thermodynamic preferences is attributed to the smaller oxo affinity of H_2S compared with H_3P, which in turn may be partly attributed to a four-electron destabilization involving the sulfur and oxygen lone pairs.

As expected, the kinetic preference for the Corey–Chaykovsky reaction is controlled by the leaving-group ability of the group next to the ylide, which is greater for the sulfide. Less obviously, *the step that kinetically differentiates the phosphorus from the sulfur in the Wittig reaction is the ring-opening of the cyclic intermediates to yield the products.* The capacity to undergo this crucial step is conditioned by the ease with which the oxygen can reach the equatorial site and the carbon the apical site and not by the fact that the S–C bond is intrinsically difficult to cleave. This interchange of groups is easy in the case of phosphorus and very difficult in the case of sulfur.

We have now at hand a convenient way to estimate the ability of a given ylide to undergo the Wittig reaction. The smaller the energy difference between the two isomers of the four-membered-ring intermediate, the easier the Wittig reaction is. As mentioned previously, the oxosulfonium ylide may fulfill this requirement since it has been shown in one case to undergo a Wittig reaction.[67a] The case of arsonium ylide, the reactivity of which is very sensitive to the nature of substituents, could be approached in that manner.

Let us conclude this study by pointing out that our calculations and results cannot be applied, at least in a straightforward manner, when lithium salt is added to the reaction mixture, since they simulate salt-free conditions. In particular, *cis*- or *trans*-betaine, which has been found to be a nonstable intermediate in our calculations, may become strongly stabilized when lithium cation is present in the reactive media.

Acknowledgment. This work has greatly beneficiated from helpful discussions with Profs. K. Morokuma and E. Vedejs and Drs. Y. Jean, J. M. Lefour, and J. Seyden-Penne. This work beneficiated from a generous donation from the computer centers of the University of Michigan (USA) and of the Institute of Molecular Science at Okasaki (Japan). In France, the calculations were done at the CIRCE (CNRS) and CRAY1 (CCVR, ATP n° 3655 and 3070). We thank these four computer centers for computational facilities and generous donation in computing time. O. E. thanks Prof. K. Morokuma for having invited her to Japan. Her stay in Japan was financially supported by the Rackham Research and Fellowship Grant from the University of Michigan. O. E. thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial financial support of this work.

Note Added in Proof. Akiba et al. (Akiba, K.-Y.; Takee, K.; Shimizu, Y.; Ohkata, K. *J. Am. Chem. Soc.* **1986**, *108*, 6320) have recently structurally characterized a strongly distorted sulfurane with an apical methyl group. However, this structure can still be viewed as a distorted episulfonium cation in weak interaction with an incoming nucleophile. Note that replacing the alkyl group by other more electronegative atoms or groups makes the sulfurane closer to a TBP structure.

Registry No. $H_3P{=}CH_2$, 36429-11-5; $H_2S{=}CH_2$, 59301-38-1; H_2CO, 50-00-0; H_2S, 7783-06-4; C_2H_4, 74-85-1; $\overline{PH_3OCH_2CH_2}$, 40110-50-7; $\overline{SH_2OCH_2CH_2}$, 104994-70-9; H_3P, 7803-51-2; ethylene oxide, 75-21-8.

Theoretical Studies of Conformations of Acrolein, Acrylic Acid, Methyl Acrylate, and Their Lewis Acid Complexes

Richard J. Loncharich, Timothy R. Schwartz, and K. N. Houk*

Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, and Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024. *Received June 17, 1986*

Abstract: Ab initio calculations have been performed on the conformations of acrolein, acrylic acid, methyl acrylate, and complexes of these species with Lewis acids, H^+, Li^+, and BH_3. Acrylic acid and methyl acrylate have small preferences for s-cis conformations, but the Lewis acid complexed acrylates prefer the s-trans conformations. Both acrolein and Lewis acid complexed acrolein prefer the s-trans conformation. These calculations confirm conformational hypotheses made to rationalize the stereoselectivities of catalyzed Diels–Alder reactions of chiral acrylates.

The regioselectivities, stereoselectivities, and rates of Diels–Alder reactions are profoundly influenced by Lewis acid catalysts.[1-5] For example, the degree of asymmetric induction observed in Diels–Alder cycloadditions to chiral acrylates is large only when the reactions are catalyzed by Lewis acids, while the corresponding thermal reactions occur with very modest stereoselectivities, at best. We have undertaken a theoretical investigation of the influence of Lewis acids upon the conformations of acrylic esters, which are perhaps the most common dienophiles in Diels–Alder cycloadditions with electron-rich dienes. The simpler molecules, acrolein and acrylic acid, were studied for comparison. We first describe the experimental results which show that stereoselectivities of asymmetric Diels–Alder reactions vary upon catalysis, suggesting that acrylate conformations are influenced by Lewis acid complexation. We then describe the theoretical results which provide a partial explanation for these phenomena.

Asymmetric Diels–Alder Reactions. Table I shows a few examples of asymmetric Diels–Alder reactions. The catalyzed reactions of three acrylic esters all exhibit a high degree of asymmetric induction. For each of the dienophiles listed, the conformation shown predicts the experimentally observed product, by endo addition to the sterically less hindered side of the dienophile.

Cycloadditions of cyclopentadiene with (−)-menthyl acrylate[6a-d] and of butadiene[7] and cyclopentadiene with di-(−)-menthyl fu-

(1) (a) Paquette, L. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, pp 456–478. (b) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.*, **1984**, *23*, 876. (c) Morrison, J. D.; Mosher, H. S. *Asymmetric Organic Reactions*; Prentice-Hall: New York, 1971 (reprinted by the American Chemical Society, 1976, pp 252–257).

(2) Arai, Y.; Kuwayama, S.-I.; Takeuchi, Y.; Koizumi, T. *Tetrahedron Lett.* **1985**, *26*, 6205.

(3) Oppolzer, W.; Chapuis, C.; Dupuis, D.; Guo, M. *Helv. Chim. Acta* **1985**, *68*, 2100.

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(5) Mulzer, J.; Kappert, M. *Tetrahedron Lett.* **1985**, *26*, 1631.

(6) (a) Sauer, J.; Kiedel, J. *Tetrahedron Lett.* **1966**, *51*, 6359. (b) Sauer, J.; Kiedel, J. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 989. (c) Farmer, R. F.; Hamer, J. *J. Org. Chem.* **1966**, *31*, 2418. (d) Sauer, J.; Kiedel, J. *Tetrahedron Lett.* **1966**, *7*, 731.

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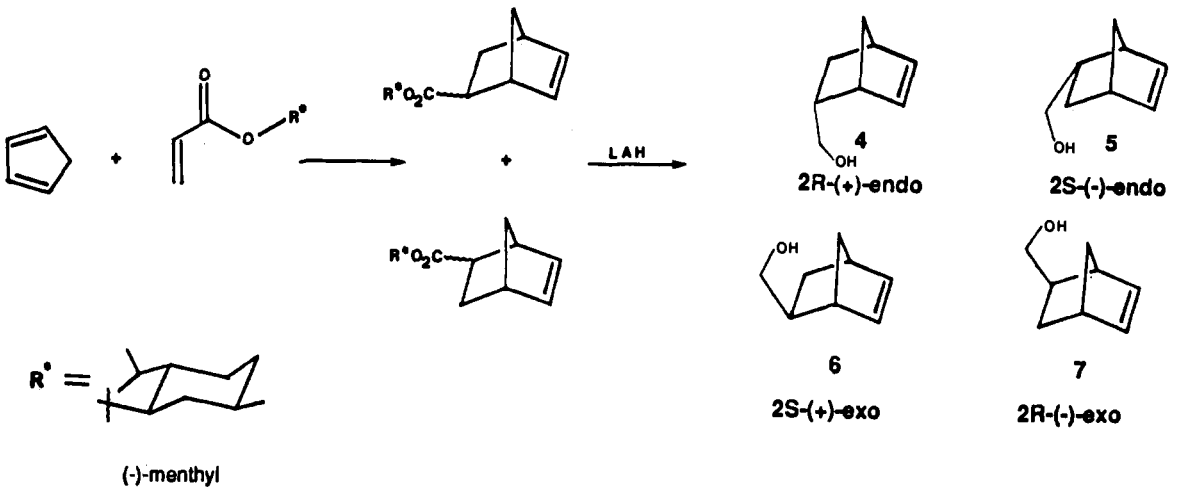


Figure 1. Definitions of asymmetric reactions of cyclopentadiene with (−)-menthyl acrylate.

