application of the FMO model to polyfunctionalized dienes tedious), electrostatic potentials do appear to behave in an additive manner, greatly facilitating their application to complex systems.

Dependence of FMO and Reactivity Models on Theoretical Level. As commented previously, the FMO model is known to be sensitive to theoretical level. An example, provided in Table X, compares HOMO coefficients for dienes substituted in the 1-position by strong electron-donating groups, obtained from STO-3G[25] and 3-21G[11] (3-21G$^{(*)}$[12]) calculations. Comparison with STO-3G is particularly appropriate; all semiempirical molecular orbital methods in common use, e.g., CNDO, INDO, and MINDO, are developed around Slater-type minimal basis sets.

Note from the data that, while the underlying polarization of the diene HOMO toward C_4 maintains, irrespective of level, both the absolute size of the effect and the ordering among the different substituents is altered significantly in going from the minimal basis set (STO-3G) to split-valence (3-21G) calculations. Unfortunately, higher level treatments, i.e., involving polarization basis sets, are not yet practical in our laboratory for systems of this size, and it is not possible to say with certainty that the results at the 3-21G level represent the limiting behavior of the Hartree–Fock model.

The data in Table X also clearly show that differences in average electrostatic potentials are sensitive to theoretical level. Again, both the magnitudes of the potentials for a given system and the ordering of potentials among related systems are affected. Indeed, the ordering of directing abilities of methoxy and acylamino substituents reverses in going from STO-3G to 3-21G level calculations, while the methylthio group moves from a close to a distant third place, insofar as its directing ability is concerned. While higher level data on these systems are presently unavailable, experience with simpler molecules[5] suggests that average electrostatic and hydride potentials evaluated at the 3-21G level are quite close to those obtained from calculations using the much larger 6-31G* polarization basis set.[26]

Improved Calculation of Proton–Substrate Interaction Energies. The Influence of the Polarization Potential on the Electrostatic Potential. The *electrostatic potential*[27] can be shown to correspond to the first-order correction to the energy of a molecular system perturbed by a point positive charge, i.e.,

$$E^{(1)} = E^{\text{electrostatic}} = \langle \Psi_0 | \hat{H}' | \Psi_0 \rangle \qquad (12)$$

where the Hamiltonian $\hat{H}'$ describes the Coulombic interactions between the test charge and the substrate. The second-order correction to the energy is termed the *polarization potential*[28] and involves contributions from all singly substituted determinants, Ψ_a, where a single electron has been promoted from an occupied molecular orbital in the ground-state (Hartree–Fock) function, Ψ_0, into a virtual orbital.

$$E^{(2)} = E^{\text{polarization}} = \sum_{a \neq 0}^{\text{determinants}} \frac{\langle \Psi_a | \hat{H}' | \Psi_0 \rangle \langle \Psi_0 | \hat{H}' | \Psi_a \rangle}{E_0 - E_a} \qquad (13)$$

The polarization correction to the electrostatic energy allows for redistribution of charge on the substrate. Its consideration presumably provides a more accurate account of the interaction of proton and substrate than available from the electrostatic potential alone.

Results for 1-methoxy-, 1-(acylamino)-, and 1-(methylthio)-butadiene (in the form of sums of electrostatic and polarization potentials) are provided in Table XI. Compared to the electrostatic potentials for the same compounds (Table VIII), these data show that the effect of the polarization correction is to direct electrophilic attack toward the position of attachment of the substituent. The overall effect is small and nearly the same for the three systems. For 1-methoxybutadiene, it reduces the preference for electrophilic addition onto the C_3C_4 bond (relative to the C_1C_2 linkage) from 4.9 to 3.7 kcal mol^{-1}; a comparable reduction from 5.8 to 4.3 kcal mol^{-1} is noted for 1-(acylamino)-butadiene. The favored site of attack in 1-(methylthio)butadiene is actually reversed (from C_3C_4 to C_1C_2), although results obtained from both electrostatic and the composite potentials show the preference to be very weak.

