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Computational Modeling of Stereoselectivity in the Diels–Alder Reactions of Dienol Esters of *O*-Methylmandelic Acid and the Question of π-Stacking

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Abstract: Ab initio calculations have been performed to determine the conformational energy profiles of methoxyacetic acid and vinyl formate. Methoxyacetic acid prefers approximately coplanar arrangements of its C=O and C_α—O bonds, with the syn arrangement favored over the anti by 0.9 kcal/mol. Vinyl formate is most stable in the conformation having a syn-periplanar C—O—C=O array and an anti-periplanar C=C—O—C array. The results of these calculations were incorporated as torsional parameters in the MM2 force field in order to assess the possible role of π-stacking interactions in the stereoselective Diels–Alder reactions of chiral diene 1,3-butadienyl *O*-methylmandelate (**1**). These force-field calculations predict that, in the lowest energy conformation of **1**, the dienyl carbons, the carbonyl group, and the C_α—O bond are approximately coplanar, and the phenyl ring is approximately perpendicular to this plane, as proposed recently by Thornton and Siegel. Conformations having a π-stacking arrangement of the dienyl and phenyl groups of **1** are predicted to lie at least 6.8 kcal/mol higher in energy. The stereoselectivity observed in this reaction can be fully understood in terms of the calculated ground-state conformational preferences of **1**, without invoking special π–π interactions between the phenyl and dienyl groups in the transition state.

Introduction

A survey of the recent chemical literature reveals an explosion of interest in the subject of π-stacking and in the possibility of exploiting π-stacking forces for controlling the stereoselectivity of organic reactions.[1-5] π-Stacking interactions between phenyl and other unsaturated groups have been widely invoked to explain high stereoselectivities in the Diels–Alder reaction,[1,2] nucleophilic additions,[3] and the ene reaction,[4] and an increasing body of data demonstrates that phenyl groups frequently act as superior stereodirecting steric barriers when compared with saturated groups of similar size such as cyclohexyl. Nonetheless, evidence for a general preference of phenyl groups to adopt a face-to-face arrangement with other unsaturated groups is lacking. A variety of crystallographic, solution, and gas-phase data suggest that aromatic hydrocarbons (and many simple heterocycles) preferentially interact with each other in a manner which minimizes face-to-face contacts between the unsaturated ring systems.[6] π-Stacking arrangements are more commonly observed for interactions between highly polarized ring systems such as DNA bases, or when there is a strong "charge-transfer" or donor–acceptor relationship between the two interacting functional groups.[7,8] In order to gain a better understanding of the forces involved in nonbonded interactions between unsaturated functional groups and how these can affect the selectivity of organic reactions, we have begun a calculational investigation into the mechanistic details of several reactions for which π-stacking forces have been invoked as driving forces for stereoselectivity. In the present work, we describe calculations which were designed to probe the origins of stereoselectivity in a system for which two different models have been proposed, one of which invokes π-stacking as the critical interaction responsible for the observed selectivity. We report ab initio calculations on some conformational effects, develop several new parameters for force-field calculations, and present model transition state calculations which support one of these models, as well as some predictions of stereoselectivity in new systems.

Background

In 1980 Trost and co-workers[1] reported that moderate to high diastereoselectivities are obtained in Diels–Alder reactions employing *O*-methylmandelic acid as a covalent chiral auxiliary. Reaction of diene **1** with acrolein or juglone under Lewis acid catalysis gives the corresponding adducts in 64 and >97% d.e., respectively. These selectivities are remarkable for a reaction in

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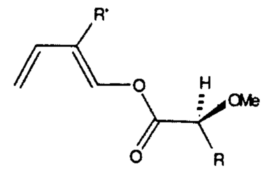


1 $R = C_6H_5$, $R' = H$
2 $R = C_6H_{12}$, $R' = H$
3 $R = C_6H_6$, $R' = CH_3$

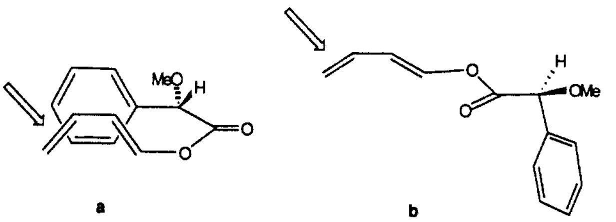


Figure 1.

Table I. Diastereoselectivity in the Diels–Alder Reactions of **1** and Related Compounds[a]

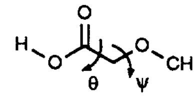
diene	dienophile	catalyst	temp (°C)	d.e. (%)	$\Delta\Delta G^\ddagger$
1	acrolein[b]	$BF_3{\cdot}Et_2O$	−20	64	0.76
1	acrolein[c]	$BF_3{\cdot}Et_2O$	−78	88	1.07
2	acrolein[c]	$BF_3{\cdot}Et_2O$	−78	78	0.81
3	acrolein[c]	$BF_3{\cdot}Et_2O$	−78	94	1.35
1	benzoquinone[c]	$BF_3{\cdot}Et_2O$	−78	92	1.23
1	benzoquinone[c]	none	20	60	0.81
2	benzoquinone[c]	$BF_3{\cdot}Et_2O$	−78	84	0.95
3	benzoquinone[c]	$BF_3{\cdot}Et_2O$	−78	92	1.23
1	methacrolein[c]	$BF_3{\cdot}Et_2O$	−78	96	1.51
1	juglone[b]	$B(OAc)_3$	0	>95	1.59

[a] Free energy differences are given in kcal/mol. The major product is that predicted by examination of either of the two models in Figure 1, or by direct analogy to these models for dienes other than **1**. [b] Reference 1. [c] Reference 9.

which the stereogenic center is located three bonds away from the nearest site of bond formation in an apparently conformationally mobile substrate. In order to explain these results, Trost proposed the π-stacking model shown in Figure 1a. According to this model, the preferred conformation of **1** has a face-to-face arrangement of the two unsaturated moieties and minimized steric interactions between the diene carbons and the methoxyl group. The major stereoisomer of the product then arises from attack of the dienophile on the less hindered face of the diene.

