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Ab Initio Study of the Thio-Ene Reaction. 1. The Enophile Substituent Effect

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The ene reaction between propene and various enophiles (ethene, methanal, methanethial, ethanethial, and cyanomethanethial) were examined at the MP4/6-31G*//MP2/6-31G* level. The transition structures are all cyclic and concerted. The activation barriers for the thiocarbonyls are significantly lower (ranging from 16.0 to 25.0 kcal mol^{-1}) than for ethene (36.3 kcal mol^{-1}) or methanal 31.1 kcal mol^{-1}). This trend, along with the trend in activation energies among the substituted thials, is completely consistent with FMO arguments. Comparison with experiment, particularly the thiol vs sulfide production, is also in complete agreement.

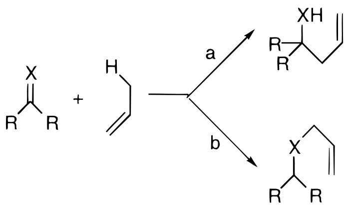
The ene reaction has largely been treated as the neglected sister to the much more famous Diels−Alder reaction.[1,2] Both involve a six-electron cyclic shift. The ene reaction is thought to proceed via a concerted mechanism, whereby the hydrogen transfers to the enophile while another σ-bond forms, and the π-bond migrates within the ene fragment.[3]

Recently, significant effort has been made to explore the ene chemistry of thio-carbonyl compounds. Since we[4−8] have been interested in the pericyclic reactions of heteroatomic systems, we decided to explore the nature of the mechanism of this reaction. In this paper, we report ab initio calculations on the thio-ene reaction, exploring the effect of substitution of the enophile.

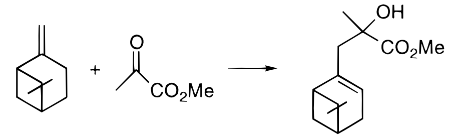
Background

In principle, the hetero ene reaction may proceed with C−C bond formation (path a) or C−X bond formation (path b), each passing through a different transition state (Scheme 1). When X is oxygen, the reaction proceeds exclusively through path a, giving just alcohol and no ether product.[2,3] An example is shown in Scheme 2, where only the alcohol is observed.[9]

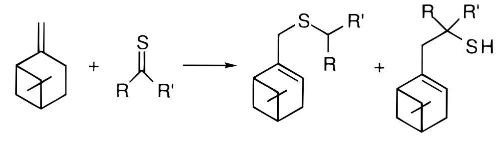
Scheme 1



Scheme 2



Scheme 3



R	R'	% sulfide	% thiol	Ref
CF_3	CF_3	only	-	10
CH_3S	CN	83	-	11
CO_2Et	CO_2Et	only	-	13
CO_2Et	H	78	21	14
CO_2Me	H	75	<2	16
Ph	H	19	38	15

On the other hand, most ene reactions of thiocarbonyls proceed preferentially via path b to yield sulfides. The earliest reported work was by Middleton[10] who reacted perfluorothioacetone with propene and β-pinene and found only sulfide products. Snider[11,12] found that two different thiones reacted with a variety of alkenes to give just the sulfide products. Kirby has found that when two ester groups[13] are attached to the thiocarbonyl group, again only sulfide is produced, but when only one ester[14] is present, the ratio of sulfide to thiol product is about 4:1. Last, Baldwin[15] has found that thiobenzaldehdye reacts with β-pinene to give a 1:2 ratio of sulfide to thiol, but the yield is dramatically lower than that seen in the other reactions. These results are summarized in Scheme 3. Vedejs reported an intramolecular ene reaction involving a thioaldehyde which produces the thiol exclu-

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[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1997.

