Competition between Diradical Stepwise and Concerted Mechanisms in Chalcogeno-Diels−Alder Reactions: A Density Functional Study

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Received March 12, 2001

The chalcogeno-Diels−Alder reactions of $H_2C{=}X$ (X = S, Se, Te) with butadiene, with *trans,trans*- and *cis,trans*-2,4-hexadiene, as well as of ethylene with thio-, seleno-, and telluroacrolein and reactions of thioformaldehyde with thioacrolein are examined theoretically. The B3LYP exchange-correlation functional with the 6-31G(d) and LanL2DZ(d) basis sets is employed. Stepwise diradical and concerted pathways are considered for all reactants. A modified concerted mechanism via a pre-reaction complex followed by a concerted transition state is studied for thioformaldehyde reacting with thioacrolein. The stepwise diradical pathways are predicted to be energetically less favorable than the concerted pathways for all cases considered. Even the sterically hindered reaction between selenoformaldehyde and *cis,trans*-2,4-hexadiene prefers a concerted path. It is a considerable challenge to reverse this energy preference for the concerted reaction given that both electronic and steric factors act to increase or decrease the activation energies of the concerted and diradical stepwise paths in the same way. A modified concerted mechanism operates for reagents with very small HOMO−LUMO gaps such as thioformaldehyde and thioacrolein. This mechanism is completely synchronous, with a vanishingly small barrier.

Introduction

The Diels−Alder (DA) reaction (Scheme 1) is symmetry allowed according to the Woodward−Hoffmann rules[1] and, thus, is presumed to proceed synchronously in a single kinetic step via a concerted transition state. A single-step mechanism for the DA reaction has been verified in many theoretical studies.[2−5] A few exceptions from the "rule of synchronicity" have been predicted theoretically by Houk and co-workers[5] for hetero-DA reactions. According to a valence bond (VB) investigation of pericyclic reactions by Bernardi, Olivucci, and Robb,[2c] the synchronicity in the formation of cyclic transition structures may be destroyed easily. There is a very delicate balance between the valence bond coulomb terms (which slightly prefer synchronicity) and the valence bond exchange terms (which slightly prefer asynchronicity). A completely asynchronous process for DA reactions yields a stepwise mechanism that proceeds via a diradical intermediate (see reaction 2, Scheme 1, as an example). An ionic stepwise pathway via a dipolar intermediate is also possible. Such a mechanism operates, for example, in the addition of singlet oxygen to *cis,trans*- and *trans,trans*-2,4-hexadiene[2i] or in the triazolinedione DA reactions with sterically hindered dienes.[2f]

The two alternate diradical and ionic stepwise mechanisms have been much less thoroughly studied. For the parent DA reaction, a stepwise mechanism was predicted theoretically by Houk and co-workers[2e,f] and by Sakai[2h] to be energetically slightly less favorable than the concerted mechanisms. One might anticipate that a stepwise mechanism would compete favorably with the concerted reaction if the diene or dienophile is so sterically hindered as to effectively block the formation of the concerted transition structure.[2f,9] The diradical stepwise mechanism is often invoked whenever there is evidence of a *nonconcerted* reaction i.e., when the DA 1,4-adduct formed does not follow from the anticipated concerted transition state. There is probably only one experimentally known example of a DA reaction where a diradical mechanism clearly operates and yields 1,4-adducts, namely the reactions of furanones with dienes. This exception was confirmed theoretically.[10] The investigations by Wilker and Erker[11] of the DA reaction between

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10.1021/jo010280g CCC: $20.00 © 2001 American Chemical Society
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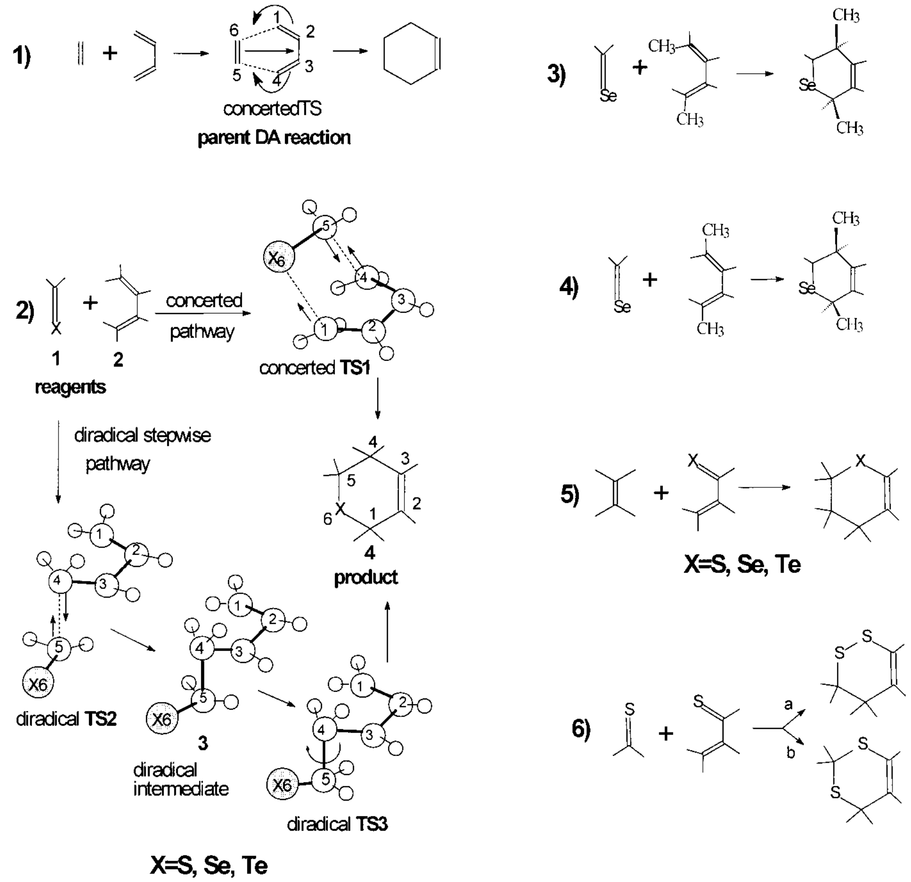
Scheme 1



cis–trans-2,4-hexadiene and diarylselenocarbonyl, which proceeds in a nonconcerted fashion, should be considered as a second possible example.