Calculated Equilibrium Structures for 1- and 2-Substituted *cis*-1,3-Butadiene. Equilibrium structures for dienes substituted at the 1-position are shown in Table XII. These have been obtained at the 3-21G level (3-21G$^{(*)}$ for molecules incorporating second-row elements). Data for 2-substituted dienes are provided in Table XIII.

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[26] Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *66*, 217. (b) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A.; *J. Chem. Phys.* **1982**, *77*, 3654.

[27] For a recent reviews, see: (a) Scrocco, E.; Tomasi, J. *Adv. Quantum Chem.* **1978**, *11*, 115. (b) *Chemical Applications of Atomic and Molecular Electrostatic Potentials*; Politzer, P., Truhlar, D. G., Eds.; Plenum Press: New York, 1981.

[28] For recent discussions, see: (a) Douglass, C. H.; Weil, D. A.; Charlier, P. A.; Eades, R. A.; Truhlar, D. G.; Dixon, D. A. In *Chemical Applications of Atomic and Molecular Electrostatic Potentials*; Politzer, P., Truhlar, D. G., Eds.; Plenum Press: New York, 1981. (b) Haymet, A. D. J.; Oxtoby, D. W. *J. Chem. Phys.* **1982**, *77*, 2466.

Communications to the Editor

Modeling Chemical Reactivity. 2. Stereochemistry of Electrophilic Additions to Chiral Allylic Double Bonds

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Electrophilic additions to carbon–carbon double bonds are among the most utilized reactions in modern synthetic chemistry. The control of their stereochemistry is of fundamental concern to rational synthesis design. The stereochemical preferences of compounds incorporating allylic double bonds has attracted considerable interest in the recent literature, and numerous reports of diastereofacial selectivity have appeared.[1]

Here we communicate an approach to the description of the stereochemistry of electrophilic addition in allylic systems,[2] based on a comparison of the relative affinities of the diastereotopic olefin faces toward a test electrophile, in our case a proton. Application follows in three stages: In the first, a surface of constant electron

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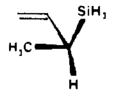
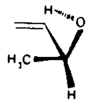
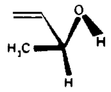
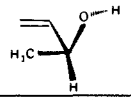
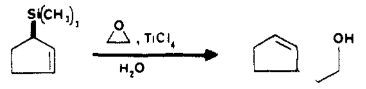
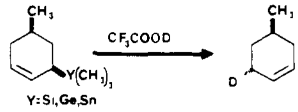
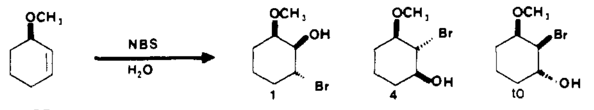
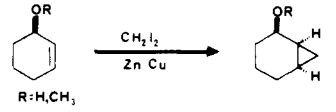
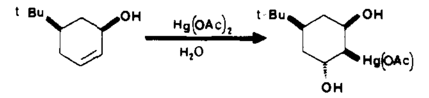
Table I. Average Electrostatic Potentials for Diastereotopic Faces in 2-Silylbut-3-ene and 3-Buten-2-ol[a]

	molecule and conformation	face	av electrostatic potential		
			C_α	C_β	av[b]
1		top, bottom	-6.7, -13.5	-8.5, -17.1	-7.6, -15.3
2a		top, bottom	2.7, -8.3	-8.2, -11.8	-2.8, -10.1
2b		top, bottom	-32.8, -8.7	-21.8, -13.6	-27.3, -11.2
2c		top, bottom	-20.5, -7.0	-16.8, -11.4	-18.7, -9.2

[a] Kcal mol^{-1}. 3-21G$^{(*)}$//3-21G$^{(*)}$ for 2-silylbut-3-ene; 3-21G//3-21G for 3-buten-2-ol. [b] $(C_\alpha + C_\beta)/2$.