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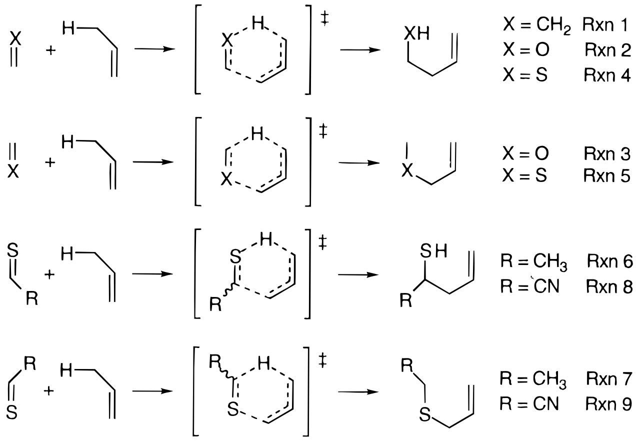
S0022-3263(97)00608-7 CCC: $14.00

Scheme 4



sively, arguing that conformational effects overcome the preference for sulfide formation.[16] Kirby reported intramolecular ene reactions that produce regioselectively either the sulfide or the thiol.[17−19]

The ene reaction has been addressed by theoreticians only a few times. We will discuss these prior results in more detail below when we compare them to our results.[20−22] Earlier theoretical studies on the Diels−Alder reactions of thiocarbonyl compounds have shown that these have lower activation energies than their carbon or oxygen analogues.[23−25] This has been attributed to the weak C−S π-bond, its high HOMO and low LUMO energies. We anticipate that these features will play an important role in the thio ene reaction as well.

Computational Methods

We have examined the ene reactions between propene and a number of enophiles: ethene (reaction 1) and formaldehyde (reactions 2 and 3) are examined as reference cases, while reactions 4−9 explore the effect of substituent on the enophile thioformaldehyde (see Scheme 4). The transition states for these reactions will be labeled **TSNm**, where **N** is the reaction number and **m** will indicate *endo* (**n**) or *exo* (**x**) attack. Similarly, the products are labled **PNm**.

The geometries of all reactants, transition states, and products were optimized at HF/6-31G* and the nature of these critical points confirmed using analytical frequencies. Optimization of the products were obtained by starting from a number of initial conformations which were obtained by 30° rotations about the C−C, C−O, and C−S single bonds. The zero-point energies were scaled by 0.89. The structures were then completely reoptimized at MP2/6-31G*, which we report here. Single-point energies were evaluated at MP4/6-31G*//MP2/6-31G*. All calculations were performed using GAUSSIAN-92[26] or GAUSSIAN-94.[27]

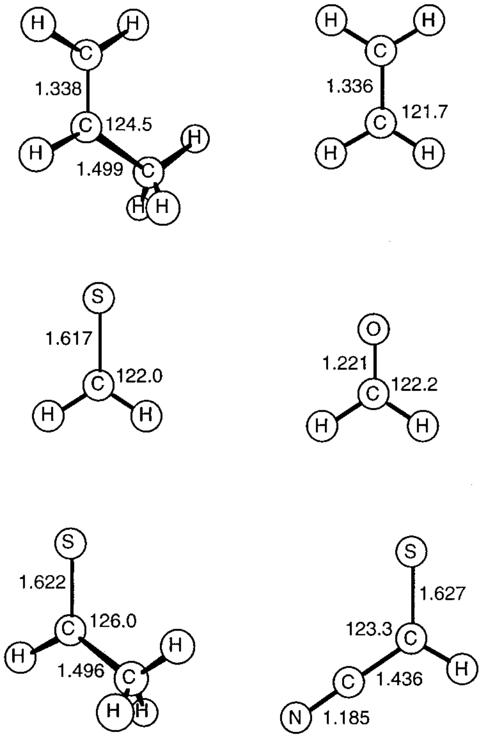


Figure 1. MP2/6-31G*-optimized geometries of the reactants. All distances are in angstroms and all angles are in degrees.

Results

Geometries. The HF and MP2 optimized geometries of the reactants and products differ by very little. The MP2 geometries of the reactants and products are drawn in Figures 1 and 2, respectively. While we cannot compare the sulfur geometries to experiments, since these structures are unknown, previous studies of model sulfur systems[28] have shown that the MP2/6-31G* provide structures in good agreement with experiment. There is very little variation in the geometries among the products—they are all in similar conformations, and distance and angles are virtually transferable among them.