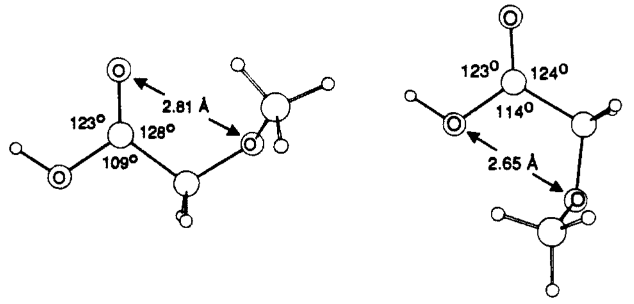
Recently, Trost's π-stacking model has been shown to be inoperative with diene **1** by Thornton and Siegel.[9] The π-stacking model requires an unfavorable s-trans arrangement of the ester group[10] and offers no explanation for Masamune's[11] observation that replacing the phenyl group of **1** by a cyclohexyl group does not greatly reduce the stereoselectivity of the reaction. These workers proposed that the selectivities observed in the reactions of **1** and structurally related dienes (Table I) are best explained in terms of a "perpendicular" model, as shown in Figure 1b. In this model the dienyl and carboxyl groups are in a coplanar arrangement, the C_α–O bond is near the carbonyl oxygen, and the phenyl group is perpendicular and turned so as to direct one face toward the carbonyl carbon. Support for this model was provided by the crystal structure of a Diels–Alder adduct of **1**, in which the conformation of the chiral auxiliary is essentially as proposed in the transition-state model. Furthermore, a variety of indirect experimental evidence supports the notion that α-alkoxy esters prefer an eclipsed arrangement of their carbonyl and methoxyl oxygens in solution.[12]

Table II. Relative Energies of Several Conformations of Methoxyacetic Acid Determined by ab Initio and MM2 Calculations[a]



	θ	ψ	E_{rel} (6-31G*//3-21G)	E_{rel} (MM2)[b]
a	0	70	0.00	0.0
b		180	1.42	1.5
c	45	−76	1.71	2.0
d		66	2.56	1.6
e	90	−75	2.71	3.2
f		79	3.80	3.8
g		180	3.29	5.0
h	135	−61	1.64	1.5
i		87	1.97	3.4
j	180	−75	0.88	1.1
k		180	1.43	1.7

[a] Energies are given in kcal/mol and angles in deg. $\theta = \angle O{-}C{-}C{=}O$ and $\psi = \angle C{-}O{-}C{-}C$. The MM2 energies refer to structures which were minimized with the MM2 force field using the same constraints and starting geometries as the ab initio structures. These structures may differ slightly from the ab initio geometries in certain structural details, such as the precise value of ψ. [b] Using the parameters developed in this work.



(θ = - 6°, ψ = 71°) (θ = 175°, ψ = -73°)

0.00 0.90 kcal/mol

Figure 2. Minimum energy conformations of methoxyacetic acid. Relative energies are MP2/6-31G*//RHF/3-21G.

Results and Discussion

In order to obtain a better understanding of the forces responsible for the stereoselectivity observed in this system, we have performed calculations to elucidate the conformational preferences of **1**, and to show how these conformational preferences lead to energetic differences between competing diastereomeric transition states. Because Allinger's[13] MM2 force field lacks accurate torsional parameters for certain bond rotations of vinyl esters and α-alkoxy esters, we began our study with a series of ab initio calculations[14] to clarify the conformational preferences of such

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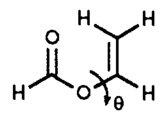
compounds and to help us to develop accurate torsional parameters for use in force-field calculations.

As a model for the conformational preferences of α-alkoxy esters,[15] we have calculated 13 points on the conformational energy surface of methoxyacetic acid at the 6-31G*//3-21G level[16] of theory. In the calculations summarized in Table II, the value of the O—C—C=O dihedral angle, θ, was held fixed at 0, 45, 90, 135, or 180°. The value of the C–O–C–C dihedral angle (ψ) was either fixed at 180° or was minimized, starting from a value of +90° or −90°. No other constraints were employed. Also shown in Table II are the results of similar calculations using the MM2 force field and the new torsional terms developed in the present work.