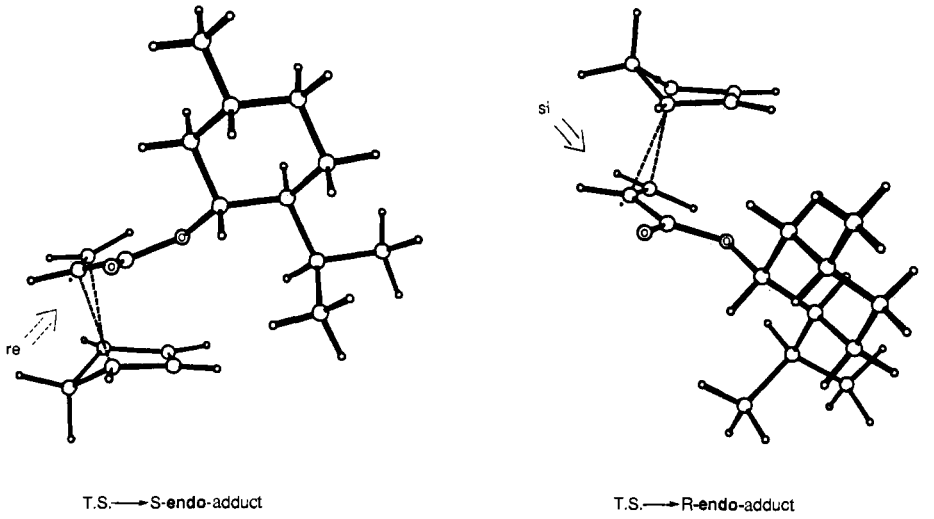


Figure 2. Model transition states for reactions of cyclopentadiene with *s-trans*-(−)-menthyl acrylate.

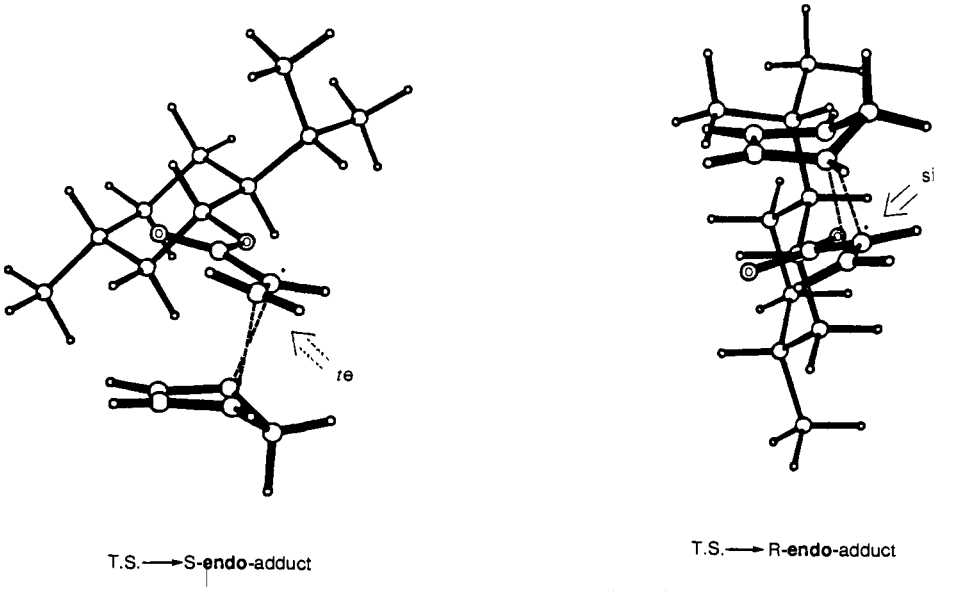


Figure 3. Model transition states for reactions of cyclopentadiene with *s-cis*-(−)-menthyl acrylate.

marate[6] are the classic examples of asymmetric induction in cycloadditions. The results of the former are summarized in Table II. In the uncatalyzed reactions of cyclopentadiene with (−)-menthyl acrylate, a modest enantiomeric excess (ee) of the 2*R*-(+)-endo (**4**) and 2*S*-(+)-exo (**6**) isomers is produced, as shown in Figure 1. In the catalyzed reactions, a much higher ee of the 2*R*-(+)-endo (**4**) and 2*R*-(−)-exo (**7**) isomers is produced. The chirality of the preferred exo product changes in the catalyzed reaction. The catalyzed reactions give a greater proportion of the

(7) (a) Korolev, A.; Mur, V. *Dokl. Akad. Nauk USSR* **1948**, *59*, 251. (b) Korolev, A.; Mur, V. *Chem. Abstr.* **1948**, *42*, 6776. (c) Walborsky, H. M.; Barash, L.; Davis, T. C. *Tetrahedron* **1963**, *19*, 2333. (d) Walborsky, H. M.; Barash, L.; Davis, T. C. *J. Org. Chem.* **1961**, *26*, 4778.

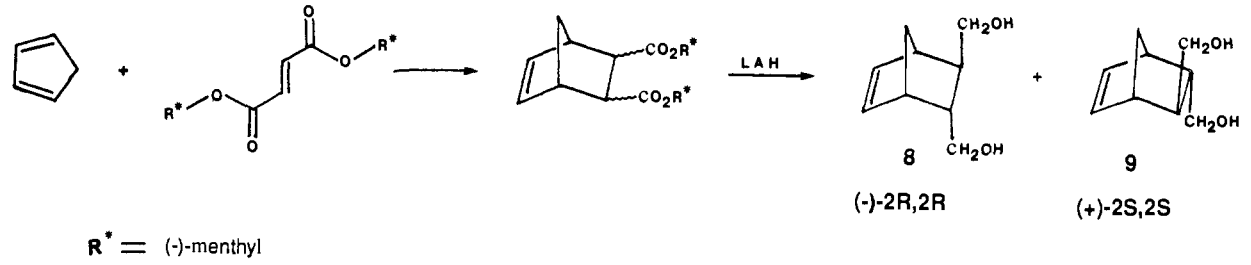
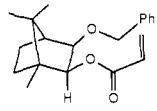
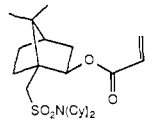
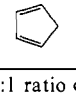
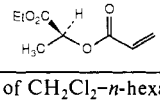


Figure 4. Definitions of asymmetric reactions of cyclopentadiene with di-(−)-menthyl acrylate.

Table I. Stereoselectivities of Asymmetric Diels–Alder Reactions

entry	diene	dienophile	catalyst	solvent	temp. [°C]	endo %d.e.	ref.
1			$TiCl_4$	CH_2Cl_2	0	88	11d
2			$TiCl_4[OiPr]_2$	benzene CH_2Cl_2	25 -20	36 93	14 11g
3			$TiCl_4$	a	-63	86	45

[a] 1:1 ratio of CH_2Cl_2–*n*-hexane.

endo adducts with much higher ee than the uncatalyzed reactions.

Inspection of models shows that the s-cis and s-trans conformers of (−)-menthyl acrylate are more crowded on opposite faces. Model transition states which we have constructed using a modified MM2 model are shown in Figures 2 and 3. These models are based on geometries computed for the transition state of the cyclopentadiene–ethylene Diels–Alder reaction. The calculations were MNDO on a constrained-synchronous (C_s) transition structure.[8] This geometry was used to build an MM2[9] model for the reaction of cyclopentadiene with menthyl acrylate. The model will be described in more detail in due course,[10] but for the moment we use the results of the model calculations to demonstrate the difference in steric hindrance of the faces of menthyl acrylate in the s-cis and s-trans conformations.

When the carbonyl of (−)-menthyl acrylate is in an s-trans conformation with respect to the olefinic double bond, approach of the diene in an endo fashion can occur from the *si* face or the *re* face to give the *R* or *S* adducts, respectively, as illustrated in Figure 2. Similarly, the s-cis conformation of the carbonyl should give the *S*- and *R*-endo adducts, respectively, with approach of the diene from the *re* face and *si* face as represented in Figure 3. The stereoselectivity of this reaction is governed by the chirality of the menthyl group. The preferred approach of the diene is from the sterically less crowded side, near the methylene group, rather than on the more crowded side, near the large isopropyl group. From perusal of Figure 2, it is obvious why for the s-trans acrylate conformation there is a preference for the *R* chirality to be induced in the product. The *R*-endo adduct is indeed the experimentally observed product (Table II). When the conformation of the acrylate is s-cis, the reaction should give a preference for the other adduct. Examination of Figure 3 shows that for this case, the preferred approach of the diene leads to the minor experimental product, namely the *S*-endo adduct.

Similar results were observed experimentally for the reaction of cyclopentadiene with di-(−)-menthyl fumarate; the uncatalyzed reaction in methylene chloride at 20 °C, followed by $LiAlH_4$ reduction, resulted in 3.6% ee of the (−) enantiomer **8**, while at −70 °C with $AlCl_3$–$O(C_2H_5)_2$, a 43% ee of the (+) enantiomer **9** was found (Figure 4). The cycloaddition of 1,3-butadiene with di-(−)-menthyl fumarate has also been studied by Korolev and Mur[7a,b] and by Walborsky and co-workers.[7c,d] In the early investigation by Korolev and Mur, the (+) diacid was observed in the condensation followed by hydrolysis, but Walborsky found that the (−) diacid actually predominates.

Recently, investigations of Lewis acid-promoted asymmetric Diels–Alder reactions have been reported by Oppolzer and coworkers,[11] and Helmchen and co-workers.[12] A multitude of menthyl, isoborneol, and camphor-type acrylates, which are either *si* face or *re* face directing in their addition to dienes, have been synthesized. A few examples of this type are presented in Table I. Oppolzer has postulated a model to elucidate the stereoselectivity of the *si* face and *re* face directing acrylates. In this model (see **1** shown in Table I), the ester is s-trans, the ester carbonyl is syn-periplanar to the O—C* bond, and the CH group at the chiral center is syn-periplanar to the O—C(=O) bond. This rigid arrangement causes the substituent on the carbon β to the ester oxygen to obstruct sterically the attack of on particular face (either *si* or *re*) of the acrylate. In contrast to this model, the stereochemical result of some other types of asymmetric Diels–Alder reactions have been rationalized in terms of a s-cis dienophile conformation,[13] since the molecules in question have large groups attached to the carbonyl group, enforcing s-cis conformations.