The optimized structures for the transition states are also relatively insensitive to the computational level. We have drawn the optimized MP2/6-31G* geometries of the TSs in Figure 3, including values of important distances.

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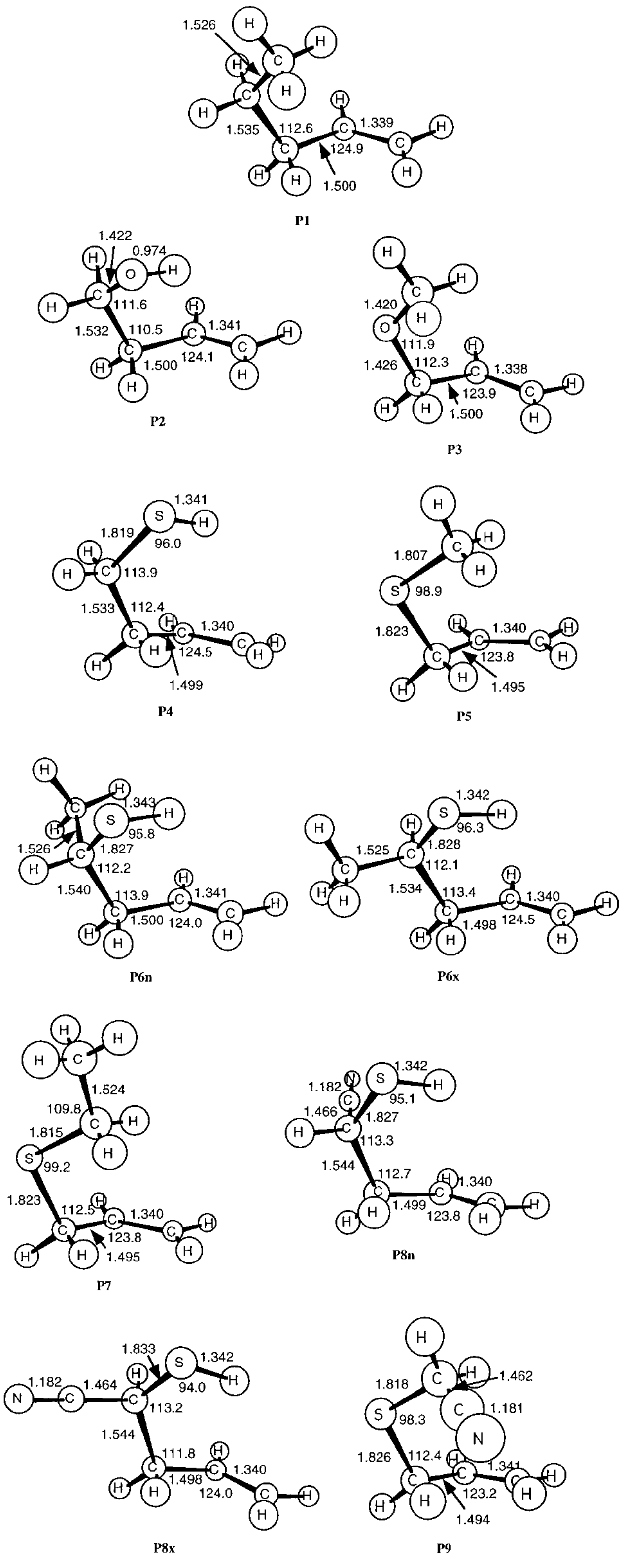

Figure 2. MP2/6-31G*-optimized geometries of the products **P1-9**. All distances are in angstroms and all angles are in degrees.