The diradical pathway for chalcogeno-DA reactions has not been examined theoretically, and there are relatively few theoretical investigations of the concerted mechanism.[6–8] Thus, we performed a theoretical study of the experimentally important[11–14] DA reactions between chalcogen-containing dienes and dienophiles including sulfur, selenium, and tellurium compounds (reactions 2–6, Scheme 1). The competition between the stepwise diradical and concerted pathways in the chalcogeno-DA reactions is the major focus of this investigation. How do steric factors that might suppress the concerted mechanism operate in the diradical pathway? Does the diradical mechanism ever become truly energetically favorable compared to the concerted mechanism?

Theoretical Methods

Reliable theoretical predictions of the activation energies of both the concerted and diradical pathways of DA reactions depend on the inclusion of electron correlation in the computational scheme. Density functional theory (DFT), which includes dynamical and, more roughly, nondynamical electron correlation,[15] has proven to be a reliable approach for the study of DA reactions[2a,c–g,5–7,9,10] and is employed in this work.

All predictions are made using the GAUSSIAN98 program suite.[16] The B3LYP exchange-correlation functional is employed throughout. B3 is a hybrid HF-DFT exchange functional,[17] and LYP is the correlation functional formulated by Lee, Yang, and Parr.[18] The 6-31G(d)[19] basis set is employed for the sulfur compounds. The LanL2DZ[20a] double-ζ valence basis sets with an effective core potential and augmented with Basch[21] d-type polarization functions for the Se and Te atoms ($\alpha_{Se} = 0.32$, $\alpha_{Te} = 0.22$) are used in predictions on the selenium-

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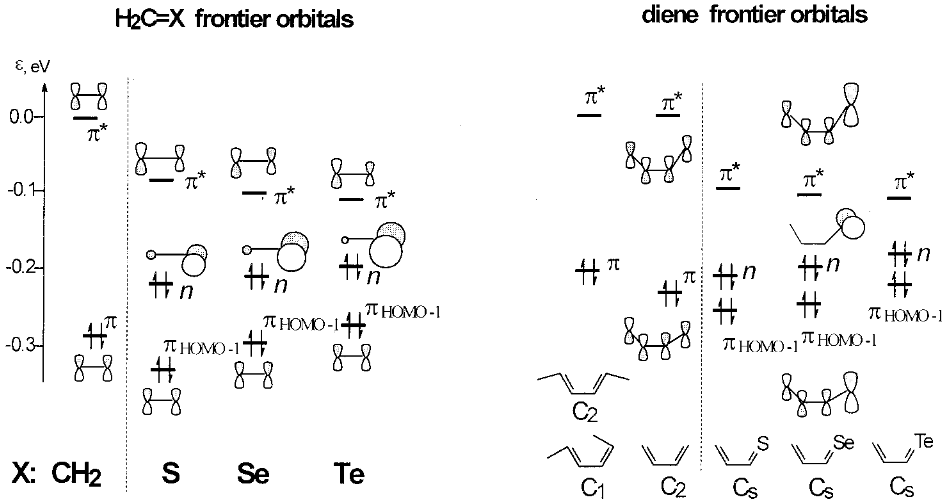

Figure 1. Sketch of the frontier Kohn−Sham orbitals and their energies (in eV) for the dienophiles and for a typical diene at the B3LYP/LanL2DZ level.

and tellurium-containing compounds. For the C and H atoms, the LanL2DZ set is equivalent to the Dunning D95 double-ζ basis set.[20b]

The nature of each stationary point (minimum, transition state) on the adiabatic potential energy surface is verified by computation of the Hessian matrix. To confirm the connection of the saddle points to minima along the reaction pathways, Minyaev's[22] gradient reaction line approach is used. Unrestricted B3LYP solutions for diradical structures are found for the formally closed-shell singlet electronic states using the guess = mix option in GAUSSIAN98. The atomic charges are obtained using NBO[23] analysis.

All relative energies include corrections for the zero-point vibrational energies.

Results and Discussion

The frontier Kohn−Sham orbitals of the dienophiles CH_2X ($X = CH_2$, S, Se, Te) and a typical set of orbitals for the dienes (reactions 2−6, Scheme 1) are sketched in Figure 1. For both the dienophiles and dienes there is a significant lowering of the energy of the π^*-LUMO on proceeding from C to S and a moderate lowering on proceeding from S to Te. As a particular feature, the actual HOMO of the chalcogenodienophiles and the chalcogenodienes is an n-orbital that corresponds to a lone pair on the chalcogen atom while the relevant π-orbital is HOMO-1. The n-orbital is not involved in formation of the new σ-bonds and continues to be the HOMO in the concerted transition structures. The energy of the HOMO and HOMO-1 decreases on proceeding from S to Te. A decrease in the HOMO-1−LUMO gap on proceeding from C to Te should lead to a decrease in the barrier of the concerted DA reaction. Simultaneously, the high-lying n-HOMO, which increases in energy on proceeding from S to Te, permits the energetically favorable formation of diradical structures on the stepwise pathways. Thus, a simple qualitative analysis of the preference for one or another of the two reaction pathways clearly suggests a competition.

1. Reactions of Chalcogenoaldehydes with 1,3-Butadiene. First, consider the cycloaddition of the chalcogenoformaldehydes **1** to the gauche conformer of 1,3-butadiene **2** (reaction 2, Scheme 1). The C_2 gauche isomer is 3.6 kcal/mol higher in energy than the most stable C_{2h} trans isomer at the B3LYP/6-31G(d) level. The potential energy profiles of the concerted and diradical pathways are depicted in Figure 2. Selected geometrical parameters of the stationary point structures along the pathways are shown in Figures 3 and 4. All reactions energetically prefer the concerted pathways. The barrier of the concerted reaction drops considerably compared to the parent ethylene plus butadiene DA reaction depicted on the top left-hand in Figure 2 and decreases from 6.6 kcal/mol to only 2.3 kcal/mol on proceeding from S to Te. Such a qualitative trend is nicely in agreement with the qualitative orbital interaction model of the concerted reaction mentioned above.