Variation of the O—C—C=O dihedral angle reveals energy minima near 0 and 180°. Full optimization of the structures represented by entries a and j of Table II leads to conformations having dihedral angles O—C—C=O = −6 and 185°, with the latter 0.90 kcal/mol higher in energy than the former at the MP2/6-31G*//HF/3-21G level[17] of theory (Figure 2). The energy difference between these two fully optimized forms is calculated to be 0.8 kcal/mol using our force-field model (see later). The overall preference for approximately coplanar arrangements of the C_α—O and C=O bonds is unexpected because such arrangements require that the methoxyl oxygen be eclipsed with one of the two carboxyl oxygens, leading to unfavorable steric and electrostatic interactions. This conformational behavior apparently results from preferential hyperconjugation of the electron-deficient C=O π bond with the C—H bonds rather than the C—O bond of the α carbon. A similar preference for coplanar or nearly coplanar arrangements of C=O and C_α-heteroatom bonds is observed for α-fluoro aldehydes, ketones, and esters.[18,19]

Of the two conformations shown in Figure 2, that having a syn arrangement of the C_α—O and C=O bonds is more stable than that having an anti arrangement, in spite of its greater dipole moment (2.2 vs 1.8 D at the HF/6-31G*//HF/3-21G level of theory). Examination of the detailed geometry of the two fully optimized structures in Figure 2 reveals that the closest contact between the methoxyl oxygen and a carboxyl oxygen is 2.65 Å in the anti form and 2.81 Å in the syn form (the van der Waals radius of oxygen is 1.4 Å). The closer O···O contact of the anti form arises in turn from the larger value of the bond angle ∠C—C=O as compared to ∠C—C—O. The former angle varies between 117 and 129° in the conformers of methoxyacetic acid discussed in this paper and the latter between 107 and 114°. These relatively small values of the bond angle ∠C—C—O are not unique to methoxyacetic acid, but appear to be common to carboxylic acids and esters in general. The minimum energy conformation of methyl acetate[10a] has ∠C—C=O = 126° and ∠C—C—O = 112°. Experimentally, the syn and anti arrangements of ethyl fluoroacetate represent energy minima with the latter 0.9 kcal/mol less stable than the former.[19] This difference in energy can be attributed to greater O–F repulsions in the anti conformer.

Table III. Relative Energies of Several Conformations of Vinyl Formate Determined by ab Initio and MM2 Calculations[a]



θ	E_{rel} (6-31G*//3-21G)	E_{rel} (MM2)[b]
0	2.80	2.8
45	3.67	3.6
90	3.61	3.9
135	1.19	1.1
180	0.00	0.0

[a] Energies are given in kcal/mol and angles in deg. θ = ∠C=C—O—C. The MM2 energies refer to structures which were minimized with the MM2 force field using the same constraints and starting geometries as the ab initio structures. These structures may differ slightly from the ab initio geometries in certain structural details. [b] Using the parameters described in the Appendix.

The energy profile for rotation about the C_α–O bond appears to be determined mainly by electrostatic interactions between the methoxyl group and the two oxygens of the carboxyl group. For each value of the O—C—C=O torsion angle in Table II, rotating about the C_α—O bond gives different geometries whose energy and dipole moment increase in the same order. These electrostatic effects are not well-modeled by the parameters given in the standard MM2 force field, which predicts that the anti (180°) arrangement of the C–O–C–C dihedral angle should always be favored. For reasons of simplicity and because we wish only to create a force field to treat this specific problem, we have chosen to correct this deficiency by modifying the torsional terms for rotation about the C_α–O bond rather than by adjusting the dipole parameters. This approach leads to errors in the relative energies of conformers which have arrangements of both the O—C—C=O and C—O—C—C dihedral angles very far from energy minima. Nonetheless, these parameters are adequate for the present study, and our parameterization produces errors only in regions of the conformational energy surface which are not relevant to our study of the conformational preferences of **1**.

Torsional parameters for rotation about the C–O bond joining the diene to the ester oxygen were developed in a similar manner. Ab initio calculations were performed on vinyl formate at the 6-31G*//3-21G level with full geometry optimization except for the C=C—O—C torsion angle, which was restrained to values of 0, 45, 90, 135, or 180°. In these calculations the starting (and optimized) geometries had an a syn-periplanar arrangement of the ester group (angle O=C—O—C near 0°), in accord with experimental and theoretical studies which indicate a strong preference for this arrangement in esters of both aliphatic and unsaturated alcohols.[10,20,21] The results of our calculations, which are summarized in Table III, indicate that the most stable conformation of vinyl formate has a C=C—O—C torsion angle near 180°, and that a second energy minimum occurs near 0°, 2.8 kcal/mol higher in energy. These calculational results are in accord with a recent experimental study by Geise and co-workers,[20] in which electron diffraction, microwave, and IR data were interpreted in terms of a planar minimum energy conformation having ∠O=C—O—C = 0° and ∠C=C—O—C = 180°. Based on their failure to observe any evidence for the presence of other conformations, these authors estimated a lower limit of 2.3 kcal/mol for the energy difference between this and the next most stable conformation. The energy profile for rotation about the

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(14) All ab initio calculations were performed using the GAUSSIAN 86 program package: Frisch, M.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Martin, R.; Stewart, J. J. P.; Bobrowicz, F.; Defrees, D.; Seeger, R.; Whiteside, R.; Fox, D.; Fluder, E.; Pople, J. A. *GAUSSIAN 86*; Carnegie-Mellon University: Pittsburgh, PA.

(15) Other workers have recently reported force-field parameters for α-alkoxy and α-hydroxy esters which are based on lower level ab initio calculations than those described here and employing incomplete geometry optimization. These parameters differ significantly from those developed in the present work, primarily because the lower level ab initio calculations give unrealistically large energy differences between forms having a syn vs an anti O—C—C=O array: Hanson, B. A.; White, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6314–6318.

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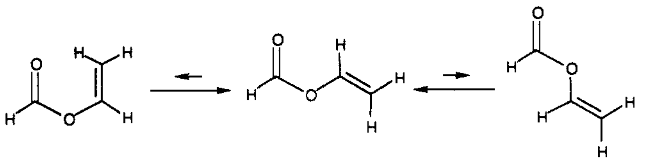
vinylic C–O bond indicated by our ab initio calculations is well-reproduced by our new force-field parameters.