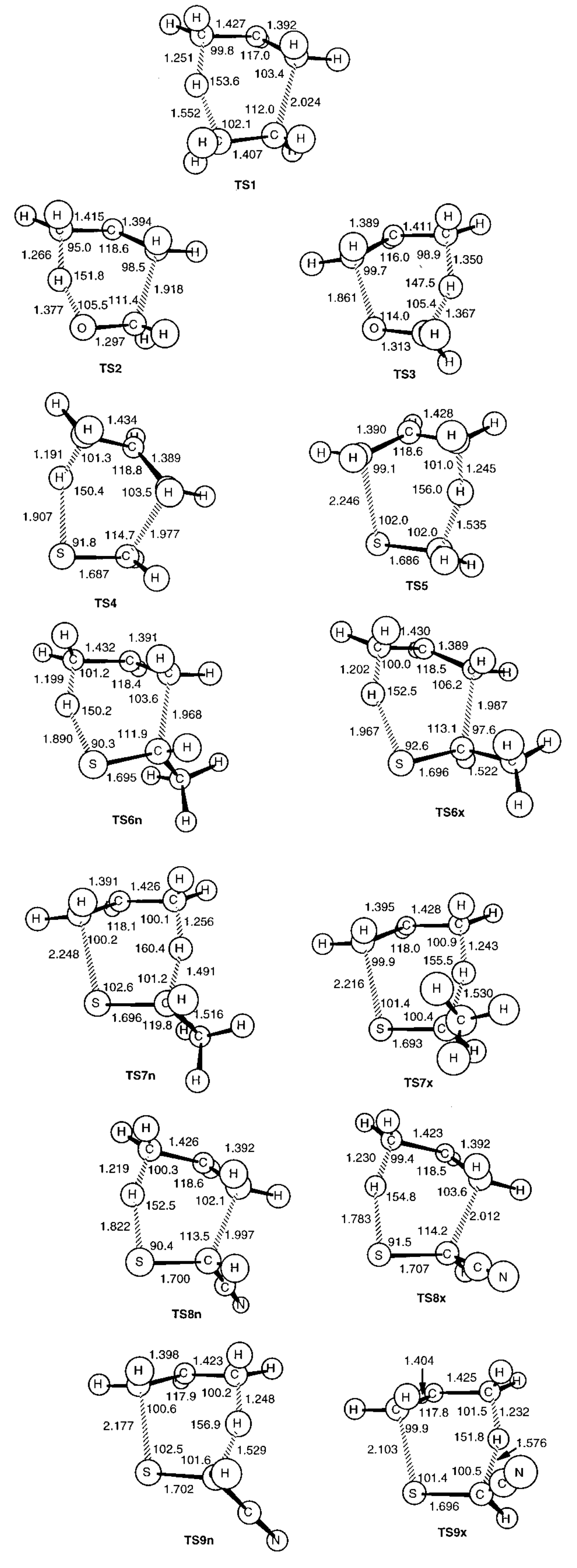

Figure 3. MP2/6-31G*-optimized geometries of the transition states **TS1-9**. All distances are in angstroms and all angles are in degrees.

Loncharich and Houk[20] optimized the structures of **TS1** and **TS2** at HF/3-21G. They claimed that these geometries should be reasonable based on small geometric variances with improved basis set and computational method in Diels−Alder and 1,5-sigmatropic shifts. However, we note some appreciable differences between the structures at this low level and our MP2 results. There is some systematic differences. The forming C−C bond distance is longer at HF/3-21G than at MP2/6-31G* while the other heavy atom bonds are all shorter at the lower level. At the HF/3-21G level, the breaking C−H bond is

Table 1. Activation Energies (kcal mol^{-1}) for Reactions 1−3

reaction	HF/6-31G*	MP2/6-31G*	MP4/6-31G*[a]
1	61.02	30.89	36.24
2	52.93	27.25	30.41
3	70.68	40.04	43.93

[a] MP4/6-31G*//MP2/6-31G*.

shorter and forming bond to hydrogen is longer than at MP2. These differences can be significant: the forming C−C bond is predicted to be about 0.1 Å longer at HF/3-21G than at the higher level. These differences are probably largely attributable to the improved basis set, given that we find little variation in the HF and MP2 geometries when the 6-31G* basis set is employed.

No stepwise or diradical intermediates were located, though no attempt was made to specifically find them. Simple pericyclic reactions have been shown to prefer concerted pathways,[29] and we did not pursue this issue further.

