–LUMO overlap more than in anti-periplanar attack and disfavor this type of attack at both C-1 and C-2. The lower drawings show that syn-periplanar attack by a nucleophile is disfavored at C-2, but favored at C-1, due to secondary orbital interactions. Interactions of a radical SOMO with both HOMO and LUMO are stabilizing. At C-2, both interactions favor anti attack, while at C-1 the two interactions favor opposite stereochemistries. The secondary orbital rationale is supported by similar calculations on H* plus 1,3-pentadiene: attack at C-1 or C-2 shows no stereochemical preference, while attack at C-3 or C-4 of pentadiene follows the same trends reported here for attack at C-1 or C-2 of propene.

Although we have focused on frontier orbital interactions to explain these results, the stereochemical rule found here can be stated in a much more general fashion to be a result of magnified torsional effects occurring in the transition states of addition reactions: *the tendency for staggering of vicinal bonds with respect to partially formed bonds is greater than for fully formed bonds.* Just as conformational preferences in ethane[14] and related molecules[15] can be rationalized on the basis of simultaneous minimization of closed-shell repulsion between bonds[16] and maximization of filled–vacant fragment orbital interactions,[14] the even larger transition-state conformational preferences that we have found can be attributed to enhancement of these effects when one bond is stretched.

The stereochemical rule is related to our recent discovery of a general pattern of alkene pyramidalization induced by asymmetric substituents.[17] That is, asymmetrically substituted alkenes or carbonyls pyramidalize so as to produce a partially staggered conformation.[17,18] This small pyramidalization (e.g., 2.1° for propene optimized in a conformation where one $HC_3C_2C_1$ dihedral angle is constrained to 90°) has a significant influence on the preference for anti-periplanar attack: anti-periplanar attacks of H^+ and H^- on planar propene are favored by 3.3 and 3.7 kcal/mol, respectively. For pyramidalized propene, the preference increases to 4.5 and 5.0 kcal/mol, respectively. That is, the slight pyramidalization of the alkene enhances the anti–periplanar preference by 1.2–1.3 kcal/mol.

Aside from providing an explanation for the stereochemical preference for exo attack on norbornene by all types of reagents,[19,20] and giving another viewpoint on the theoretically thoroughly trodden S_N2' reaction,[21] this stereochemical rule has ramificiations in the reactivity realm, as well. For example, (1) the anomalously high reactivities of norbornene derivatives (Huisgen's "factor *x*")[22] can be attributed to the fact that the forming bond(s) in additions or cycloaddtions to norbornenes are more perfectly staggered with respect to allylic bonds than in additions to molecules such as bicyclo[2.2.2]octane. (2) The unusually low reactivities of cyclohexenes relative to cyclopentenes in cycloaddition reactions[20] may be attributed to the ~6 kcal/mol of strain[23] required to distort cyclohexene into a boat conformation which has allylic bonds staggered with respect to forming bonds in cycloaddition transition states. (3) The differences in reactivities of geometrical isomers of acyclic alkenes may be attributed to the differences in energy required to rotate allylic bonds into geometries preferred in transition states,[24] which our model calculations imply will differ from preferred ground-state conformations. (4) The "eclipsed alkene model", which rationalizes the stereochemistry of electrophilic attack on asymmetric alkenes,[1b] should be modified since the preferred geometry of an alkene differs in the isolated molecule and in transition states.

Full details of these effects as well as studies of the influence of polar substituents and reagent structure on magnified torsional effects in addition transition states will be reported in future publications.

Acknowledgment. We are grateful to the National Science Foundation and the NATO Research Foundation for financial support of this research, Professor E. M. Burgess for extensive discussions, and Professor John A. Pople for the use of GAUSSIAN 80 for MP2 calculations.

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Superconductivity in an Organic Solid. Synthesis, Structure, and Conductivity of Bis(tetramethyltetraselenafulvalenium) Perchlorate, $(TMTSF)_2ClO_4$

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Recently it was reported that a series of quasi-one-dimensional organic cation radical salts $(TMTSF)_2X$,[1] where X is a symmetrical octahedral anion, PF_6^-,[2,3] AsF_6^-,[4] SbF_6^-,[5] and TaF_6^-,[5] exhibit

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