A variety of theoretical and experimental studies support the notion that the energy profile for rotation about the carboxyl C–O bonds of enol esters is very similar to that for rotation about the same bond in saturated esters.[10,20,21] The 4.9-kcal/mol preference for conformation of **4b** over **4c** found at the ab initio 6-31G*//3-21G level of theory is not, however, correctly reproduced by direct application of the MM2 torsional parameters for saturated esters, in part because MM2 assigns a nonzero dipole moment to aliphatic but not to olefinic C–O bonds. Our calculations used the standard MM2 2-fold torsional parameter to describe the preference of enol esters for planar over nonplanar O=C—O—R arrays, and the 1-fold torsional parameter used to describe the energetic preference for a syn-periplanar over an anti-periplanar O=C—O—R array was set to correctly reproduce our ab initio results.

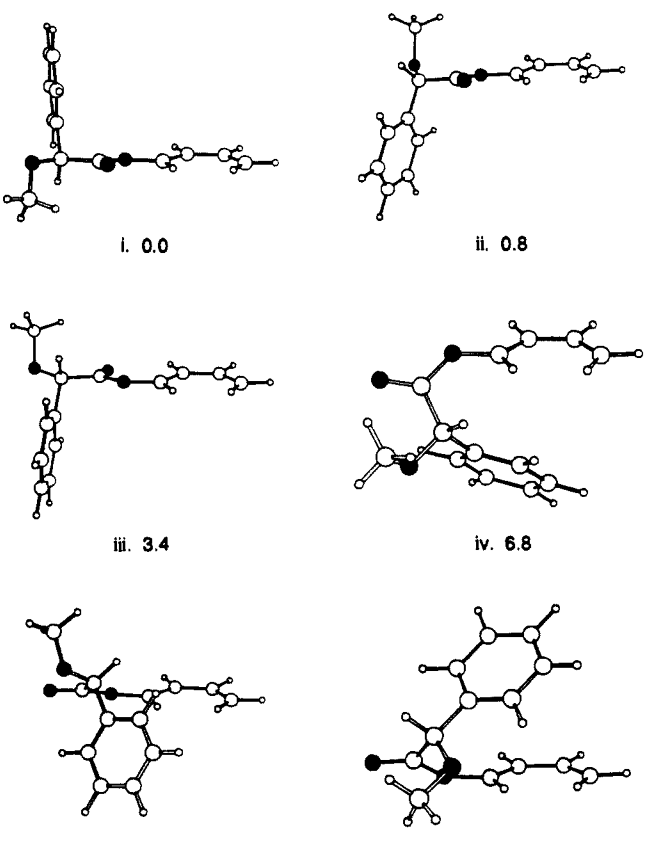


4a (2.8 kcal/mol) **4b** (0.0) **4c** (4.9 kcal/mol)

In addition to these torsional parameters, the calculations described below made use of Allinger's[22] recent reparameterization of C_{Ar}–H and C_{Ar}–C_{sp3} bonds. Independent work by Allinger and Lii and by Pettersson and Liljefors[23] has shown that assigning dipole moments of 0.6 and 0.9 (C_{Ar} negative) to these two bond types results in a dramatically improved description of the heat of sublimation of benzene, the geometry of the gas-phase benzene dimer, and the conformational preferences and strain energy of compounds containing aryl rings. The standard MM2 force field, which assigns a much smaller dipole moment to C_{Ar}–C_{sp3} bonds and zero dipole moment to C_{Ar-H} bonds, fails to correctly reproduce the quadrupolar nature of the benzene nucleus.[24]

The results of our investigation of the conformational properties of **1** are shown in Figure 3, which shows the structures and relative steric energies of six fully optimized conformational minima of this compound, using the modified MM2 force field. Our study included only conformations of **1** having an s-cis arrangement of the dienyl moiety, as this arrangement is required in the Diels–Alder transition state.

The lowest energy conformation of compound **1** has an arrangement of its atoms which is similar to what one would expect based on the conformational preferences of methoxyacetic acid and vinyl formate. In conformation i the two double bonds of the dienyl group, the carbonyl group, and the C_{α}–O bond all lie in an approximately coplanar arrangement. The arrangement of atoms about the vinylic C–O bond is anti-periplanar, and that about the ester C_{sp2}–O bond is syn-periplanar with respect to the carbonyl oxygen. The C_{α}–O bond is very nearly eclipsed with C=O. The methoxyl group is arranged so that its methyl group is anti to phenyl and gauche to the carbonyl. This arrangement simultaneously minimizes unfavorable steric interactions between methyl and phenyl and repulsive electrostatic interactions between the methoxyl lone pairs and the carbonyl oxygen. The two alternative arrangements of the methoxyl group (not shown) have a gauche relationship between methyl and phenyl and are 0.5 and 0.9 kcal/mol higher in energy, respectively. Overall, the lowest energy conformation of **1** is very similar to that suggested in Thornton's[9] perpendicular model, although Thornton emphasizes the perpendicular phenyl rather than the in-plane C_{α}–O bond, which we believe determines the favored conformation.



i. 0.0 ii. 0.8

iii. 3.4 iv. 6.8

v. 7.8 vi. 8.7

Figure 3. Minimum energy conformations of **1** and their relative steric energies (kcal/mol).