In an overall sense, the geometries of all of these TSs are quite similar. The structures are clearly cyclic, in a half-chair conformation. Many of the analogous bonds of these TSs are of similar length; the C_2−C_3 bond in the propene fragment varies from 1.411 to 1.434 Å, the C_1−C_2 falls in the range 1.389−1.404 Å, and the breaking C−H distances are from 1.191 to 1.245 Å (with an outlier of 1.350 Å in **TS3**). For the TSs having a forming C−C bond, this distance is from 1.918 to 2.024 Å, which is within the normal range for forming C,C bonds as compiled by Houk.[29] The angle about the transferring H is also in a small range, from 147.5 to 160.4°.

With that said, there are some differences worth commenting upon. For all of the TSs except **TS3**, the position of the transferring hydrogen suggest an early TS—the C−H distance is much shorter than the distance to the enophile. However, in **TS3** these two distances are nearly equal, suggesting a much later TS. The other geometric parameters are in accord with this notion—the forming C−O distance is quite short and the C−C distances in the propene fragment indicate more bond change than in any of the other TSs.

The bond distances in **TS4** and **TS5** show less change from reactants than in **TS1-3**, indicating that the thio-ene TSs are earlier than the C or O analogues.

Energies. The first issue to address is the adequacy of the computational method to provide reasonable reaction and activation energies. The reaction energies are relatively insensitive to computational method, varying by no more than 3 kcal mol^{-1} between the HF, MP2, and MP4 methods.

On the other hand, as might be anticipated since partial bonds are involved, the activation energies are dependent on the basis set and computational method. Loncharich and Houk[20] had noted that the HF/3-21G and HF/6-31G*//HF/3-21G activation energies for reactions 1 and 2 are much higher than those predicted at MP2/6-31G*//HF/3-21G*. We also observe this trend and list the activation energies evaluated with different methods for reactions 1−3 in Table 1. Further, we note that the MP4 activation energies are slightly higher than the MP2 values, a trend completely consistent with that observed in Diels−Alder reactions.[30−35] Loncharich and Houk[20] have estimated that the activation energy for reaction 1 should be about 35 kcal mol^{-1} based on their calculations and comparison with the experimental value for the reaction of ethylene with *cis*- and *trans*-2-butene, in excellent agreement with the MP4 result. The estimate for reaction 2 is 26.4 kcal mol^{-1} which is in poorer agreement with our calculated value. There are no experimental or theoretical data on the thermochemistry of the thio-ene reaction to provide a benchmark. Nevertheless, the estimates for reactions 1 and 2 are reasonable; this level of computation has been successfully exploited for a variety of pericyclic reactions and should prove quite adequate here for estimating the relative energies and trends among this series of related ene reactions. Therefore, we report and discuss here the MP4/6-31G*//MP2/6-31G* energies only. These are listed in Table 2.

Table 2. Activation and Reactions Energies (kcal mol^{-1}) for Reactions 1−9[a]

reaction	E_a	E_{rxn}
1	36.34	−23.30
2	31.12	−7.97
3	44.73	−1.04
4	20.15	−18.75
5	21.44	−19.70
6	22.90 *endo*24.22 *exo*	−15.12
7	25.04 *endo*24.03 *exo*	−16.87
8	17.79 *endo*19.57 *exo*	−18.81
9	17.86 *endo*15.98 *exo*	−20.00

[a] MP4/6-31G*//MP2/6-31G* with ZPE/HF/6-31G* scaled by 0.89.

As noted by Loncharich and Houk,[20] the activation energy for reaction 2 is less than for reaction 1, though we find a slightly larger difference at the MP4 level than they report for the MP2 level. The activation energies for reaction 3 is 13.6 kcal mol^{-1} higher than for reaction 2, and it is also less exothermic by nearly 7 kcal mol^{-1}. Both of these results are consistent with the experimental finding[2,3] of only alcohol product and no ether—the alcohol product is both the thermodynamic and kinetic product.