The stepwise paths for the chalcogen-DA reactions have topologies similar to that predicted earlier for the parent DA diradical reaction.[2h] A diradical intermediate, **3**, is formed through a diradical transition structure, **TS2**. For all chalcogens, the diradical transition structures, **TS2**, were predicted to be notably higher in energy than the concerted transition structures, **TS1**. The activation barriers are 15.9, 13.6, and 10.7 kcal/mol for S, Se, and Te, respectively. For the parent DA reaction, the corresponding value predicted earlier was 30.0 kcal/mol.[2f] The second step of the diradical pathway corresponds to a rotation of the terminal CH_2X group of the diradical intermediate, **3**, around an essentially single C−C bond through the diradical transition structure, **TS3**, with the subsequent formation of the DA 1,4-adduct, **4**. This step involves a low barrier of ca. 2 to 3 kcal/mol. Such a barrier is clearly typical for internal rotation about a carbon−carbon single bond.

Several noteworthy features of the chalcogeno-DA reaction pathways are revealed. For the stepwise reactions, the stability of the diradical intermediate, **3**, referred to reactants or products increases significantly on proceeding from S to Te. For S, the diradical intermediate, **3**, is even higher in energy than the concerted **TS1** and is 6.3 kcal/mol lower than diradical **TS2**. For the parent DA reaction, the corresponding value is 4.6 kcal/mol.[2e] For Se, the diradical intermediate, **3**, is lower in energy than the concerted **TS1** but is still somewhat

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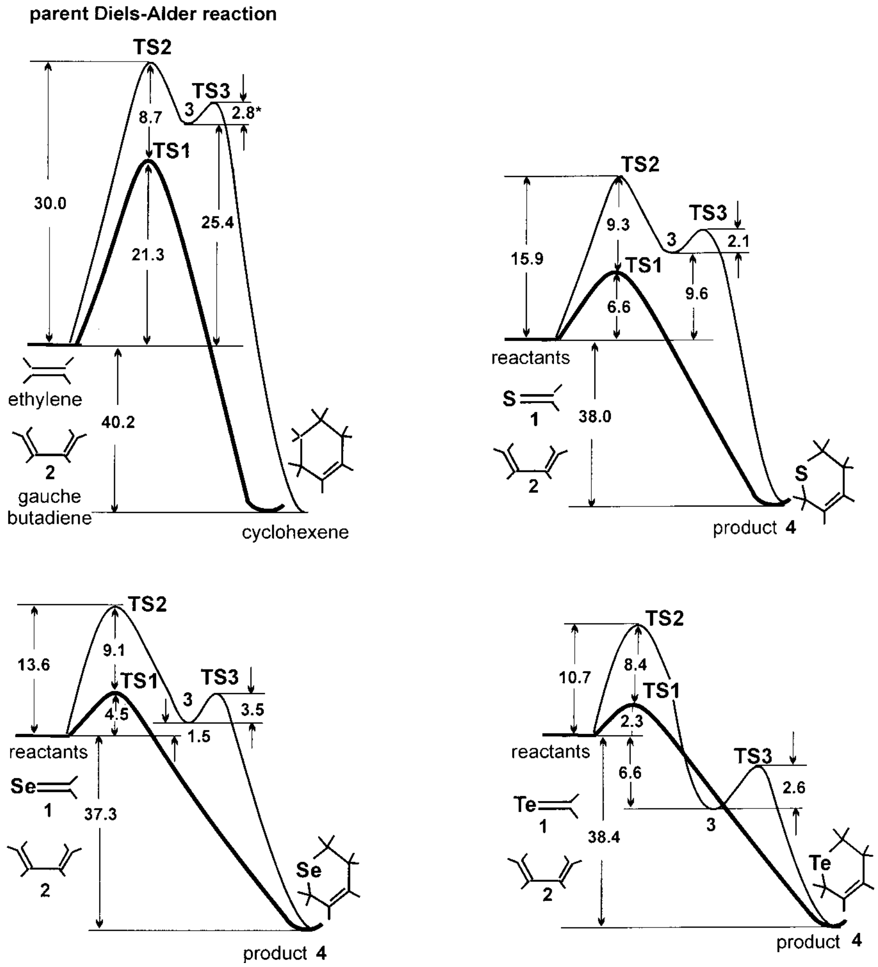

Figure 2. Potential energy profiles for the concerted (heavy lines) and stepwise diradical (light line) pathways for reaction 2 in Scheme 1 between $HC_2{=}X$ (X = S, Se, Te), **1**, and gauche-1,3-butadiene, **2**, as predicted by B3LYP with the 6-31G(d) basis set for X = S and with LanL2DZ(d) for X = Se, Te. The relative energies (in kcal/mol) include zero-point vibrational energy corrections. Potential energy profiles for the parent DA reaction as predicted previously[2e,f] with B3LYP/6-31G(d) are shown for comparison. *The second barrier, TS3, for the parent DA reaction was predicted previously[2h] with CAS-MP2/6-311+G(dp).

higher than the reactants. For Te, the diradical intermediate is 6.6 kcal/mol lower in energy than the reactants. This trend reflects the strengths of the chalcogen−carbon chemical bonds and appears to be a feature particular to the chalcogenocarbonyl dienophiles. The stability of the C=X (X = S, Se, Te) double bond decreases[24] and the stability of the $C{-}X^{\bullet}$ bonding arrangement with a lone electron on the terminal chalcogen increases on proceeding from S to Te[25] and is critical to diradical stability. Note that the diradical intermediate **3** is almost a pure singlet diradical in the case of Se and Te ($<S^2> = 1.02$) but there is a somewhat smaller value of $<S^2>$ (0.92) for X = S.

The energy difference between the two transition states for the two different mechanisms (“the energy of concert”) is almost constant and decreases only slightly on proceeding from S, through Se, and on to Te: 9.3, 9.1, and 8.4 kcal/mol, respectively. For the parent DA reaction, a very similar value of 8.7 kcal/mol for this energy of concert was predicted previously.[2e] Another energy “constant” of the gauche butadiene plus chalcogenoaldehyde cycloaddition is the overall reaction energy. Very similar values of ca. 38 kcal/mol were predicted for S, Se, and Te. This value also is quite close to the reaction energy of 40.2 kcal/mol predicted earlier for the parent DA reaction.[2f]

The barrier of the concerted reaction is mainly determined by the changes in electron coupling upon the bond-making and bond-breaking processes. For the diradical stepwise reaction, the barrier is mainly due to the electron uncoupling upon the change of a closed shell electronic state to a “singlet diradical like” one with the $<S^2>$ greater than zero and less than one.[2h] We propose that the nearly constant energy of concert for the $H_2C{=}X$ (X = CH_2, S, Se, Te) plus butadiene reactions is due to the nearly constant difference between the energies of electron coupling (the $C{=}X \rightarrow -C{-}X-$ process) and electron uncoupling (the $C{=}X \rightarrow -C{-}X^{\bullet}$ process) for the $CH_2{=}X$ dienophiles. The very similar reaction energies probably reflect the effects of aromaticity in the formation of the $(4n + 2)$ six-membered cyclic product relative to the 4π electron butadiene and 2π electron ethylene-like reagents.