The stereofacial directing dienophile, 10-(dicyclohexylsulfonamido)isobornyl acrylate (**2**), has also been employed in studies of the asymmetric Diels–Alder reaction.[11,14] The thermal reaction of **2** with cyclopentadiene has been found by Curran and Kim to give the *S*-endo adduct in a 36% de at 25 °C.[14] This product is that which is that which is expected to be obtained from the reaction proceeding via the s-cis arrangement of the acrylate. When the reaction is catalyzed with $TiCl_2(O\text{-}i\text{-}Pr)_2$, a 93% de of the *R*-endo adduct is observed at −20 °C.[11] Here the reaction has been rationalized to take place through the s-trans arrangement of the acrylate **2**. Again, it is interesting that the thermal and catalyzed processes of this reaction give products of opposite configuration.

(8) Brown, F. K.; Houk, K. N., unpublished results.

(9) (a) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, D.C., 1982. (b) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *79*, 8127. (c) Quantum Chemistry Program Exchange (QCPE), No. 395.

(10) Loncharich, R. J., unpublished results.

(11) (a) Oppolzer, W.; Chapuis, C.; Kelly, M. J. *Helv. Chim. Acta* **1983**, *66*, 2358. (b) Oppolzer, W.; Kurth, M.; Reichlin, D.; Chapuis, C.; Mohnhaupt, M.; Moffatt, F. *Ibid.* **1981**, *64*, 2802. (c) Oppolzer, W.; Chapuis, C. *Tetrahedron Lett.* **1983**, *24*, 4665. (d) Oppolzer, W.; Chapuis, C.; Dao, G. M.; Reichlin, D.; Godel, T. *Ibid.* **1982**, *23*, 4781. (e) Oppolzer, W.; Kurth, M.; Reichlin, D.; Moffatt, F. *Ibid.* **1981**, *22*, 2545. (f) Oppolzer, W.; Chapuis, C.; Bernardinelli, G. *Helv. Chim. Acta* **1984**, *67*, 1397. (g) Oppolzer, W.; Chapuis, C.; Bernardinelli, G. *Tetrahedron Lett.* **1984**, *25*, 5889. (i) Oppolzer, W.; Chapuis, C. *Ibid.* **1984**, *25*, 5383.

(12) (a) Helmchen, G.; Schmierer, R. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 205. (b) Poll, T.; Helmchen, G.; Bauer, B. *Tetrahedron Lett.* **1984**, *22*, 2191.

(13) (a) Choy, W.; Reed, L. A., III; Masamume, S. *J. Org. Chem.* **1983**, *48*, 1137. (b) Masamune, S.; Reed, L. A., III; Davis, J. T.; Choy, W. *Ibid.* **1983**, *48*, 4441. (c) Evans, D. A.; Chapman, K. T.; Bisaha, J. *Tetrahedron Lett.* **1984**, *25*, 4071. (d) Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1984**, *106*, 4261.

(14) Curran, D. P.; Kim, B. H.; Piyasena, H. P.; Loncharich, R. J.; Houk, K. N., submitted for publication.

Table II. Stereoselectivities of Cycloaddition of Cyclopentadiene to *R*-(−)-Menthyl Acrylate

solvent	temp, °C	catalyst	yield, %	endo, %	exo, %	predominant product: endo conf (% ee)	predominant product: exo conf (% ee)	ref
CH_2Cl_2	0		63	84	16	*R* (9.1)		6a,d
CH_2Cl_2	35		100	78	22	*R* (7.4)	*S* (3.1)	6a,d
	25		77	*a*	*a*	*R* (8)		6c
CH_2Cl_2	0	$AlCl_3$-$O(Et)_2$	84	93	7	*R* (49)	*R* (36)	6a,d
CH_2Cl_2	−70	$AlCl_3$-$O(Et)_2$	67–81	97	3	*R* (66–67)		6a,d
CH_2Cl_2	0	BF_3-$O(Et)_2$	74–81	*a*	*a*	*R* (74)	*R* (43)	6a
CH_2Cl_2	−70	BF_3-$O(Et)_2$	45–80	*a*	*a*	*R* (82–85)		6a

[a] Values were not reported.

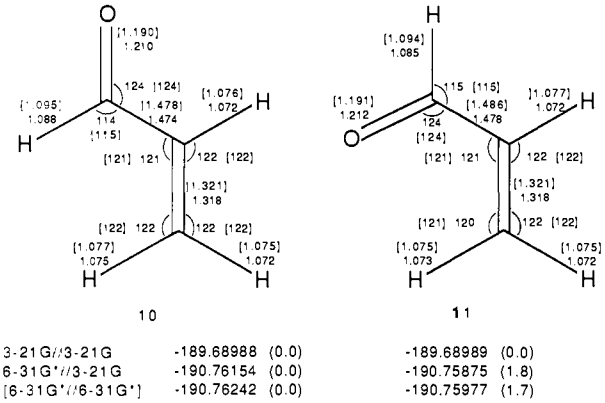


Figure 5. 6-31G* and 3-21G geometries of the s-cis and s-trans conformers of 2-propenal. C_s symmetry was maintained. Total energies (au) at the different levels, along with relative energies (in parentheses, kcal/mol), are given below the figures. Bond distances are in ångströms, and angles are in degrees.

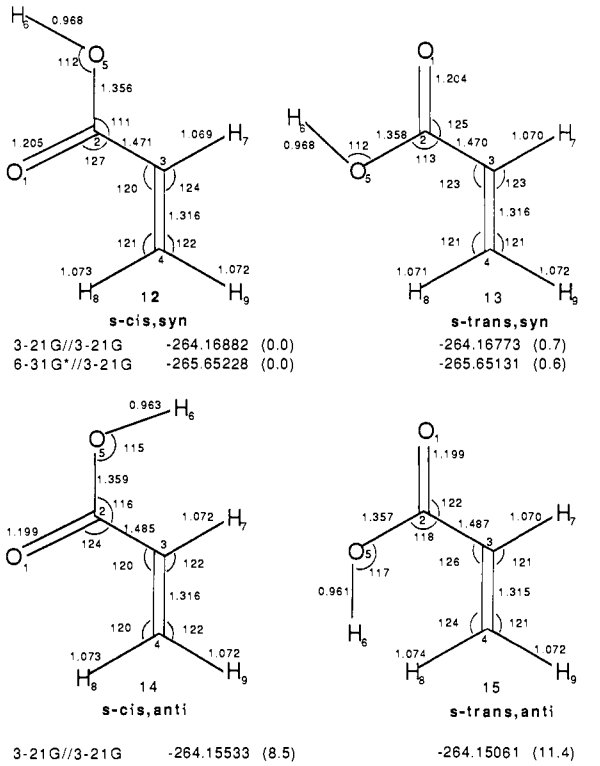


Figure 6. 3-21G geometries of the different conformers of acrylic acid; for meaning of symbols see Figure 5.

Calculations

Acrolein, Acrylic Acid, and Methyl Acrylate. In order to learn more about the conformations of uncomplexed and Lewis acid complexed acrylates, we have performed ab initio[15] calculations on acrolein, acrylic acid, and methyl acrylate. The protonated forms of these three compounds, Li^+-complexed acrolein, Li^+- and BH_3-complexed acrylic acid, and BH_3-complexed methyl acrylate, have also been studied computationally.

The s-cis and s-trans conformers of acrolein were optimized with ab initio gradient optimizations using the split-valence 3-21G basis set,[16a] or the split-valence 6-31G* basis set, which includes d-orbital polarization functions on C and O.[16b] The geometries and energies are shown in Figure 5. At the 6-31G* level, the s-trans conformation is preferred by 1.7 kcal/mol over the s-cis conformation. Calculation of the harmonic frequencies for the 6-31G* planar s-cis acrolein resulted in only real frequencies (none imaginary), indicating that the planar species is an energy minimum. The 3-21G calculations erroneously predict both conformers to have the same energy, but the s-trans conformer was found to be 1.8 kcal/mol more stable at the 6-31G*//3-21G level. These results are in excellent agreement with experiment (see below).

There have been many rationalizations of relative energies of s-cis and s-trans isomers of conjugated diene systems. It has been argued that electrostatic interaction of the diene termini,[17] π–π and π–π^* MO interactions,[18] and most often, destabilizing steric repulsions[19] (i.e., H–H repulsion and interaction among substituents) account for the difference in the s-trans and s-cis conformational energies. The s-cis conformation should be disfavored because of O–H repulsions at the termini of the conjugated system. The distance between these atoms is only 2.85 Å. George et al. have concluded that the C···O termini distance for s-cis acrolein is closer than normally expected as compared to the corresponding geometries of the s-trans series,[17] because of an electrostatic attraction, but this is insufficient to make this geometry preferred.