Relative to the most stable conformation, the diastereotopic face of the dienyl group which is most closely associated with the phenyl group of the stereogenic center can be inverted by rotating 180° about either the C_{sp2}–C_{α} bond of the ester group (conformation ii), the vinylic C–O bond (conformation iii), or the C_{sp2}–O bond of the ester group (conformation v). Rotation about the C_{sp2}–C_{α} bond of the ester group is predicted to be endothermic by 0.8 kcal/mol, a value which is very similar to the energy difference between the two conformations of methoxyacetic acid in Figure 2. The other two processes are predicted to be much more energetically demanding. Rotating the C=C—O—C array into a syn-periplanar arrangement is predicted to be endothermic by 3.4 kcal/mol. The slightly greater endothermicity calculated for this process relative to the corresponding conformational motion in vinyl formate appears to be related to steric interactions between the carbonyl oxygen and the nearby vinylic proton, and to the greater force constant assigned in MM2 for deformation of a C_{sp2}–C_{sp2}–H as opposed to a H–C_{sp2}–H bond angle. Rotating the O=C—O—C array into an anti-periplanar arrangement is endothermic by 7.8 kcal/mol.

In addition to the conformations already discussed, we have also attempted to assess the relative stability of conformations having a π-stacking arrangement of the aryl and dienyl moieties of **1**. According to the model originally proposed by Trost,[1] the hydrogen and the methoxyl group attached to C_{α} each orient themselves in a gauche arrangement relative to the C=O bond. π-Stacking then occurs preferentially on the face of the diene shown in Figure 1a, because a similar face-to-face arrangement of the phenyl and the other face of the dienyl group would lead to unfavorable steric interactions between the methoxyl and the olefinic carbon β to oxygen. In our calculations, we found that arrangements of **1** having the phenyl and dienyl groups in parallel or nearly parallel planes must also have O=C—O—C and/or

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(22) Allinger, N. L.; Lii, J. H. *J. Comput. Chem.* **1987**, *8*, 1146–1153.

(23) Pettersson, I.; Liljefors, T. *J. Comput. Chem.* **1987**, *8*, 1139–1145.

(24) Ab initio calculations at the HF/3-21G level indicate that bringing a hydrogen fluoride molecule and a benzene molecule together with their principle symmetry axes colinear and fluorine "inward" is repulsive at all separations (best plane of benzene to F) between 3.0 and 5.0 Å (Brédas, J. L.; Street, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 7001–7005). This behavior is reproduced by MM2 in a qualitatively correct manner using the benzene parameters in ref 22 and the ab initio 3-21G hydrogen fluoride dipole of 2.17 D, although the repulsion is too low (0.8 vs 2.4 kcal/mol at 3.0 Å). In contrast, the original MM2 parameters for phenyl rings predict an attractive interaction (–0.7 kcal/mol at 3.0 Å).

C═C—O—R arrays which deviate significantly (>60°) from planarity and do not represent conformational energy minima. Optimization of structures similar to that shown in Figure 1a leads to either conformation v or vi. Conformation vi has the dienyl and phenyl groups in a partially cofacial arrangement, but the angle formed by the best planes of the two functional groups is about 60°.

Conformation iv has a relative arrangement of the phenyl and dienyl groups which is very similar to that in conformation vi, only the opposite face of the diene is shielded. Conformer iv is calculated to be 1.9 kcal/mol more stable than conformation vi, largely because it has an energetically favorable eclipsed arrangement of O═C—C—O array.[25] These calculations suggest that if the selectivity of this reaction resulted from attack on the most stable conformation of **1** having a face-to-face arrangement of the phenyl and dienyl groups, the major product would be the opposite of that observed experimentally.

An important question that is raised by examination of the data in Table I and in Figure 3 is how the high stereoselectivity which is observed in reactions of **1** can arise in spite of its preference for a highly extended conformation, and in spite of the availability of a second low-energy conformation (conformation ii) in which the relationship between the dienyl group and the chiral barrier is approximately reversed. In order to develop an understanding of how the conformational behavior described in Figure 3 might be translated into energy differences between competing diastereomeric transition states, we developed a force-field model for the uncatalyzed reaction between **1** and benzoquinone. In this model, the relative orientations of the six carbon atoms undergoing bonding changes and their attached hydrogens were constrained to be the same as found in the ab initio 3-21G transition state for the reaction of butadiene with *s-trans*-acrolein.[26] The positions of other atoms were minimized using the MM2 force field and the parameters developed in the present work. Parameters describing the positions of "normal" atoms relative to those undergoing bonding changes were estimated in the following manner. The 2-fold barrier for rotation about partial double bonds was set to 20 kcal/mol. The 2-fold torsional barrier for rotation about C_{sp^2}–C_{sp^2} single bonds (i.e., C═C—C═O) was set to 10 kcal/mol.[27] Torsional parameters involving partial single bonds were set to zero. All other undefined torsional parameters and bond lengths were defined by treating the carbons undergoing bonding changes as normal sp^2 carbons. Parameters for bond angles A–B–C were defined in the same manner if B is a normal atom and either A or C is a carbon undergoing bonding changes. If B is an atom undergoing bonding changes, the force constants for angle deformation were set to 0.25 mdyn/deg, and the natural bond angles A_0 were chosen to be those which correctly reproduce the bond angles about B when this same force field is used to calculate the transition structure for butadiene reacting with *s-trans*-acrolein. Overall, the approximations in this model are based on an assumption of an early transition state, which is reasonable considering the relatively early ab initio transition state for the reaction of acrolein with butadiene. Furthermore, this choice of torsional parameters favors a conjugated arrangement of the reacting double bonds with their attached electron-donating and electron-withdrawing substituents, as would be expected in the Diels–Alder transition state.