In agreement with a modified Hammond’s postulate, the geometries of the concerted transition structures, **TS1**, in Figure 3 reflect the trends in energetics. Telluroformaldehyde, **1**, X = Te with the smallest energy barrier (2.3 kcal/mol) forms the earliest transition state with the

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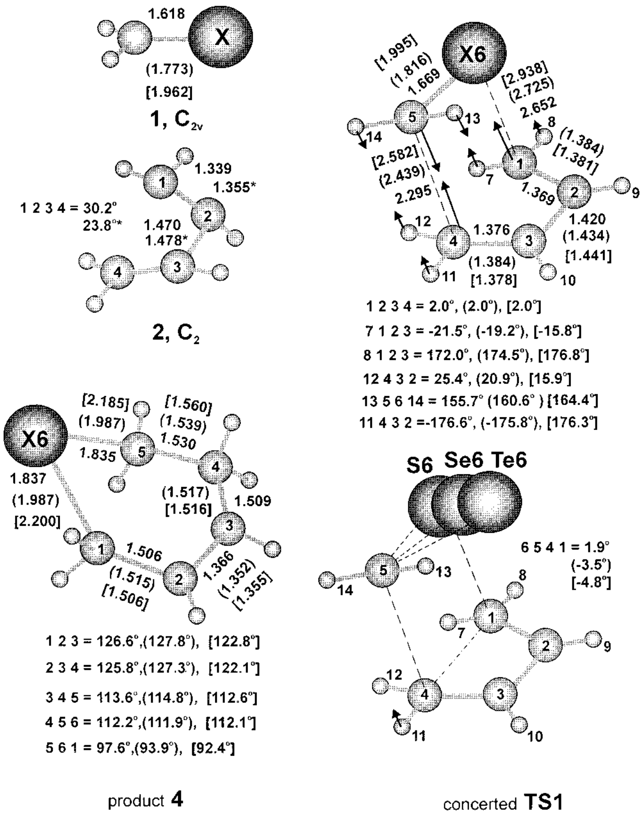

Figure 3. Selected geometrical features for the stationary point structures (reactants **1** and **2**, transition state **TS1**, and product **4**) of the concerted pathway for reaction 2 in Scheme 1 predicted using B3LYP/6-31G(d) for X = S and B3LYP/LanL2DZ(d) for X = Se (values in parentheses) and X = Te [values in square brackets]. For butadiene, the values from B3LYP /6-31G(d) are plain and from B3LYP /LanL2DZ are marked with an asterisk. The geometries are reported in Å and deg. For the transition structures, the transition vector is sketched. The deviation of the chalcogen atom from the C5C4C1 plane in **TS1** is given by the 6541 dihedral angle as shown at the bottom of the figure.

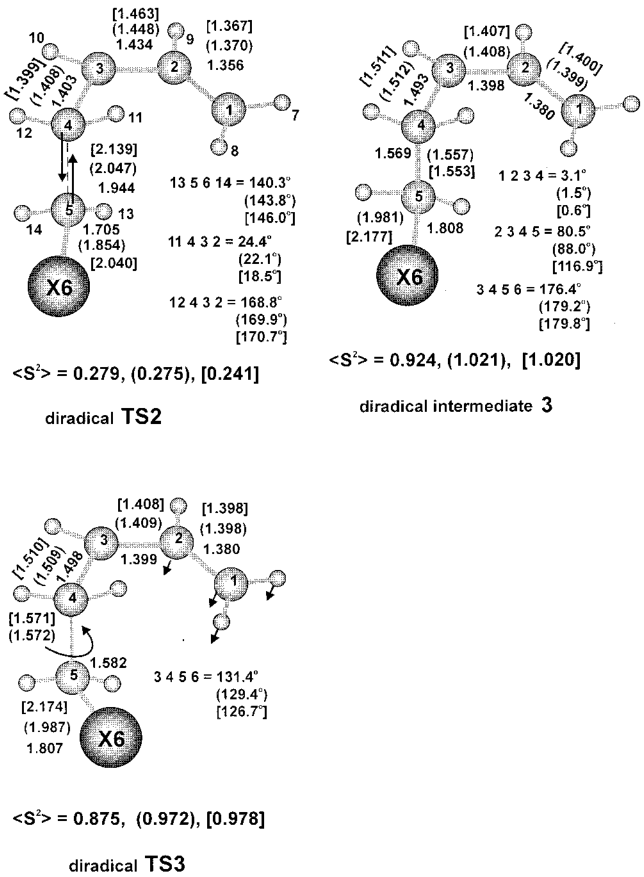

Figure 4. Selected geometrical features for the diradical intermediates and transition state structures for the stepwise pathway of reaction 2 in Scheme 1 as predicted with B3LYP/6-31G(d) for X = S and B3LYP/LanL2DZ(d) for X = Se (values in parentheses) and X = Te [values in square brackets]. Geometries are in Å and deg. For the transition structures, the transition vector is sketched. The expectation values of S^2 also are reported.