An experimental preference for the s-trans conformation of 2.1 kcal/mol has been obtained from ultrasonic studies in liquid acrolein.[20] Ultraviolet spectroscopy studies indicate that 4% of acrolein exists in the s-cis conformation at room temperature in the vapor phase, which indicates a free-energy difference of 1.9 kcal/mol.[21]

The geometries are in reasonable agreement with a recent microwave spectroscopy study in the vapor phase of planar *s-cis*- and *s-trans*-acrolein.[22] Many other ab initio studies have also

(15) (a) Binkley, J. S.; Whiteside, R. A.; Raghavachari, K.; Seeger, R.; Defrees, D. J.; Schlegel, H. B.; Frisch, M. J.; Pople, J. A.; Kahn, L. R. GAUSSIAN 82, Carnegie-Mellon University, Pittsburgh, PA, 1982. (b) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. GAUSSIAN 80, QCPE 406, Indiana University, Bloomington, Ind.

(16) (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(17) George, P.; Bock, C. W.; Trachtman, M. *J. Mol. Struct.* **1980**, *69*, 183.

(18) (a) Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 6941. (b) Devaquet, A. J. P.; Townshend, R. E.; Hehre, W. J. *Ibid.* **1976**, *98*, 4068.

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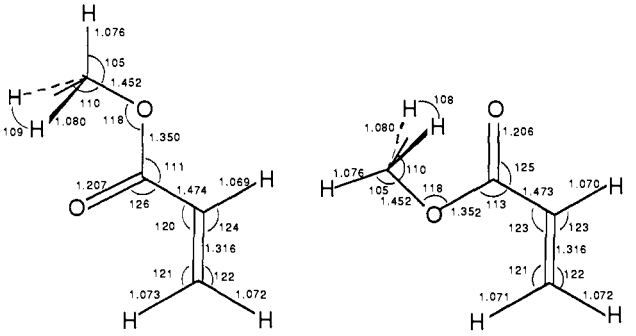
(20) DeGroot, M. S.; Lamb, J. *Proc. R. Soc. London, Ser. A* **1957**, *242*, 36.

(21) (a) Blom, C. E.; Müller, R. P.; Gunthard, Hs. H. *Chem. Phys. Lett.* **1980**, *73*, 483. (b) Alves, A. C. P.; Christoffersen, J.; Hollas, J. M. *Mol. Phys.* **1971**, *20*, 625.



	16 s-cis,syn	17 s-trans,syn
3-21G//3-21G	-302.98200 (0.0)	-302.98079 (0.8)
6-31G*//3-21G	-304.67836 (0.0)	-304.67722 (0.7)

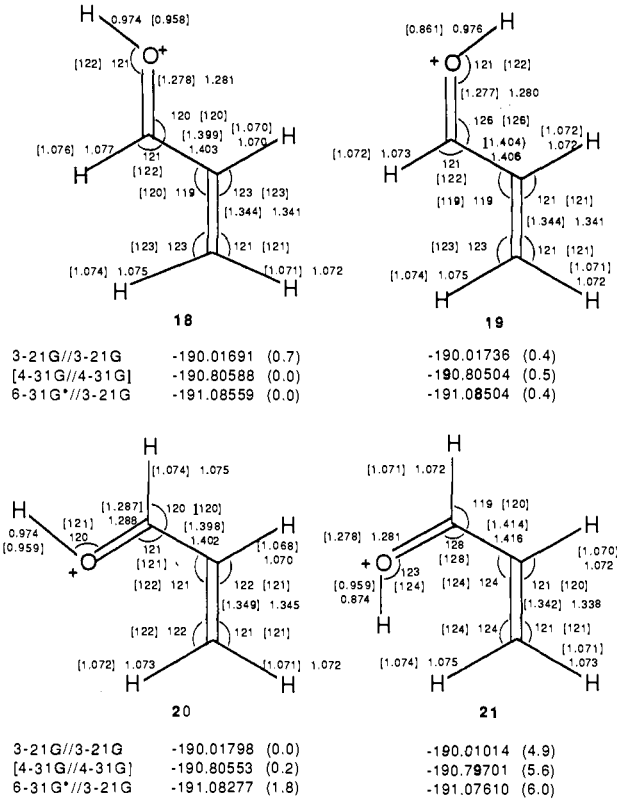
Figure 7. 3-21G geometries of the syn conformers of methyl acrylate; for meaning of symbols see Figure 5.

been done on the conformers of acrolein.[17,23] Among them Topsom and Marriott[23a] have found that the s-trans conformer is 1.7 kcal/mol more stable than the s-cis at the 6-31G*//4-31G level.

The rotational barrier of acrolein was also estimated. In order to model the rotational barrier, acrolein was optimized with the C=C—C=O dihedral angle constrained to 90°. The barrier in going from the s-trans to the s-cis conformer was found to be 8.9 kcal/mol at the 6-31G*//3-21G level. This is larger than the value of 5.0 kcal/mol obtained in liquid-phase ultrasonic studies.[20] Two rotational barriers were found by a gas-phase microwave spectroscopy study:[24] a barrier of 4.0 kcal/mol in going from the s-trans to a gauche conformation, and a barrier of 6.6 kcal/mol from the gauche to the s-cis conformation.

Both theory and experiment agree that acrolein is s-trans and has a barrier to rotation of 4–9 kcal/mol to form the less stable s-cis conformer, which is about 2 kcal/mol higher than the s-trans.

Four planar conformers of acrylic acid, shown in Figure 6, were fully optimized at the 3-21G basis level. Single-point calculations with a 6-31G* basis set were also done on the 3-21G geometries. According to a multitude of experimental[25,26] and computational[26,27] investigations, there is a strong preference for the syn conformation in carboxylic acids and esters. This is found here also, since the s-cis,anti and s-trans,anti isomers of acrylic acid are disfavored by 8.5 and 11.4 kcal/mol, respectively. Among the explanations offered to rationalize this syn preference are stabilizing $n-\sigma^*_{C-O}$ interactions,[28] the minimization of dipole–dipole (electrostatic) interactions,[27] and destabilizing interactions of nonbonded electron pairs on the two oxygen atoms.[29] The



	18	19
3-21G//3-21G	-190.01691 (0.7)	-190.01736 (0.4)
[4-31G//4-31G]	-190.80588 (0.0)	-190.80504 (0.5)
6-31G*//3-21G	-191.08559 (0.0)	-191.08504 (0.4)

	20	21
3-21G//3-21G	-190.01798 (0.0)	-190.01014 (4.9)
[4-31G//4-31G]	-190.80553 (0.2)	-190.79701 (5.6)
6-31G*//3-21G	-191.08277 (1.8)	-191.07610 (6.0)

Figure 8. 4-31G and 3-21G geometries of the four conformers of protonated acrolein; for meaning of symbols see Figure 5.

s-cis,syn and s-trans,syn conformations of acrylic acid were found to have energies of 0.0 and 0.6 kcal/mol, respectively, at the 6-31G*//3-21G level. This result is in agreement with a microwave spectroscopy study[29] of acrylic acid, which indicates that the s-cis,syn conformer is more stable than the s-trans,syn in the vapor phase by 0.15 kcal/mol. In the present study, preference of the s-cis,syn isomer of acrylic acid can be rationalized by steric arguments. There is a slight preference of the s-cis,syn conformers over the s-trans,syn conformer which can be attributed to a steric interaction between the hydroxyl oxygen, O_5, and hydrogen, H_8, on the terminal end of the olefin in the s-trans,syn conformer. This distance is 2.38 Å, whereas the $O_1\cdots H_8$ distance is 2.56 Å for *s-cis,syn*-acrylic acid.

A rotational barrier for acrylic acid was also estimated. The barrier was calculated from optimization of acrylic acid with the C=C—C=O dihedral angle constrained to 90°. The rotational barrier from the minimum energy s-cis,syn conformer was found to be 7.5 kcal/mol. This is larger than that calculated by Kiss and Lukovitz[31] of 5.5 kcal/mol using the NDDO method. Experimentally, the rotational barrier from cis to trans was found to be only 3.8 kcal/mol by Bolton et al.[30]

Two planar symmetric conformers of methyl acrylate were also fully optimized, and the results are shown in Figure 7. The s-cis,syn conformer **16** was again more stable than the s-trans,syn conformer **17**, by 0.7 kcal/mol. The energy difference between the s-cis,syn and s-trans,syn conformers of both acrylic acid and methyl acrylate are about the same. Our calculations of methyl acrylate are in accord with a recent experimental study in which the s-cis,syn was found to be favored in the vapor phase.[32] However, two older experimental investigations[33,34] by IR spec-

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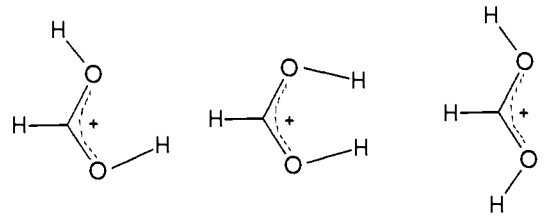


Figure 9. The sickle-, U-, and W-shaped conformations of protonated formic acid.

troscopy in solution indicate that the s-trans,syn conformer is the more stable. This reversal of the preferred conformation in solution can be rationalized by consideration of dipole moments. The s-trans,syn and s-cis,syn conformers have dipole moments of 2.55 and 1.65 D, respectively. This indicates that the former should be stabilized to a larger extent than the latter in the liquid state or in a polar solvent.