Table II. Experimental Regio- and Stereochemical Preferences for Electrophilic Additions to Cyclic Alylic Silanes and Allylic Alcohols

reaction	ref[a]	regiochemistry[b]	stereochemistry[c]
	1	*β*	*anti*
	2	*β*	*anti*
	3	*α* (major)	*syn* (major)
	4		*syn*
	5	*α*	*syn*
	6	*α*	*syn*

[a] References to experimental work: (1) Hayashi, T.; Kabeta, K.; Yamamoto, T.; Tamao, K.; Kumeda, M. *Tetrahedron Lett.* **1983**, *24*, 5661. (2) Reference 13a. (3) Bannard, R. A. B.; Casselman, A. A.; Hawkins, L. R. *Can. J. Chem.*, **1965**, *43*, 2398. (4) Poulter, C. D.; *Freidrich*, E. C.; Winstein, S. *J. Am. Chem. Soc.* **1969**, *91*, 6892, and references therein. (5) Bellucci, G.; Bianchini, R.; Ingrosso, G.; Mastrorilli, E. *Gazz. Chim. Ital.* **1978**, *108*, 643. (6) Chamberlain, P.; Whitham, G. H. *J. Chem. Soc.* B **1970**, 1382. [b] Attachment of the electrophile with respect to the directing group ($SiMe_3$ or OR). [c] Diastereotopic face attacked by the electrophile with respect to the directing group.

density, corresponding to $\psi^2 = 0.002$ electron/bohr^3,[3] is obtained for the substrate from an appropriate quantum-mechanical wavefunction.[4] Next a point positive charge (the test electrophile) is placed at a series of uniformly distributed locations on the

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(1) See, for example: (a) Morrison, J. D.; Mosher, H. S. *Asymmetric Organic Reactions*; Prentice Hall: New York, 1971. (b) Bartlett, P. A.; *Tetrahedron* **1980**, *36*, 2. (c) *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. 2; 1984; Vol. 3.

(2) For related work, see: (a) Pau, C. F.; Hehre, W. J. submitted for publication in *J. Comput. Chem.* (b) Hehre, W. J.; Pau, C. F.; Hout, R. F., Jr.; Francl, M. M. *Molecular Modeling. Computer-Aided Descriptions of Molecular Structure and Reactivity*; Wiley: New York, in press. (c) Kahn, S. D.; Pau, C. F.; Overman, L. E.; Hehre, W. J. *J. Am. Chem. Soc.*, preceding paper in this issue. (d) Kahn, S. D.; Hehre, W. J. *J. Am. Chem. Soc.*, following paper in this issue.

(3) See: Francl, M. M.; Hout, R. F., Jr.; Hehre, W. J. *J. Am. Chem. Soc.* **1984**, *106*, 563.

(4) All calculations have been performed at the single-determinant Hartree-Fock level by using the 3-21G basis set[5] (3-21G$^{(*)}$ for molecules incorporating second-row atoms[6]). Optimum geometries have been used throughout and will be reported in an upcoming full paper. The GAUSSIAN 85 program system[7] has been utilized.

(5) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(6) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Brinkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.

(7) Hout, R. F., Jr.; Francl, M. M.; Kahn, S. D.; Dobbs, K. D.; Blurock, E. S.; Pietro, W. J.; DeFrees, D. J.; Pollack, S. K.; Levi, B. A.; Steckler, R.; Hehre, W. J., *Quantum Chemistry Program Exchange*; Indiana University, Bloomington, IN, submitted for publication.

density surface, and an energy of interaction between reagent and substrate evaluated at each of these locations. In the simplest model, this energy is termed the *electrostatic potential*.[8,9] Finally, information relating to the relative electrophilic affinities of the diastereotopic faces is extracted from the calculated potentials, either visually, by direct inspection of the reactivity information as superimposed onto the substrate electron-density surface, or by constructing average potentials.[10]

Electrostatic potentials corresponding to the diastereotopic faces of the conformer of 2-silylbut-3-ene (**1**) in which the terminal methyl group is in the plane of the double bond (mimicking the situation found in cyclic allylic silanes) are shown in Figure 1. These have been color-encoded on top of the substrate electron-density surfaces; colors near the red end of the visible spectrum represent maximum attraction of the substrate for the test electrophile, while those near the blue represent minimum attraction. Visual inspection suggests greater reactivity of the olefin face which is *anti* to the silyl group and preferentially at the β-carbon. This is confirmed by the average potentials provided in Table I.