smallest changes in the geometries of the interacting fragments. Thioformaldehyde, **1**, X = S with the highest barrier (6.6 kcal/mol) forms the latest transition state with the largest geometrical changes. The following geometrical changes may be noted in Figure 3 upon the formation of **TS1.** The X6−C1 and C5−C4 bonds are nearly formed, and the C1, C4, and C5 atoms begin to pyramidalize. The butadiene fragment flattens, the C1−C2 and C3−C4 double bonds of butadiene elongate, and the C2−C3 bond shortens. In the chalcogenoaldehyde, the C5−X6 double bond elongates. Of these processes, only the flattening of the butadiene fragment from a gauche to a nearly cis conformation is essentially constant for all chalcogens and results in a C1−C2−C3−C4 dihedral angle of 2°. This very low energy process of flattening corresponds to the lowest harmonic vibrational frequency and, thus, may occur at the earliest stage of the reaction. Naturally the X6−C1 and C5−C4 σ-bonds formed in **TS1** are considerably longer for X = Te and shorten on proceeding to X = S. The C1−C2 and C3−C4 double bonds of the gauche butadiene **2** elongate upon interaction with H_2CX by 0.026 and 0.023 Å, 0.029 and 0.029 Å, and 0.030 and 0.037 Å, respectively, for X = Te, Se, and S. The CH_2Te, CH_2Se, and CH_2S moieties cause the C2−C3 bond of butadiene to decrease in length by 0.037, 0.044, and 0.050 Å, respectively. For comparison, the parent DA reaction, which proceeds via a significantly later concerted transition state, has the C2−C3 bond length decreased by a significantly larger amount, 0.063 Å. The pyramidalizations of the carbon atoms that are formally sp^2 hybridized are higher energy processes and the degree of pyramidalization of the C1, C4, and C5 atoms in **TS1** changes slightly (a small increase) on proceeding from Te to S. The natural charges on the $H_2C{=}X$ fragments of the concerted **TS1** are −0.147, −0.105, and −0.075 for S, Se, and Te, respectively. This trend in negative charges nicely reflects a weaker withdrawal of electron density from the diene to the dienophile by the less electronegative chalcogen in the earlier transition structures.

The H_2CX fragments are slightly twisted with respect to the butadiene fragment in **TS1.** For X = S, the sulfur atom is shifted *away* from the butadiene fragment, while for X = Se and Te, the chalcogen atom is shifted *inward* (see the structure of **TS1** at the bottom of Figure 3). For formaldehyde and thioformaldehyde, this effect has been observed earlier by McCarrick et al.[5a] and has been attributed to a repulsive interaction between the lone pair on the oxygen (moderate repulsion) and the lone pair on sulfur (considerably weaker repulsion) with the electron density of the butadiene. For Se and Te, which

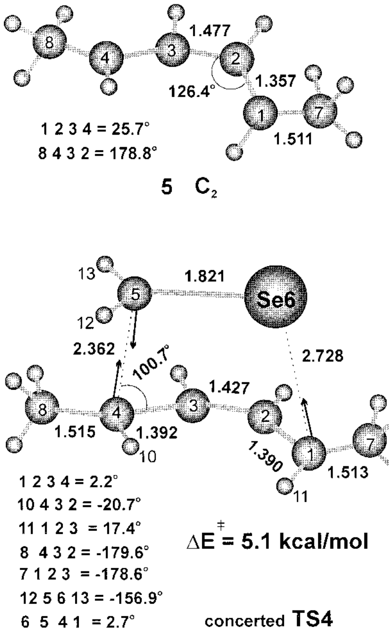

Figure 5. Geometries of *trans,trans*-2,4-hexadiene **5** and the concerted transition structure **TS4** as given by B3LYP/LanL2DZ(d). The barrier referred to reactants for reaction 4 in Scheme 1 as predicted by B3LYP/LanL2DZ(d) is reported. Geometries are in Å and deg. The transition vector is sketched.

form considerably longer bonds to the carbon atom than sulfur, the repulsive interaction does not appear to be as strong.

On the diradical pathway, as on the concerted one, telluroformaldehyde forms the earliest **TS2** with the longest C4−C5 bond and the smallest degree of pyramidalization of C4 and C5 (see Figure 4). Judging by the value of $<S^2>$ of 0.279, 0.275, and 0.241 for S, Se, and Te, respectively, the diradical character of **TS2** decreases slightly on proceeding from S to Te. For the parent DA reaction, a greater diradical character of "later" diradical transition state ($<S^2> = 0.56$) was predicted previously at the B3LYP/6-31G(d) level.[2e]

Electronic factors that increase or decrease the barrier of the concerted mechanism of the DA reaction between H_2CX and gauche butadiene operate in the same sense and to much the same degree in the first step of the diradical stepwise mechanism. Thus, despite considerable changes in the activation energies for both the concerted and the stepwise diradical pathways on proceeding from ethylene to telluroaldehyde, the energetic preference for the concerted pathway over the diradical remains constant at ca. 9 kcal/mol for all interacting partners.

2. Does Steric Hindrance Favor the Diradical Pathway? The Reactions of Selenoformaldehyde with *cis,trans*-2,4-Hexadiene and with *trans,trans*-2,4-Hexadiene. Sterically hindered dienes possess a structure that is inherently somewhat unfavorable to the formation of a concerted transition states. Similar steric obstacles also may affect any diradical stepwise pathway. To study the relative influence of steric effects on the concerted and stepwise diradical mechanisms, we considered the DA reactions of $H_2C{=}Se$ with the sterically hindered *cis,trans*-2,4-hexadiene (reaction 3, Scheme 1) and with its sterically unhindered trans,trans isomer (reaction 4, Scheme 1). The energies of the frontier orbitals of these dienes are very close and are close to those for the twisted gauche butadiene (see Figure 1). Thus, the difference in the reactivity of these dienes should be determined by steric and not orbital energy derived electronic factors.