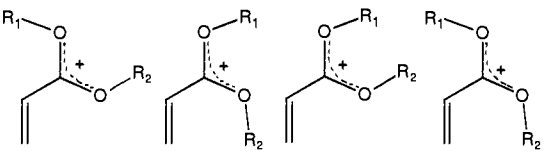
A rotational barrier of 7.4 kcal/mol, relative to the s-cis,syn conformation, was computed for methyl acrylate. The rotational barrier of methyl acrylate was calculated from optimization with the constraint of the C=C—C=O dihedral angle at 90°.

The structurally similar molecule, methyl crotonate, has also been studied experimentally. Montaudo[35] has reported a 51:49 ratio of the s-cis,syn:s-trans,syn conformations in solution by lanthanide-induced shift measurements in $CDCl_3$.

Protonated Acrolein. Four planar conformers of protonated acrolein have been computed at the 3-21G, 4-31G (by Ditchfield, Hehre, and Pople[36]), and the 6-31G*//3-21G basis levels. The results presented in Figure 8 show a dependence of the conformational energies of this system on the basis set. The relative energies at the 6-31G*//3-21G level are expected to be the most reliable. In both the s-trans and s-cis conformers of acrolein, protonation anti to the C–C single bond (syn to CH) is most favorable. According to a proton NMR study, only the anti (to CC) isomer is observed for protonated α,β-unsaturated aldehydes in superacid media.[37] This is evidenced by a sharp doublet with a coupling constant J_{HH} = 8–9 Hz for the proton on oxygen. The syn isomer is believed to be sterically unfavorable. In this NMR study, only the s-cis conformer of the α,β-unsaturated aldehydes was described. There is no mention of the conformational preference due to rotation about the C–C single bond. In a theoretical study of proton affinities of monosubstituted carbonyl compounds,[38] only the s-trans isomer of acrolein was studied. The anti isomer was found favored by 0.3 kcal/mol for the fully optimized structures of planar protonated acrolein at the STO-3G level.

Protonated Acrylic Acid and Methyl Acrylate. Protonated formic acid (Figure 9) has been the subject of several experimental[39] and computational[40,41] studies. NMR studies[39] at −60 °C indicate that the sickle-shaped isomer of protonated formic acid predominates over the W-shaped isomer by a factor of about 2:1. Other NMR studies[39a,c] at low temperatures indicate that this preference is slightly greater than 3:1. Hopkinson and coworkers[40] have studied protonated formic acid in detail by ab initio calculations with the minimal basis set. The sickle-shaped isomer was found to be the most stable, while the U-shaped and W-shaped isomers were higher in energy by 5.7 and 7.1 kcal/mol, respectively.

Table III. 3-21G Calculated Conformations of Protonated α,β-Unsaturated Esters and Their Relative Energies[a]



	22	**23**	**24**	**25**
$R_1=R_2=H$	0.0	4.2	5.6	10.4
$R_1=CH_3, R_2=H$	0.1 (0.0)	3.6 (4.4)	(3.7)	(11.3)
$R_1=H, R_2=CH_3$	0.0 (0.6)	(14.5)	(3.9)	(23.6)

[a] All structures have C_s symmetry. Single-point calculations are enclosed in parentheses.

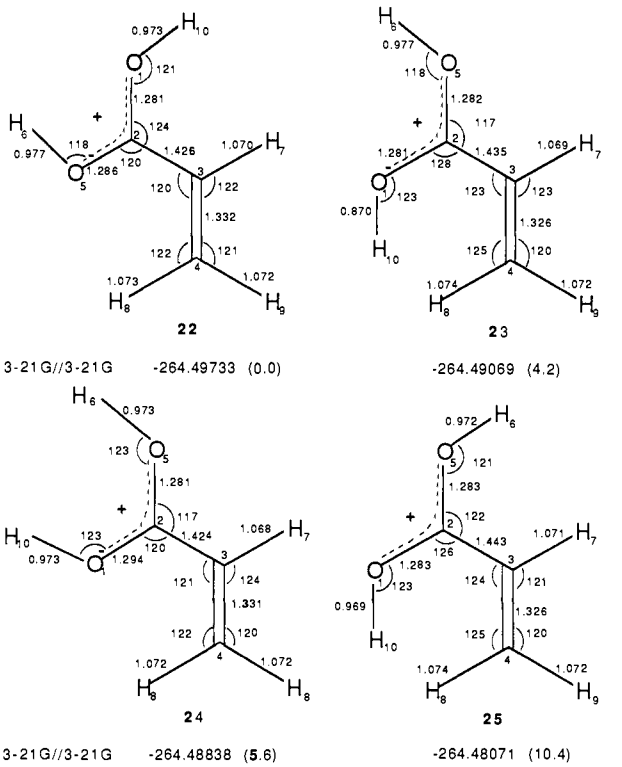


Figure 10. 3-21G geometries of the four conformers of protonated acrylic acid; for meaning of symbols see Figure 5.

Several conformers of protonated acrylic acid and protonated methyl acrylate have been investigated by ab initio calculations using full geometry optimizations or single-point calculations (see Table III). The four conformations of protonated acrylic acid, shown in Figure 10, increase in relative energy from structures **22** to **25**. Structure **25** is highest in energy because of a large lone-pair–lone-pair repulsion and a small steric interaction between H_8 and H_{10}. Structure **24** is disfavored because of steric interactions between H_6 and H_{10} and between O_1 and H_8. Unlike protonated formic acid, there are two possible sickle-shaped isomers of protonated acrylic acid. These sickle-shaped isomers are generally favored for protonated carboxylic acids and esters. In our calculations of protonated acrylic acid, we also found that the sickle-shaped isomers are favored over the U- and W-shaped isomers. Although we investigated four conformations of protonated acrylic acid, in a proton NMR study by Olah and Calin[42] only isomers **22**, **24**, and **25** were considered to be in equilibrium in solution. Olah found that isomer **22** is observed at low tem-

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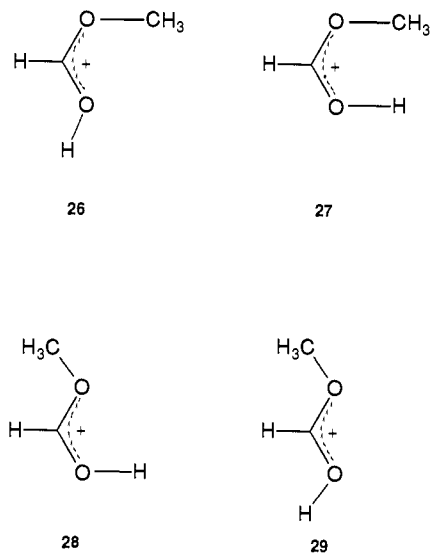

Figure 11. Four conformers of protonated methyl formate.

perature (−95 °C), while at higher temperatures, coupling constant changes indicate that both **24** and **25** are present also.

In a study by Ohkubo et al.[41] a series of protonated aliphatic methyl esters were investigated by the INDO–MO method using standard geometries. For protonated methyl formate (Figure 11), they report isomer **26** as the most stable, while isomers **27**, **28**, and **29** have the relative energies of 0.6, 1.3, and 4.4 kcal/mol. They suggest that isomer **27** appears much more stable than expected because of inaccurate estimates of electron–electron repulsions in INDO calculations. The NMR spectrum of protonated methyl formate[39] shows the existence of two isomeric forms. The major isomer (90%) has been assigned as **26** and the minor isomer (10%) as **28**.

The relative energies of isomeric protonated methyl acrylates are estimated from 3-21G single-point calculations, performed on acrylic acid structures in which a standard methyl group (r_{C-H} = 1.09 Å, r_{OC} = 1.43 Å, ∠OCH = 109.5°, and ∠COCH = 60.0, −60.0, and 180.0°) is substituted in place of the corresponding hydrogen (Table III). The energies from single-point calculations may overestimate or underestimate the difference in conformational energies as compared to the energies at optimized geometries, since no geometrical relaxation of the structure was permitted. This may be why the energetics of the protonated methyl acrylates do not follow the expected ordering based upon the results of the protonated acrylic acid series. Three of the sickle-shaped isomers of protonated methyl acrylate were fully optimized and are shown in Figure 12a. The energies of the fully optimized structures indicate that the potent Lewis acid, H^+, has a considerable bearing on the conformation of acrylates. Isomer **30** is an s-trans,syn acrylate with respect to the methyl ester fragment. Isomers **31** and **32** are s-cis,anti and s-cis,syn acrylates, respectively, with respect to the methyl ester fragment in each case.