Figure 4 summarizes the results of our transition state modeling for the uncatalyzed reaction of **1** with benzoquinone. As might reasonably be expected, the lowest energy transition structure found for this reaction corresponds to attack of the benzoquinone on the less hindered face of the most stable conformation of **1**. This transition structure (vii) corresponds to the formation of the experimentally observed major product. In principle, the minor product might arise via one of two paths: attack of benzoquinone on the more hindered face of the most stable conformation of **1**, or attack on the less hindered face of one of the higher energy conformations ii–v. Our calculations suggest that formation of the minor product occurs via two competing mechanisms. Attack on the more hindered face of conformation i and attack on the less hindered face of conformation ii leads to transition states viii and xi, respectively, which are predicted to have similar energies. Transition structures x–xii are higher in energy and are expected to make only a very small contribution to the overall selectivity of the reaction. Overall, our crude force-field model predicts a selectivity of 1.7 kcal/mol for attack on the *si* face of **1**, compared to an experimental value of 0.8 kcal/mol. Taken in sum, these calculations do not prove the validity of the perpendicular model, but they do demonstrate that the stereoselectivity of this reaction can be rationalized in terms of the ground-state conformational preferences of **1** and a reasonable model for the transition-state geometry, without postulating unusual or unprecedented potentials for nonbonded interactions.

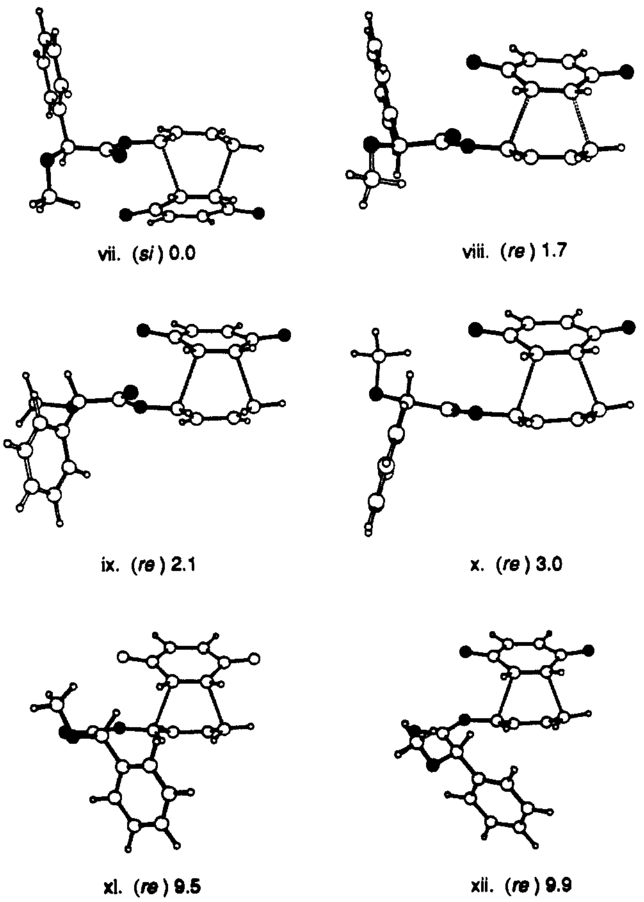
vii. (*si*) 0.0
viii. (*re*) 1.7
ix. (*re*) 2.1
x. (*re*) 3.0
xi. (*re*) 9.5
xii. (*re*) 9.9

Figure 4. Transition structures for the Diels–Alder reaction of **1** with benzoquinone and their relative steric energies (kcal/mol).

Examination of the partitioned energy terms from our calculations provides some interesting suggestions concerning the origins of stereoselectivity in this system. Transition structure viii is disfavored relative to vii in spite of the highly extended conformation of the diene. In our calculations the sterically unobtrusive phenyl group interacts with the incoming dienophile in part through unfavorable electrostatic interactions with the carbonyl oxygen of the quinone. When we repeated our calculations with the C_{Ar}–H and C_{Ar}–C_{sp^3} dipoles set to zero, transition structure viii was calculated to be only 0.4 kcal/mol less stable than vii. Transition structure ix is calculated to be 2.1 kcal/mol higher in energy than vii, in spite of the fact that these two transition structures correspond to attack on the less hindered face of conformations of **1** which are only 0.8 kcal/mol apart in energy. This difference arises in part from an interesting dichotomy in the role of the methoxyl group in these competing transition states. Attack of benzoquinone on the less hindered face of conformation i leads to transition structure vii, in which the interaction between the methoxyl group and the carbonyl oxygen of the dienophile is

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(25) Conformations iv and vi both correspond to points on the conformational energy surface that are well-described by our parameters for α-alkoxy esters.

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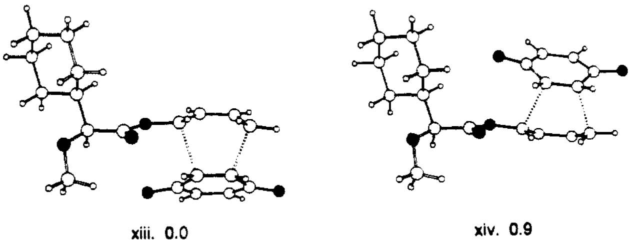
xiii. 0.0 xiv. 0.9

Figure 5. Transition structures for the Diels–Alder reaction of **2** with benzoquinone and their relative steric energies (kcal/mol).