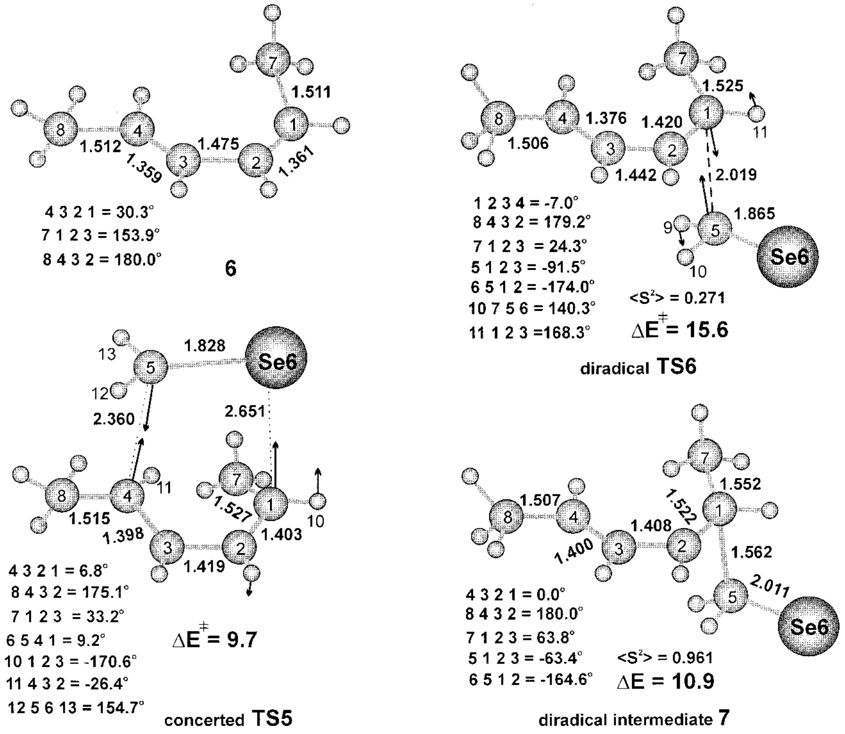

Figure 6. Geometries for the structure of *cis,trans*-2,4-hexadiene **6**, the concerted transition structure **TS5**, the diradical transition structure **TS6**, and the diradical intermediate **7** as predicted with B3LYP/LanL2DZ(d) for reaction 3 in Scheme 1. Relative energies (in kcal/mol) are referred to the reactants. Geometries are in Å and deg. The transition vectors are sketched. For the diradicals, the expectation values of S^2 are reported.

The experimentally known[11] DA reaction between diarylselenocarbonyls and *trans-trans*-2,4-hexadiene proceeds rapidly via a concerted mechanism and yields the trans,trans adduct. The same trans,trans adduct was obtained with *cis,trans*-2,4-hexadiene, and thus, the probability of a stepwise diradical pathway was raised.[11] The preference for the diradical pathway in this case was attributed to the sterically unfavorable conformation of the *cis,trans*-2,4-hexadiene, which is experimentally well known to be considerably less reactive in the concerted DA cycloaddition than the trans,trans isomer.[11] Figure 5 shows *trans,trans*-2,4-hexadiene, **5**, and the corresponding concerted transition state structure, **TS4**. The geometries of the butadiene fragment in *trans,trans*-2,4-hexadiene, **5**, and in gauche butadiene, **2** (Figure 3), obviously are very similar. Selenoformaldehyde reacts with the *trans,trans*-2,4-hexadiene, **5**, through an early concerted transition structure, **TS4**, which is only slightly "later" than the transition structure, **TS1**, for the reaction with unsubstituted gauche butadiene, **2** (Figure 3). The barrier to the concerted reaction of CH_2Se with *trans, trans*-2,4-hexadiene, **5**, is only 0.6 kcal/mol higher than that for the reaction with gauche butadiene **2** as would be anticipated given similar electronic factors and an absence of steric effects.

Selected geometrical features of *cis,trans*-2,4-hexadiene, **6**, the concerted transition structure, **TS5**, the diradical transition structure, **TS6**, and the diradical intermediate, **7**, along with the relative energies referred to reagents are shown in Figure 6. Wilker and Erker have proposed[11] that experimentally observed trans,trans product may be a result of $Ar_2C{=}Se$ attack at C1 with subsequent rotation about the C1−C2 bond. The structure of the *cis,trans*-2,4-hexadiene, **6**, is notably twisted compared to the trans,trans isomer, **5**, due to the unfavorable steric interactions of the methyl group in the cis position with the hydrogen atom in the cis position. The H_2CSe molecule oriented so that selenium atom attacks the carbon with the *cis*-methyl substituent forms a later concerted transition structure, **TS5**, with shorter C4−C5 and Se6−C2 σ-bonds than with the unsubstituted butadiene and with well-developed π-character in the C2−C3 bond. The predicted reaction barrier for this concerted reaction of 9.7 kcal/mol increases by more than a factor of 2 compared to the concerted reaction with the unsubstituted gauche butadiene but is still low.

For the stepwise diradical pathway (Figure 6), the *cis*-methyl group also poses a steric obstacle. The barrier of the stepwise reaction increases by 2.0 kcal/mol compared to the CH_2Se plus unsubstituted gauche-butadiene case. The diradical transition state, **TS6**, is 5.9 kcal/mol higher than the concerted **TS5**. The stability of the diradical intermediate, **7**, relative to the concerted **TS5** decreases significantly so that the diradical becomes 0.8 kcal/mol higher in energy than concerted **TS5**. Recall that in the unsubstituted case the diradical was 3.0 kcal/mol more stable than the concerted transition state structure. Given that the aryl substituents in $Ar_2C{=}Se$, as used in the experiments, do not hinder the formation of the concerted transition structure with *trans,trans*-2,4-hexadiene, we suggest that aryl substitution would not change the predicted relative energetics for the concerted and stepwise pathways determined for the model reactions between *cis−trans*-2,4-hexadiene and unsubstituted H_2CSe. We conclude therefore that the "classical" diradical mechanism is unlikely to operate in the DA reaction of $Ar_2C{=}Se$ with *cis,trans*-2,4-hexadiene. Wilker and Erker have noted[11] that a more complex stepwise mechanism that involves the radical cation cannot be excluded on the basis of their experimental data.

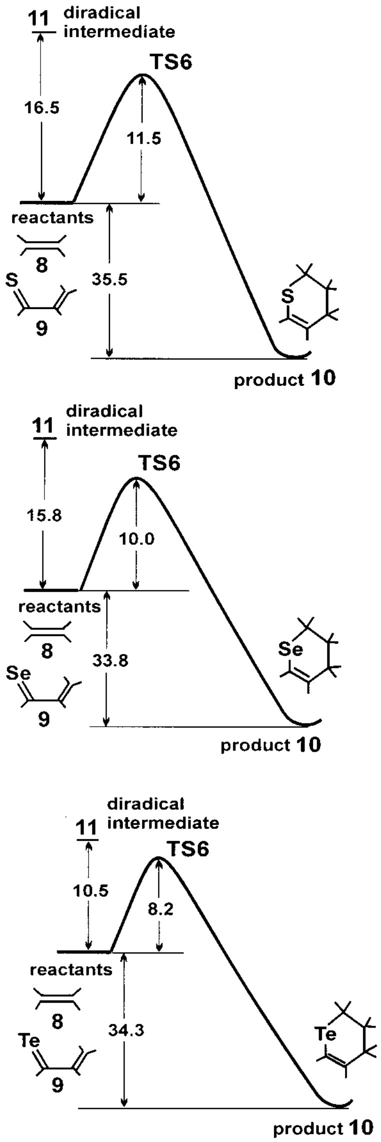

Figure 7. Potential energy profiles for the concerted reaction between ethylene, **8**, and the chalcogenoacroleins, **9** (reaction 5, Scheme 1), as predicted by B3LYP/6-31G(d) for S and B3LYP/LanL2DZ(d) for Se and Te. The relative energies of the biradical intermediates, **11**, also are reported. These energy differences (in kcal/mol) include the zero-point vibrational energy corrections.