In order to understand the implications of these conformations of protonated methyl acrylate on the stereochemical result of a Diels–Alder cycloaddition to a chiral acrylate, we arbitrarily assign the Prelog conformation[43] to a chiral ester fragment of the protonated acrylates. For example, by using this Prelog model, a chiral group replacing the methyl group of isomer **30** would have the configuration represented by **30b**, as shown in Figure 12b. Rotation about the CC single bond of **30b** will give **32b**. Likewise **31b** can be generated from **32b** by rotation about the OC* and OC single bonds. For each of these acrylates the favored approach of a diene should be from the sterically less crowded side, i.e., that of the small group, as shown by the arrows. Analysis shows that isomers **30b** and **31b** are topologically equivalent, favoring attack from the front, while isomer **32b** is topologically different, favoring

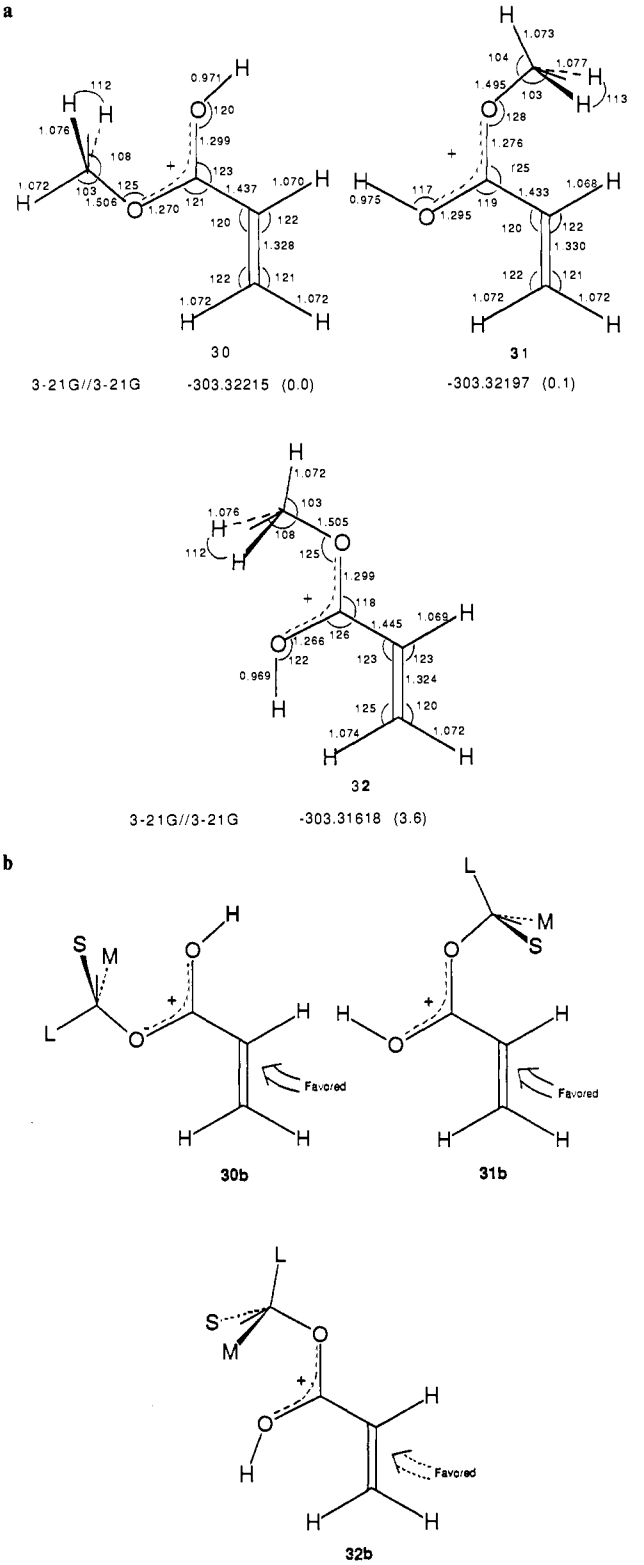

Figure 12. (a) 3-21G geometries of three sickel-shaped conformers of protonated methyl acrylate; for meaning of symbols see Figure 5. (b) Prelog-type model for attack on the conformers of protonated methyl acrylate.

attack from the back side. It is interesting that the preferred conformation of a Lewis acid coordinated chiral acrylate is generally assumed to be the conformation of isomer **30b**, while both isomers **30b** and **31b** would predict the same product. Furthermore, the results of the 3-21G calculations on protonated methyl acrylate suggest that the two conformations **30b** and **31b** are similar in energy. Also if we compare only the topologically different isomers **30b** and **32b**, then the 3-21G calculations on protonated methyl acrylate suggest that coordination of the

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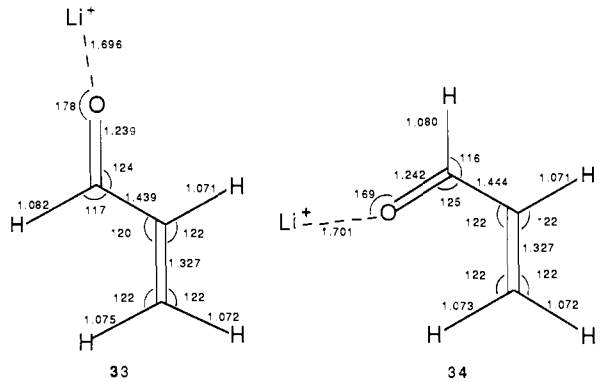


Figure 13. 3-21G geometries of the anti isomers of lithium-complexed acrolein; for meaning of symbols see Figure 5.

acrylate with a proton in a catalyzed Diels–Alder reaction favors the s-trans acrylate conformation by 3.6 kcal/mol.

Lithium-Complexed Acrolein and Acrylic Acid. To further study the effect of Lewis acids on conformations of acrylates, we studied the milder Lewis acid, Li^+. The calculated coordination energies for H^+, Li^+, and BH_3 with acrylic acid are 206.8, 62.9, and 18.7 kcal/mol, respectively. In the gas phase, the unsolvated Li^+ is still a potent Lewis acid, although its interaction with the carbonyl oxygen is primarily electrostatic in nature.

The two anti isomers of acrolein complexes by lithium were fully optimized with planar symmetry (Figure 13). The s-trans complexed conformer was found to be 3.2 kcal/mol more stable than the s-cis conformer, which is an increase in stability of 1.4 kcal/mol relative to the uncomplexed structure. Analysis of the geometries show that several bond angles change by only as much as 3° in the complexed structures relative to the uncomplexed structures. Presumably this change occurs to relieve steric crowding. However, the geometrical changes cannot account for all the stabilization energy of Lewis acid complexation; the difference must therefore be accounted for by an electronic stabilization. Complexation increases the total atomic charge on the carbonyl oxygen so that is is more negative in the Li complex than in the parent structure. We believe that this increases the nonbonded electron pair–H repulsion of the diene termini in the s-cis conformer and gives rise to the larger preference for the s-trans conformer upon complexation. There may also be some repulsion involving the Li^+ cation and the acrolein terminus.

A rotational barrier of 12.0 kcal/mol with respect to the minimum-energy s-trans structure was also computed for lithium-complexed acrolein. The rotational barrier was modeled from optimization of lithium-complexed acrolein with the C=C—C=O dihedral angle constrained to 90°. This indicates a relatively large barrier to rotation about the C–C single bond upon coordination. Several geometrical changes are apparent in the 90° conformation of lithium-complexed acrolein as compared to the planar s-trans conformer. First, the C–C single bond increases in length by 0.038 Å to a bond distance of 1.477 Å. This increase is larger than expected as compared to the bond length increase of 0.020 Å for the corresponding uncoordinated structures. Secondly, the C=O···Li^+ angle increases from 178 to 185° for the 90° conformer relative to the minimum-energy s-trans conformer. For the 90° conformer, the lithium is actually coordinated at a H—C=O···Li^+ angle of 185°. These geometrical changes presumably contribute to the larger barrier of rotation for the lithium-coordinated structure.

The four possible lithium-coordinated acrylic acid structures were fully optimized with C_s symmetry. Results are shown in Figure 14. As compared to uncoordinated acrylic acid, the relative energies of the s-cis,syn and s-trans,syn conformations reverse. Furthermore, the anti conformations of this series are not disfavored by as much as they are in the acrylic acid series. Presumably, this can be attributed to a greater electrostatic interaction of the nonbonded electron pairs on the oxygen atoms in acrylic

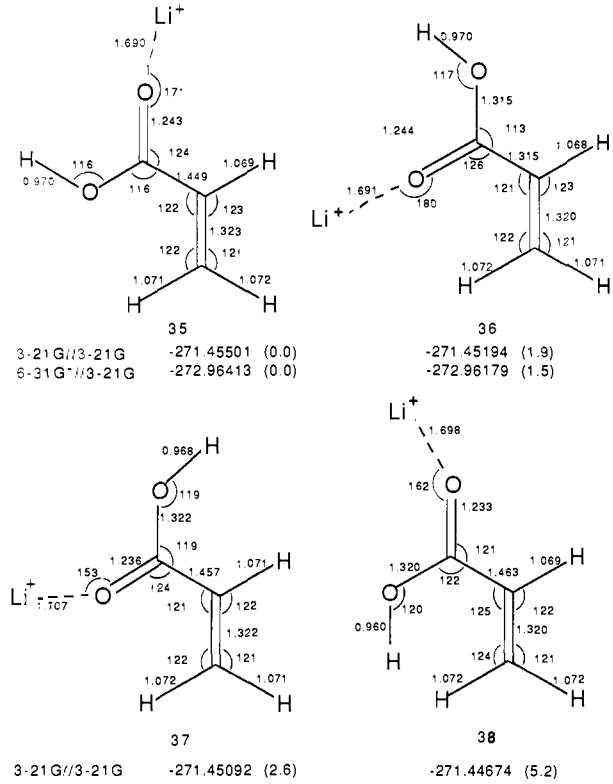


Figure 14. 3-21G geometries of the different conformers of lithium-complexed acrylic acid; for meaning of symbols see Figure 5.