A number of interesting features are evident in the energetics of the thio-ene reactions. While all of the ene reactions examined are exothermic, the reactions involving formaldehyde are much less so ($\Delta E_{rxn} = -7.9$ and -1.04 kcal mol^{-1} for reactions 2 and 3) than the others ($\Delta E_{rxn} \approx -20$ kcal mol^{-1}). This is likely attributable to the much stronger π-bond in a carbonyl than in either an alkene or thiocarbonyl. The activation energies for all of the thio-ene reactions are much below the barriers found for reactions 1−3. This result is consistent with the less harsh reaction conditions needed to affect the thio-ene reaction relative to the carbon and oxygen analogues.[10]

Unlike the ene reaction with formaldehyde, where the alcohol product is substantially favored kinetically over the ether, for the parent reaction using thioformaldehyde (reactions 4 and 5), the thiol route has a lower barrier by only 1.3 kcal mol^{-1} than the path producing the sulfide. Placing a methyl group on the thiocarbonyl

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Table 3. LUMO Energies (au)

reactant	E_{LUMO}
ethene	0.1839
methanal	0.1459
methanethial	0.0566
ethanethial	0.0700
cyanomethanethial	−0.0038

(reactions 6 and 7) reduces the difference between the two activation energies marginally (to 1.1 kcal mol^{-1}) with the thiol remaining the favored product. Both barriers are higher than in the parent reactions. However, attaching a cyano group to the thiocarbonyl reverses the barrier heights so that the sulfide product is now favored, having a barrier that is 1.8 kcal mol^{-1} lower than the one leading to the thiol. Both barriers are also lower than for the parent reactions. The trend is that electron-donating substituents increase the activation barriers while electron-withdrawing substituents reduce the activation barriers, but preferentially reducing the barrier to formation of sulfide so that it becomes the expected product.

Last, we have explored the question of *endo* vs *exo* selectivity in these thio-ene reactions. Loncharich and Houk[20] have argued that the *exo* position in reaction 1 is more crowded than the *endo* position. For both reactions 6 and 8, the *endo* position is favored, having a lower barrier by 1.3 kcal mol^{-1} in reaction 6 and 1.8 kcal mol^{-1} in reaction 8. The situation is reversed in the reactions leading to sulfides, reactions 7 and 9. Here the *exo* TS is preferred by 1.0 kcal mol^{-1} in reaction 7 and 1.9 kcal mol^{-1} in reaction 9.

Discussion

The transition states for all reactions examined here indicate a single-step reaction. Bond changes, while certainly not synchronous, indicate a concerted reaction.

In general the ene reactions involve early transition states with moderately low activation energies. This is true for all of the reactions examined here except for reaction 3. The ene reaction of formaldehyde and propene to give methyl allyl ether is less exothermic, has a later transition state, and a markedly higher activation energy than the other reactions. These features are typically unified under the Hammond Postulate. The very high activation energy for production of ethers is completely consistent with the observed exclusive production of alcohols in ene reactions of carbonyl compounds.

As anticipated, the activation energies for thio-ene reactions are smaller than for the carbon or oxygen cases. They can be understood using FMO theory. The dominant orbital interaction is between the HOMO of propene (the C−C π-bond), the C−H antibond of propene, and the LUMO of the enophile.[36] In Table 3 we list the LUMO energies of the enophiles. The LUMO energy of ethene, formaldehyde, and thioformaldehyde decreases in that order, which corresponds precisely with their decreasing activation energies. The weaker C=S π-bond makes these ene reaction more favorable than in reactions 1−3 which involve cleaving the stronger C=C and C=O π-bonds.

While carbonyls react to give only alcohols, thiocarbonyls predominantly undergo the ene reaction to give sulfides. Hoffmann has argued that this is due primarily to the much stronger O−H bond than the S−H bond.[3] We see this reflected in the fact that the sulfide products are slightly lower in energy than the thiols, while the alcohol **P2** is much lower in energy than the ether **P3**.

We next examine the substituent effect on the activation barrier. The electron-donating methyl group raises the activation energy for the ene reaction (relative to H) while the electron withdrawing cyano group reduces the barriers. This is consistent with the LUMO of the enophile being the FMO involved in the reaction, as was suggested by Fukui.[36] Examination of Table 3 shows that the LUMO energy increases in the order: cyanomethanethial < methanethial < ethanethial, again duplicating the ordering of their activation barriers.