There are three conformers of 3-buten-2-ol in which the terminal methyl group has been constrained to be coplanar with the CC double bond.[11] According to 6-31G*//3-21G[12] calculations, the most stable of these, **2a**, positions the hydroxyl hydrogen directly over the double bond. Conformers **2b** and **2c**, in which the OH bond is *trans* to the vinyl group and to the terminal methyl group, respectively, are 1.4 and 1.6 kcal/mol higher in energy. Electrostatic potentials for both diastereotopic faces of these three conformers are provided in Figure 1 and in Table I. While the three surfaces describing electrophilic attack onto the olefin face away from the CO bond are nearly the same, the electrostatic potentials corresponding to addition onto the other diastereotopic face are quite sensitive to the conformation of the OH bond. Here, the two conformers **2b** and **2c**, in which one or the other lone pairs on oxygen is positioned "over the double bond", are indicated to be much more reactive than the arrangement **2a**, in which the OH linkage is overhead. A balance needs to be struck between relative equilibrium abundance and relative reactivity.[13] Conformers **2b** and **2c**, which favor electrophilic attack syn to oxygen, contribute only 14% to the total population (according to 6-31G*//3-21G calculations), although these are by far the most reactive.

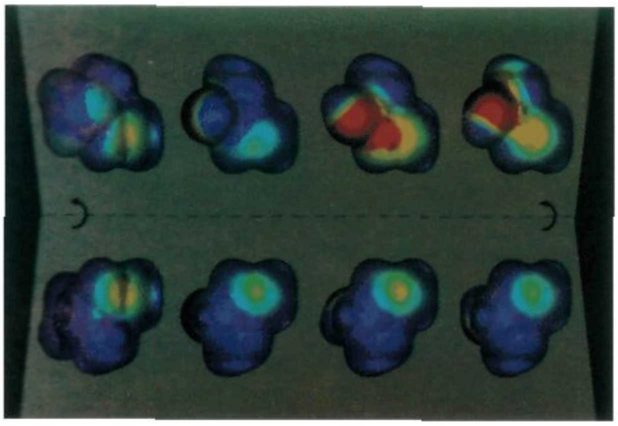

Figure 1. Electrostatic potentials for 2-silylbut-3-ene (**1**) (left) and 3-buten-2-ol **2a** (middle, left), **2b** (middle right), and **2c** (right). Upper and lower images for each correspond to "top" and "bottom" diastereotopic faces designated in Table I. Scale: −30 (red) to 0 kcal mol^{-1} (blue). 3-21G//3-21G ($3\text{-}21G^{(*)}//3\text{-}21G^{(*)}$ for 2-silylbut-3-ene).

Experimental regio- and stereochemical data for electrophilic additions to a variety of cyclic allylic silanes, alcohols, and ethers are summarized in Table II. The general trends, addition *anti* to silicon at the β-carbon and *syn* to oxygen at the α-carbon, are in accord with the reactivity models.[14] A number of qualitative interpretations for the observed stereochemistry of the two classes of electrophilic additions dealt with in this paper have already been advanced.[16] Among them are arguments based on the Fukui hypothesis,[17] that addition will occur preferentially onto the olefin face in which the π orbital is the more heavily localized. We find no evidence for polarization of the π bond in any of these systems.[18,20] An alternative explanation for the noted stereochemistry that an incoming electrophile will "associate" with the lone pairs on oxygen in allylic alcohols and ethers and "avoid association" with the electropositive silicon center in allylic silanes seems preferable.

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(8) For recent reviews, see: (a) Scrocco, E.; Tomasi, J. *Adv. Quantum Chem.* **1978**, *11*, 115. (b) *Chemical Applications of Atomic and Molecular Electrostatic Potentials*; Politzer, P., Truhlar, D. G., Eds.; Plenum Press: New York, 1981.