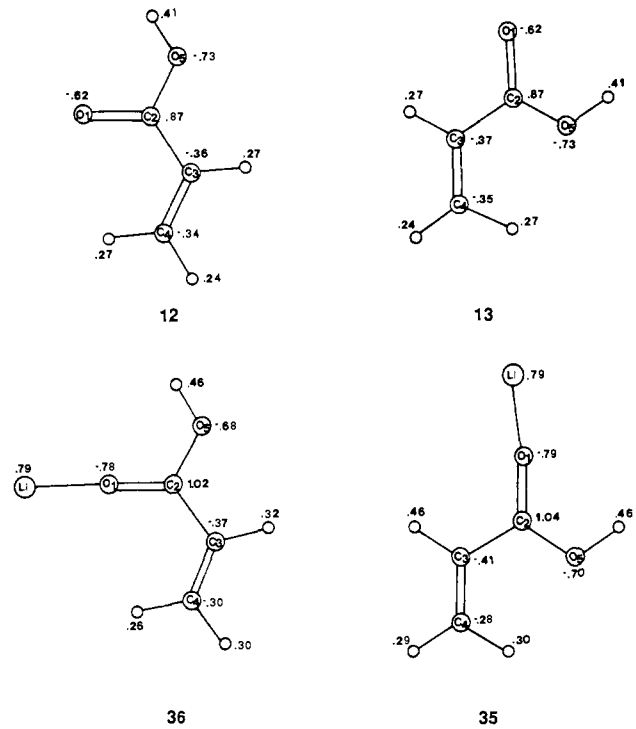
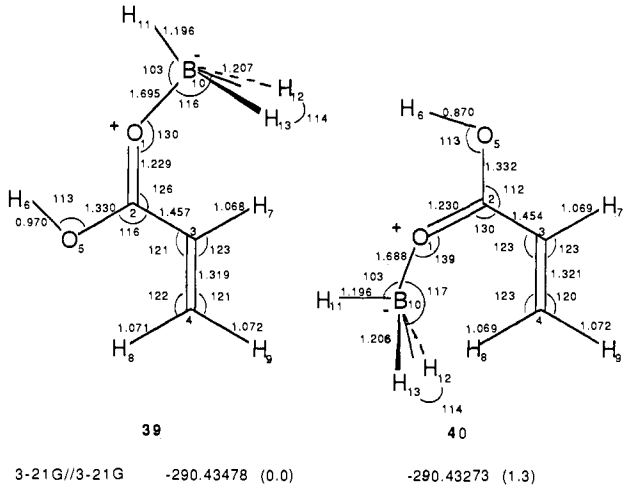


Figure 15. Total atomic charges (electrons) of *s-cis,syn*-acrylic acid, *s-trans,syn*-acrylic acid, lithium-complexed *s-cis,syn*-acrylic acid, and lithium-complexed *s-trans,syn*-acrylic acid.

acid than in the lithium-complexed acrylic acid. In addition, none of the geometries of the lithium-coordinated structures are very different from that of the parent acid. The bond angles change only by a few degrees, and the bond lengths by a few hundredths of an Ångström. However, the total atomic charges of the heavy atoms do change drastically. Figure 15 shows the total atomic charges of structures **35** and **36** along with those of the parent acids. Comparison of the atomic charges of the parent acid and



3-21G//3-21G -290.43478 (0.0) -290.43273 (1.3)

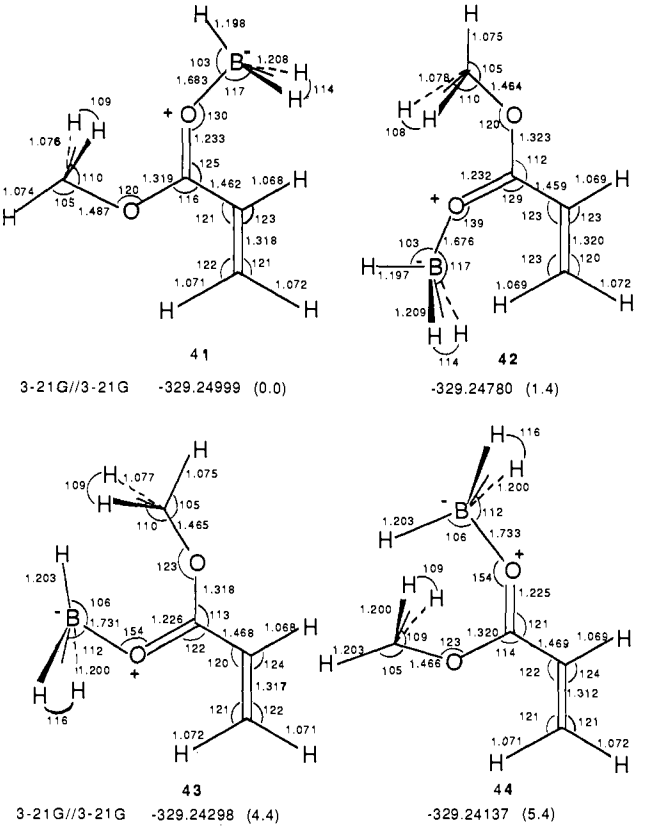
Figure 16. 3-21G geometries of the syn conformers of acrylic acid complexed by borane; for meaning of symbols see Figure 5.

the lithium-coordinated acids reveals two interesting features. First, the atomic charge of O_5 is more negative than the charge of O_1 for the parent acid. Secondly, the charges of atoms O_1 and C_3 are more negative and the charge of atom C_2 is more positive in the lithium-coordinated structures **35** and **36** than in the parent acids **12** and **13**. The net result upon coordination is that O_1 now has an atomic charge that is more negative than O_5. These factors cause a destabilization of conformer **36** and a stabilization of the conformer **35** relative to the parent acids.

The rotational barrier of lithium-coordinated acrylic acid was estimated to be 8.5 kcal/mol. Again the barrier was found by optimization of lithium-coordinated acrylic acid with the C=C—C=O dihedral angle constrained to 90°. Comparisons with the results for acrylic acid and methyl acrylate indicate that Lewis acid complexation stabilizes the s-trans conformation and introduces a slightly larger barrier of rotation about the CC single bond.

Borane-Complexed Acrylic Acid and Methyl Acrylate. Calculations were also performed on the s-cis,syn conformers of acrylic acid complexed with BH_3, as shown in Figure 16. Full geometry optimizations with C_s symmetry were carried out. The s-trans,syn-coordinated structure is again favored. It should be noted that with the Lewis acid BH_3 there is a weaker coordination to the acrylic acid than with Li^+ or H^+. As previously mentioned, the calculated coordination energies for H^+, Li^+, and BH_3 with acrylic acid are 206.8, 62.9, and 18.7 kcal/mol, respectively. Upon complexation of BH_3, there is no large change in the electronic character of these structures. The preference of isomer **39** can be rationalized by steric arguments. In structure **39**, atom H_7 is 2.59 Å away from H_{12} or H_{13}, and 2.77 Å from the boron atom. And in structure **40**, atom H_8 is 2.29 Å away from either H_{12} or H_{13}, and 2.54 Å from the boron atom. In order to verify a steric preference, single-point calculations were also performed on BH_3-complexed acrylic acid. In these calculations, the geometries of acrylic acid moieties of structures **39** and **40** were assumed, and a standard BH_3 species (BO = 1.69 Å, BH = 1.20 Å, ∠OBH$_{11}$ = 102.7°, ∠OBX = 116.0°, and ∠HBH = 56.9°) was placed at an angle of 180.0° from atom C_2. In this case there is only a 0.1-kcal/mol preference for the s-trans-coordinated structure over the s-cis,syn-coordinated structure. This leads us to believe that **39** is favored for primarily steric reasons.

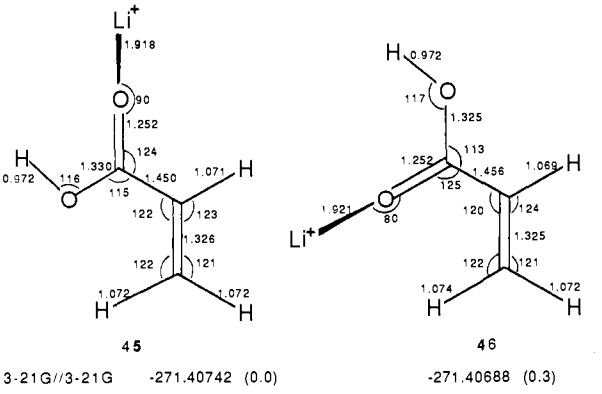
Further calculations were done on methyl acrylate complexed by borane. This system more closely models the larger Lewis acids and chiral acrylic esters that have recently been used in catalyzed Diels–Alder reactions. Four conformers of methyl acrylate complexed by borane were calculated at the 3-21G level with full geometry optimizations and C_s symmetry (Figure 17). The results are now predictable: the s-trans complexed conformer is the most stable. The preference is about the same as for the borane complexed acrylic acid system. As expected, the anti complexed isomers are largely favored over the syn owing to greater steric crowding.