The substituent has a further effect. Thiol is the predicted kinetic product for ene reactions of both methanethial and ethanethial, with its barrier about 1 kcal mol^{-1} lower than the barrier to produce sulfide. However, when a withdrawing group is placed on the enophile, sulfide becomes the kinetic product. The barrier for reaction 9 is 1.81 kcal mol^{-1} lower than for reaction 8. In terms of the thial LUMO, the carbon character increases with electron-donating ability (leading to selection toward formation of the C−C bond) while the sulfur character increases with electron-withdrawing ability (leading to selection toward formation of the C−S bond). As discussed in the background section above, the experiments have been mostly performed with electron-withdrawing groups, and these produce predominantly sulfide product. When only one withdrawing group is present, the yields reduce and some thiol is recovered, and when the substituent is phenyl, the yield is poorer still and thiol is the major product. The calculations are consistent with these studies. Further, they indicate that the energy differences for the barriers for the two paths is small. Therefore, other effects can certainly play a major role, such as the conformational restrictions in the intramolecular case examined by Vedejs.[16]

Last, we note that reactions 6−9 can proceed through two diastereomeric TSs having the substituent in the *endo* or *exo* position. On the basis of the structure of the TS, Loncharich and Houk[20] suggested that the *exo* position is more crowded than the *endo* position in **TS1**. At MP4, *endo* substitution is favored for reactions 6 and 8. Steric interactions explain this result in part: the distance between the substituent carbon and the nearest hydrogen of the propene fragment is longer by about 0.2 Å in the *endo* TSs.

The preference reverses in the TSs leading to the sulfide product, where the *exo* TSs are now lower in energy for both reactions 7 and 9. The distance between substituent on the enophile and the nearest hydrogen on propene do not explain this preference as the longer distance is in the higher energy *endo* TSs. Rather, an understanding of the energies of the *endo* vs. *exo* TSs lies in conformational analysis. The dihedral angles about the ring in the half-chair conformation of cyclohexane are about ±30° or ±60°. In Table 4 we list the dihedral angle C_1XYH, where X and Y are either the C or S of the thiacarbonyl and C_1 is the first carbon of propene, for **TS6-9**. The higher energy TS of each *exo*/*endo* pair always has the smaller absolute value of this dihedral angle, indicating greater conformational strain in the form of increased eclipsing interactions. Therefore, a combination of steric and conformational interactions explain the *endo* preference for reactions 6 and 8 and the

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Table 4. C_1XYH^a Dihedral Angles (deg) in TS6-9

compound	angle
TS6n	29.00
TS6x	15.25
TS7n	−14.06
TS7x	−26.30
TS8n	24.11
TS8x	14.51
TS9n	−18.38
TS9x	−29.98

[a] Where X and Y are the C and S of the thiacarbonyl group, C_1 is the first carbon of propene, and H is the hydrogen transferred to the enophile.

exo preference for reactions 7 and 9. We also note that the energy differences between the *endo* and *exo* TSs is rather small (less than 2 kcal mol^{-1}), indicating that other conformational and substituent effects can certainly change this situation, as suggested by Vedejs.[16]

Conclusion

MP4 calculations on the ene reactions involving thiocarbonyls provide a number of insights. The reaction proceeds through a concerted, cyclic transition structure. The greater ease of reaction for the thiocarbonyls than for carbonyls is understood in terms of the weak C═S π-bond, exemplified by its low LUMO. Substituents on the thiocarbonyl affect the activation barrier in ways completely consistent with FMO theory, an important result in that it confirms the notion that these simple ideas, i.e., FMO theory, are applicable to second-row heteroatoms. The changes in activation energy with substituent are completely consistent with the observed thiol vs sulfide production.

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Supporting Information Available: Coordinates of the MP2/6-31G*-optimized structures of **TS1-9** (7 pages). This material is contained in libraries on microfiche, immediately follows the article in the microfilm version of the journal, and can be obtained from the ACS; see any current masthead page for ordering information.

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