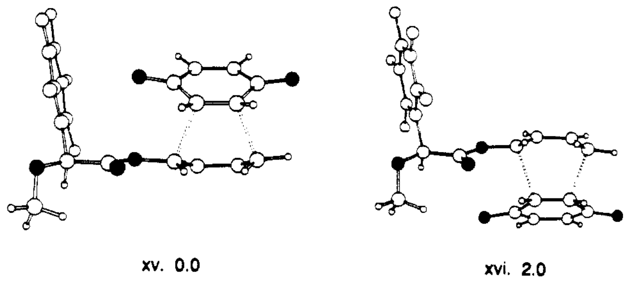
xv. 0.0 xvi. 2.0

Figure 6. Transition structures for the Diels–Alder reaction of **5** with benzoquinone and their relative steric energies (kcal/mol).

overall slightly attractive, due to a stabilizing arrangement of the C=O and C_{sp3}–O bond dipoles. With respect to the plane of the page, this structure has the methoxyl group "forward" and the dienophile carbonyl oxygen "back". Attack of the dienophile on the less hindered face of conformation ii leads to a structure in which methoxyl group and the carbonyl oxygen are much closer, both being behind the plane of the page of Figure 4. The resulting unfavorable steric interactions force the methyl group to rotate away from the incoming dienophile and into an unfavorable arrangement gauche to the phenyl group (ix).

We have applied this same model to make some interesting predictions concerning stereoselectivity in reactions of dienes closely related to **1** which have not yet been studied experimentally. Replacing the phenyl steric barrier of **1** with a cyclohexyl ring gives diene **2**. The lowest energy transition structures corresponding to the uncatalyzed reaction of benzoquinone on the *re* and *si* faces of **2** are shown in Figure 5. The calculations predict a 0.9-kcal/mol selectivity for attack on the same face of the diene which is preferentially attacked in the corresponding reaction of **1**. In transition structure xiv, the unfavorable electrostatic interactions between the phenyl group and benzoquinone oxygen of viii are absent, but the cyclohexyl group is somewhat more sterically demanding than phenyl. Because of the crudeness of our transition-state model, we conclude only that the selectivity should be in the same direction as observed for **1** and that it should be of significant magnitude. Experimentally, the boron trifluoride catalyzed reaction of **2** with benzoquinone gives the same major product as the corresponding reaction of **1**, but in somewhat lower selectivity. A more interesting prediction arises from a calculation which was prompted by our observations concerning electrostatic repulsions between the electron-rich phenyl ring and a quinone oxygen in transition structure viii. In diene **5** the five electron-donating aryl C–H bonds are replaced by electron-withdrawing C–F bonds. In our calculations the resulting partial positive charge on the aryl carbons of **5** leads to an overall *attractive* interaction between the quinone oxygen and the perfluorophenyl group in transition structure xv (Figure 6). Although these calculations have mainly qualitative significance, they suggest the tantalizing possibility that the uncatalyzed reaction of **5** with benzoquinone will result in a reversal of stereoselectivity as compared to the corresponding reaction of **1**.[28] This prediction depends in part on the assumption that perfluorination of the phenyl group of **1** will not result in a dramatic change in the energy profile for rotation of the ester C_{sp2}–C_α bond. Such a change might conceivably arise because of the increased electronegativity of a perfluorophenyl group as compared to a phenyl group, but it is difficult to assess this possibility in a quantitative manner by ab initio methods owing to the large number of heavy atoms present in even the simplest model compounds.[29]

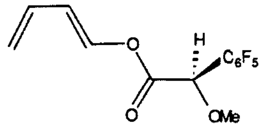

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Table IV

	torsional parameters (kcal/mol)		
	V_1	V_2	V_3
2-2-6-3	1.05	1.90	−0.45
5-2-6-3	−1.05	1.90	0.45
7-3-6-2	−3.40	8.98	0.00
1-3-6-2	0.00	1.39	0.00
5-3-6-2	0.00	1.39	0.00
6-1-3-6	0.40	2.00	0.00
6-1-3-7	−0.40	2.00	0.20
3-1-6-1	−3.10	0.00	0.00

	bending parameters	
	A_0	k_b
2-6-3	121.0	0.60

[a] Angles in degrees, bending constants in mdyn Å/rad^2.

Taken in sum, our calculations provide support for a relatively extended conformation of chiral diene **1** and related compounds, similar to that embodied in Thornton's perpendicular model. Moreover, calculations utilizing a simple force-field model for the reaction of **1** with benzoquinone support the idea that the stereoselectivity which is observed in this reaction (at least) can be explained in terms of the ground-state conformational preferences of **1**, without invoking special π–π interactions between the dienyl and phenyl groups of **1** in the transition state. A rigorously face-to-face (parallel planes) arrangement of the phenyl and dienyl groups of **1** requires the induction of considerable torsional strain in the remainder of the molecule, while in more relaxed structures, which represent conformational minima, the phenyl ring prefers to lie against the wrong face of the diene relative to that which would explain the observed selectivity. We conclude that the critical interactions responsible for stereoselectivity in this system are not nonbonded interactions between the phenyl and dienyl groups of **1**, but the same forces responsible for the conformational preferences of methoxyacetic acid and vinyl formate. Of these, the former are of particular interest, owing to the widespread use of compounds having similar structures[30] (e.g., tartrates), as chiral auxiliary in a variety of reaction types.