Similar to the electronic factors, the steric factors operate in the same direction in both the concerted and diradical mechanisms of the DA reaction. Activation energies are increased for both pathways in the substituted cases although the effect is somewhat greater for the concerted mechanism. Thus, the energy of concert decreases only slightly in sterically hindered case.

3. Reactions of Ethylene with Chalcogenoacroleins. The $HOMO_{diene}{-}LUMO_{dienophile}$ and $HOMO_{dienophile}{-}LUMO_{diene}$ energy gaps for the ethylene plus chalcogenoacrolein partners are greater than for the chalcogenoformaldehydes and butadiene (Figure 1). Thus, the DA reactions between ethylene and the chalcogenoacroleins (reaction 5, Scheme 1) have higher activa-

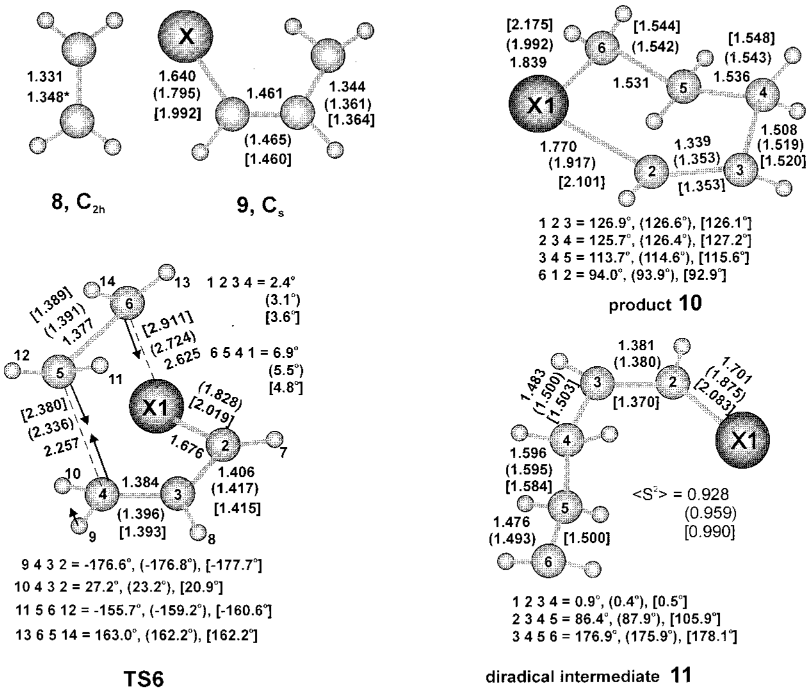

Figure 8. Geometries of the stationary point structures on the concerted pathways and the diradical intermediates for reaction 5 in Scheme 1 as predicted by B3LYP/6-31G(d) for X = S and B3LYP/LanL2DZ(d) for X = Se (values in parentheses) and X = Te [values in square brackets]. For ethylene, the values predicted by the B3LYP/6-31G(d) basis set are plain and with B3LYP/LanL2DZ are marked by an asterisk. Geometries are in Å and deg. For the transition structures, the transition vector is sketched. For the diradicals, the expectation values of S^2 are reported.

tion energies compared to the parent chalcogeno-DA reaction (reaction 2, Scheme 1). For reaction 5, between ethylene and the chalcogeno-butadienes, the $\mathrm{HOMO_{dienophile}}$–$\mathrm{LUMO_{diene}}$ gap is smaller than the $\mathrm{HOMO_{diene}}$–$\mathrm{LUMO_{dienophile}}$ one. Therefore, the cycloaddition of ethylene and chalcogenoacrolein may be attributed to a DA reaction with inverse electron demand (from the dienophile to the diene). The formation of the diradical TS for the ethylene plus chalcogenoacrolein reaction is also a less favorable process compared to the chalcogenoformaldehyde plus butadiene reaction. Electron “uncoupling” in the C═C double bond in the ethylene fragment is a higher energy process than for the chemically less stable C═X (X = S, Se, Te) bonds in the chalcogenoformaldehydes. The potential energy profiles of the concerted DA reactions of ethylene, **8**, with the chalcogenoacroleins, **9**, via the concerted **TS6** to the DA adduct, **10**, and the energies of the corresponding diradical intermediates, **11**, are shown in Figure 7. Selected geometrical features of these structures are presented in Figure 8.

All ethylene plus chalcogenoacrolein reactions have similar exothermicities (ca. 34–36 kcal/mol), which are close to those for the chalcogenoformaldehyde plus butadiene reactions. The concerted pathways are energetically preferable. In accord with the FMO analysis, concerted reactions between ethylene and chalcogenoacroleins have notably higher activation barriers compared to the chalcogenoformaldehydes plus butadiene partners. The barrier decreases only slightly on proceeding from S to Te. Geometries of the concerted transition structures, **TS6**, in Figure 8 correspond to late transition states. The total natural charges on the ethylene fragment in transition structure **TS6** are positive: +0.059, +0.028, and +0.002 for X = S, Se, Te, respectively. These positive charges are entirely consistent with an inverse electron demand DA reaction.

Electronic factors operate in a similar manner for the diradical pathway. The diradical intermediate, **11**, is higher in energy than the concerted **TS6** for all chalcogens. Therefore, the complete diradical path remains higher in energy then concerted one. The expectation values of S^2 for the diradical intermediates, **11**, of 0.928, 0.959, and 0.990 for S, Se, and Te, respectively, are slightly less than the corresponding $\langle S^2 \rangle$ values for the diradical intermediates **3** (Figure 4) and reflect a small decrease in singlet diradical character.