(9) This accounts only for Coulombic interactions between the point charge and the substrate and does not allow for redistribution of the substrate electron density, transfer of charge from the substrate to the test electrophile, or nuclear relaxation. For a discussion of the possible effects of these corrections, see: Reference 2. (a) Douglass, C. H.; Weil, D. A.; Charlier, P. A.; Eades, R. A.; Truhlar, D. G.; Dixon, D. A. In *Chemical Applications of Atomic and Molecular Electrostatic Potentials*, Politzer, P., Truhlar, D. G., Eds.; Plenum Press: New York, 1981. (b) Haymet, A. D. J.; Oxtoby, D. W. *J. Chem. Phys.* **1982**, *77*, 2466.

(10) This is accomplished by first assigning points on the electron density surface to specific atoms (based on a distance criterion) and then weighting the electrostatic potentials at the individual points according to the cosine of the angle that the surface normal makes with the approaching reagent. In this manner, surface regions which are directly "in front" of the reagent contribute more than those which are "turned awaw". Full details are available elsewhere.[2a,c]

(11) None of these forms are minima on the 3-21G conformational profile and have been chosen to mimic arrangements found in cyclic allylic alcohols and ethers. For further discussion of the conformational energy surface of 3-buten-2-ol, see: Kahn, S. D.; Hehre, W. J. *Tetrahedron Lett.* **1985**, *26*, 3647.

(12) 6-31G* basis set: Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *66*, 217.

(13) (a) Curtin, D. Y. *Rec. Chem. Prog.* **1954**, *15*, 111. (b) Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83.

(14) OsO_4 oxidation of allylic alcohols and ethers generally leads to opposite stereochemical preferences to those noted here.[15] These and other apparent exceptions will be discussed at length in an upcoming full paper.

(15) Cha, J. K.; Christ, W. J.; Kishi, Y. *Tetrahedron,* **1984**, *40*, 2247 and references therein to earlier work.

(16) Allylic silanes: (a) Wickham, B.; Kitching, W. *J. Org. Chem.* **1983**, *48*, 614. Allylic alcohols and ethers: (b) Dauben, W. G.; Berezin, G. H. *J. Am. Chem. Soc.* **1963**, *85*, 468. (c) Chan, J. H. H.; Rickborn, B. *Ibid.* **1968**, *90*, 6406. (d) Srivastava, R. M.; Sweet, F.; Murray, T. P.; Brown, R. K. *J. Org. Chem.* **1971**, *36*, 3633. (e) Barili, P. L.; Bellucci, G.; Berti, G.; Golfarini, M.; Marioni, F.; Scartoni, V. *Gazz. Chim. Ital.* **1974**, *104*, 107. (f) Houk, K. N.; Moses, S. R.; Wu, Y. D.; Rondan, N. G.; Jäger, V.; Schohe, R.; Fronczek, F. R. *J. Am. Chem. Soc.* **1984**, *106*, 3880 (1984).

(17) (a) Ingaki, S.; Fukui, K. *Chem. Lett.* **1974**, 509. (b) Fukui, K. *Theory of Orientation and Stereoselection*; Springer-Verlag: New York, 1975. See also: (c) Anh, N. T.; Eisenstein, O.; Lefour, J. M.; Dâu, M. E. T. H. *J. Am. Chem. Soc.* **1973**, *95*, 6146. (d) Klein, J. *Tetrahedron Lett.* **1973**, 4307. (e) Klein, J. *Tetrahedron* **1974**, *30*, 3349. (f) Eisenstein, O.; Klein, J.; Lefour, J. M. *Ibid.* **1979**, *35*, 225. (g) Burgess, E. M.; Liotta, C. L. *J. Org. Chem.* **1981**, *46*, 1703. (h) Anh, N. T. *J. Chem. Soc., Chem. Commun.* **1968**, 1089.

(18) Visual examination[19] of the 3-21G//3-21G molecular orbitals corresponding to the π bond in these systems shows no evidence for polarization. Details will be provided in our full paper.

(19) See: Hout, R. F.; Pietro, W. J.; Hehre, W. J. *A Pictorial Approach to Molecular Structure and Reactivity*; Wiley: New York, 1984.

(20) This has previously been noted. Houk, K. N. *Methods Stereochem. Anal.* **1983**, *3*, 1.