3-21G//3-21G -329.24999 (0.0) -329.24780 (1.4)

3-21G//3-21G -329.24298 (4.4) -329.24137 (5.4)

Figure 17. 3-21G geometries of the four conformers of methyl acrylate complexed by borane; for meaning of symbols see Figure 5.



3-21G//3-21G -271.40742 (0.0) -271.40688 (0.3)

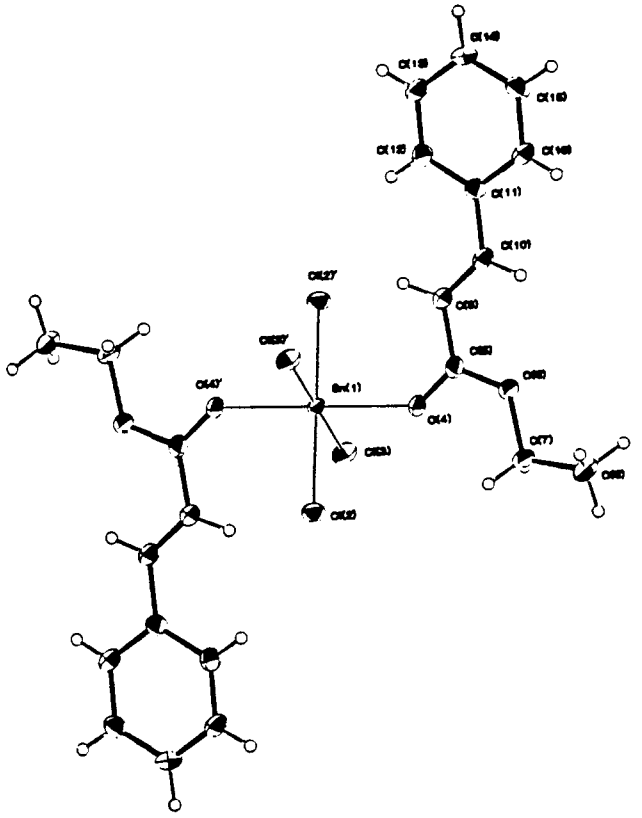
Figure 18. 3-21G geometries of two conformers of lithium-complexed acrylic acid with the constraint of angle C=O—Li at 90°; for meaning of symbols see Figure 5.

It should be emphasized that an energy difference of 1.3 kcal/mol is enough to give a significant conformational preference. For a Diels–Alder reaction run at 0 °C, this energy difference would correspond to a 92:8 ratio of major and minor isomers. Our calculations of Lewis acid complexed acrylates show an energy difference between the s-trans and s-cis conformations of at least 1.3 kcal/mol or greater. This does not imply that this conformational preference should apply to the transition state. However, since these catalyzed Diels–Alder reactions proceed very rapidly, and the transition state occurs at an early stage along the reaction coordinate, then the conformational preferences of the complexed acrylates may also be manifested in the transition state.

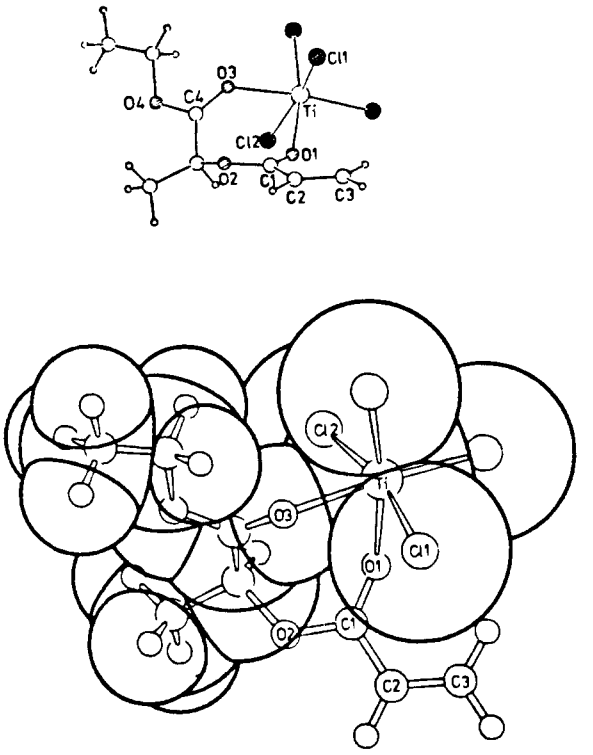
Recent experimental work has addressed the question of the conformational preference of acrylates.[11,44] The uncomplexed 10-(phenylsulfonyl)isobornyl acrylate and 10-(dicyclohexylsulfonamido)isobornyl acrylate, **2**, have been shown to adopt the

(44) Lewis, F. D.; Oxman, J. D.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 466. **47** is reprinted with permission of the American Chemical Society.

Chart I



47



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s-trans conformation by X-ray diffraction.[11g,h] The topicity of the reaction of either of these acrylates with cyclopentadiene agrees with the free acrylate conformation. Evidence for the s-trans conformational preference of Lewis acid complexed α,β-unsaturated esters comes from the crystal structure of an (ethyl cinnamate)$_2$–$SnCl_4$ complex, **47**, shown below.[44] The molecular structure of this complex is octahedral with Sn at the center of inversion. Both ethyl cinnamate molecules are s-trans.

The crystal structure of a $TiCl_4$ complex of an acrylate of ethyl lactate, **48**, has also been determined recently.[45] This is the first crystal structure of a Lewis acid chiral dienophile complex. This structure is rather interesting in that the largest group (the $CH_3CH_2O_2C$ ester group) does not have the expected anti-periplanar arrangement, but is syn-periplanar (see **3** shown in Table I). The conformation of the acrylate in this complex is s-cis. This is surprising, since all of the work presented here has supported the preference of the s-trans acrylate conformation in catalyzed reactions. We believe this s-cis conformation is the result of the unusual geometry of the complex. First, the titanium is chelated in a seven-membered ring. Secondly, the OC=OTi dihedral angle is 63.6° instead of the usual 180° found in our model calculations and in X-ray and spectroscopic studies.[44,46]

In order to investigate the possible bearing of the position of the Lewis acid on the conformational preference, we have done ab initio calculations on our model lithium-complexed acrylic acid systems. Optimizations were carried out on complexes of the planar s-trans and s-cis acrylic acid with the constraint of the O—C=O—Li dihedral angle equal to 90°. For these calculations the s-trans,syn-coordinated structure is favored by 0.3 kcal/mol (Figure 18). Here the preference for the s-trans,syn-coordinated structure is greatly diminished from previous calculations, where planar lithium-complexed s-trans acrylic acid was favored by 1.9 kcal/mol (Figure 14). Although this result does not show a preference of the s-cis acrylic acid, it does indicate the relevance of Lewis acid position on the degree of rotational isomerism of acrylates. Further studies of this geometrical dependence will be carried out.

Conclusion

In summary, our calculations have shown that the s-cis conformation of uncomplexed acrylates is slightly favored over the s-trans conformation. Furthermore, Lewis acid complexation of these acrylates dramatically stabilizes the s-trans conformation relative to the s-cis by either electronic or steric effects. This implies that the uncatalyzed Diels–Alder reactions may proceed via the s-cis conformation of the acrylate, or with little preference, while the use of a Lewis acid catalyst greatly enhances the preference for the reaction to proceed via the s-trans conformation. This work supports Oppolzer's assumption that an s-trans conformation is present in catalyzed Diels–Alder reactions involving *si*-face- or *re*-face-directing acrylates. The observed enantiomer in these reactions can only be predicted if the s-trans conformation of the acrylate is assumed. We are developing models to assist in the understanding of the conformation about asymmetric centers which direct the stereofacial approach of the attacking diene. The results will be reported soon.

Acknowledgment. We are grateful to Professor Wolfgang Oppolzer for suggesting this problem to us, and to the National Institutes of Health for financial support of this research.

(45) Poll, T.; Metter, J. O.; Helmchen, G. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 112. **48** is reprinted with permission of *Angew. Chem.*

(46) (a) Childs, R. F.; Lindsay, M.; Nixon, A. *Can. J. Chem.* **1982**, *60*, 801. (b) Brun, L. *Acta Crystallogr.* **1966**, *20*, 739. (c) Brunn, J.; Radeglia, R.; Lewanscheck, B.; Peust, S. *Z. Phys. Chem. (Leipzig)* **1977**, *258*, 681.

Registry No. Acrolein, 107-02-8; acrylic acid, 79-10-7; methyl acrylate, 96-33-3; protonated acrolein, 57344-16-8; protonated formic acid, 16961-31-2; protonated acrylic acid, 64833-99-4; protonated methyl formate, 39014-35-2; protonated methyl acrylate, 67457-05-0; cyclopentadiene, 542-92-7; (−)-menthyl acrylate, 4835-96-5.