Appendix

The force-field (MM2) parameters given in Table IV were employed to reproduce the conformational behavior of α-alkoxy esters and vinyl esters, as revealed in the ab initio calculations described in the text. Atom types are the same as those in the

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(28) Replacing a phenyl steric barrier with a perfluorophenyl group dramatically affects the stereoselectivities of reactions of iron enolates. See ref 5f.

(29) (a) Similar considerations might lead one to question whether the perfluorophenyl group of **5** might have a strong preference for an eclipsed arrangement with its benzylic C–O bond. Model calculations were performed in which the standard MM2 parameters for the torsions C_{Ar}–C_{Ar}–C_{sp3}–O and H–C_{Ar}–C_{sp3}–O were replaced by a 2-fold torsional preference of 3.0 kcal/mol for such an eclipsed array. This change in torsional parameters actually leads to a slight increase in the predicted selectivity of this reaction.

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MM2 force field, i.e., type 1 = aliphatic C, type 2 = olefinic C, type 3 = carbonyl C, type 5 = H, type 6 = divalent O, and type 7 = carbonyl O.

Acknowledgment. We are grateful to the National Institutes of Health for financial support of this research.

Supplementary Material Available: Details of transition-state modeling calculations including Cartesian coordinates for the RHF/3-21G transition state of the Diels–Alder cycloaddition of *s-trans*-acrolein and butadiene and force-field parameters (4 pages). Ordering information is given on any current masthead page.

Arene Exchange by P Donors in the 19-Electron Complexes Fe^{I}Cp(arene): Kinetics, Mechanism, and Salt Effects. Interconversion, Radical-Type Reactions, and Electron-Transfer Chemistry of the New 17-Electron and 19-Electron Radicals Fe^{I}CpL$_n$ (L = Phosphine, Phosphite; n = 2, 3)

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Abstract: The 19e complexes Fe^{I}Cp(C$_6$H$_{6-n}$Me$_n$), **1** ($0 \leqslant n \leqslant 6$), react with P donors (PMe$_3$, PPh$_3$, PPh$_2$H, PPh$_2$D, dppm, dppe, P(OMe)$_3$, P(OPh)$_3$) to give products resulting from arene exchange and radical reactions of the 17e radicals FeCpL$_2$, **2** (H or Cl abstraction, Arbuzov-type reaction, P–O cleavage, and coupling with Hg). These reactions are potentially side reactions in the electrocatalytic exchange starting from the 18e complexes **1**$^+$, but reduction of **1**$^+$ by the 19e species Fe^{I}CpL$_3$, **3**, proceeds faster except for L = P(OPh)$_3$. Complex **1** was used as an electrocatalyst (1%) for the quantitative synthesis of [FeCp(PMe$_3$)$_3$]$^+$, **3a**$^+$, [FeCp{P(OMe)$_3$}$_3$]$^+$, **3b**$^+$, [FeCp(dppe)(NCMe)]$^+$, **13**$^+$, and [FeCp(dppm)(NCMe)]$^+$, **10**, in a THF suspension at 20 °C. The 19e complex **3a** (L = PMe$_3$) is also formed in stoichiometric reactions of **1** with PMe$_3$ in the presence of reducible substrates (CO$_2$, perylene, *p*-dicyanobenzene, and methyl *p*-cyanobenzoate) as well as in disproportionation reactions of **1** induced by sodium salts. Double ion exchange in the latter reactions gives reactive ion pairs containing the organoiron anion and the Na$^+$ counter cation. This disproportionation can also be catalyzed by NaPF$_6$. The kinetics of the ligand exchange of **1** with P donor is shown to follow a second-order process according to the following rate law: $-\mathrm{d}[\mathrm{FeCp(toluene)}]/\mathrm{d}t = k[\mathrm{FeCp(toluene)}][\mathrm{P\ donor}]$. The reaction rate depends on the nature of the P donor and on the arene. The associative mechanism is confirmed by the large, negative entropy of activation ($\Delta S^{\ddagger} = -22 \pm 3$ cal mol^{-1} K^{-1} for P(OMe)$_3$). A fast preequilibrium, FeCp(η^6-arene) $\rightleftharpoons$ FeCp(η^4-arene), is proposed, which avoids a high-energy 21e intermediate or transition state. In the course of the reaction of **1** with L = PPh$_3$, the 17e species Fe^{I}CpL$_2$ was characterized by its ESR spectrum at 10 K showing three *g* values around 2 and a characteristic triplet indicating the coupling with two P ligands. Another entry into the 19e species **3a** is the one-electron reduction of the cathodic precursor. For example, Na/Hg reduction of [FeCp(PMe$_3$)$_3$]$^+$PF$_6^-$, **3a**$^+$, gives Hg[FeCp(PMe$_3$)$_2$]$_2$, **9**, while its reduction on sodium mirror gives [FeCp(PMe$_3$)$_2$H], **4a**, as the reactions of **1** with PMe$_3$. This confirms the fast equilibrium Fe^{I}CpL$_2$ + L $\rightleftharpoons$ Fe^{I}CpL$_3$ (L = PMe$_3$).

Organometallic and inorganic radicals might play an important role in material science[1] as well as in catalytic processes.[2] Their intermediacy in organometallic reactions is now being increasingly recognized.[2,3] The main focus thus far has been on the structure of main group radicals[4] and metal sandwich radicals[5] and on the reactivity of transition-metal carbonyl radicals.[6] However, stable 19e radicals are relatively rare, and their reactivity[7] is not very

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