4. A Modified Concerted Mechanism: The Role of a Pre-reaction Complex in the Reactions of Thioformaldehyde with Thioacrolein. We have noted that the low-barrier chalcogeno-DA reaction has an early transition state, with long distances between the interacting diene and dienophile fragments. A decrease of the $\mathrm{HOMO_{diene}}$–$\mathrm{LUMO_{dienophile}}$ gap may modify the detailed mechanism of a concerted DA reaction somewhat due to the formation of a pre-reaction charge-transfer complex. The existence of a pre-reaction complex (PRC) on the pathway for DA reactions between selenocarbonyls substituted with cyano groups, which are strongly electron withdrawing, and butadiene has been proposed previously by Bachrach and Jiang.[6]

Thioformaldehyde and thioacrolein appear to be suitable candidates to form a PRC due to the very small $\mathrm{HOMO_{diene}}$–$\mathrm{LUMO_{dienophile}}$ gap. Two possible orientations for the attack of $H_2C{=}S$ on thioacrolein, (a) one with the C–C and S–S bonds forming and (b) one with C–S bonds forming were considered (reactions 6a and 6b, Scheme 1). Potential energy profiles for these two reactions are shown in Figure 9. Selected geometrical fea-

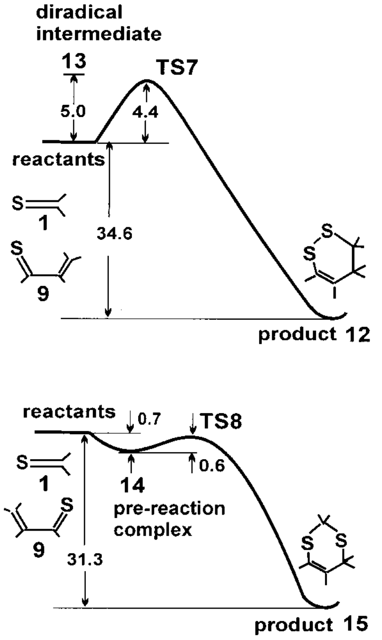

Figure 9. Potential energy profiles for the concerted reaction between thioformaldehyde, **1**, and thioacrolein, **9** (reaction 6, Scheme 1), as predicted with B3LYP/6-31G(d). The relative energy of the biradical intermediate, **13**, also is shown. These energy differences (in kcal/mol) include the zero-point vibrational energy corrections.

tures of the stationary point structures are shown in Figure 10.

The potential energy profile of reaction 6a corresponds to a conventional single-step concerted DA reaction with a low activation barrier of 4.4 kcal/mol. The concerted transition structure, **TS7**, is early, with smaller changes in the geometries of the interacting fragments than for ethylene plus thioacrolein or thioformaldehyde plus butadiene. The diradical intermediate, **13**, is predicted to be very close to but still very slightly, 0.6 kcal/mol, higher in energy than the concerted **TS7**. Therefore, the whole diradical stepwise pathway is at least very slightly energetically less favorable than the concerted one. The predicted geometries of **TS7**, with a long C2$-$C3 distance, correspond to an early transition state. The H_2CS fragment is twisted by 9.8° with respect to the thioacrolein fragment due to a repulsive interaction between the lone-pairs of the sulfur atoms. This factor hinders the formation of any PRC. For the low lying diradical intermediate, **13**, a shorter C5$-$C1 bond and an increase in singlet biradical character compared to the ethylene plus thioacrolein or the thioformaldehyde plus butadiene partners are observed.

The potential energy profile for reaction 6b reveals the change in the concerted mechanism and a flattening of the potential energy surface. A very loose PRC, **14**, forms, with a binding energy of only 0.7 kcal/mol. From this complex, the reaction path leads to the DA adduct, **15**, via the cyclic transition state, **TS8**, with a vanishingly small barrier of 0.6 kcal/mol. The geometry of the PRC, **14**, shows that in the first step of the reaction the formation of the cyclic structure occurs synchronously, with virtually no difference (ca. 0.001 Å) between the C1$-$S6 and S4$-$C5 bond lengths. This synchronicity is destroyed slightly upon the decrease in the distance between the interacting moieties. In transition structure **TS8**, the difference in lengths between the two bonds being formed reaches 0.040 Å. These results are in excellent agreement with the VB interpretation of the DA reaction by Bernardi et al.[2c] The total exchange term that favors asynchronicity in the formation of cyclic structures depends mainly on the distances between the atoms involved in bond making.

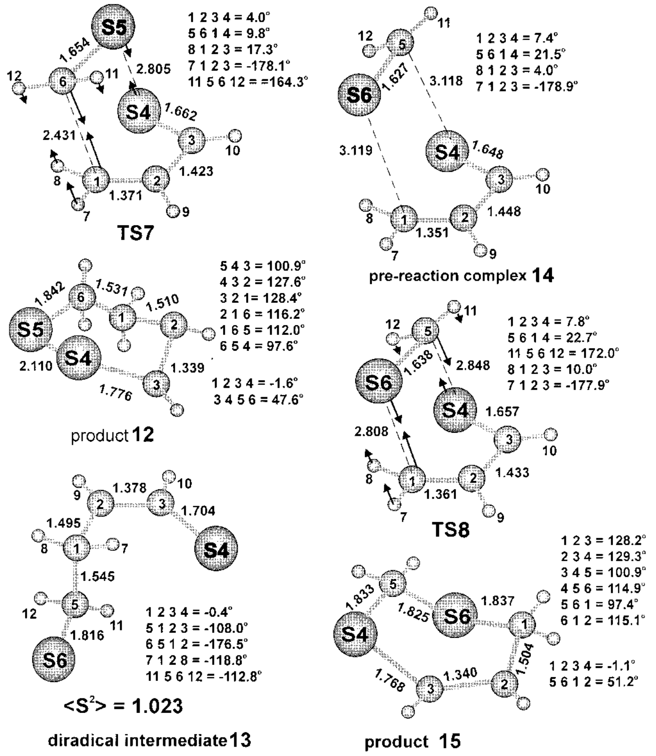

Figure 10. Geometries for the stationary points on the concerted pathways and the diradical intermediate, **13**, for reactions 6a and 6b in Scheme 1 predicted with B3LYP/6-31G(d). Geometries are in Å and deg. For the transition structures, the transition vectors are sketched. For the diradical intermediate, **13**, the expectation value of S^2 is reported.

Conclusions

For all chalcogeno-DA reactions considered, concerted pathways via cyclic transition structures, or via a cyclic pre-reaction complex and a subsequent cyclic "concerted like" transition state, are predicted to be energetically more favorable than diradical stepwise mechanisms. The stability of the diradical intermediate on the stepwise pathway increases on proceeding from S to Te.

The "energy of concert", i.e., the difference between the activation energies of the concerted and diradical transition states of ca. 9 kcal/mol for the chalcogenoaldehydes plus butadiene series, is close to the comparable quantity for the parent DA reaction. It is a very considerable challenge to eliminate or reverse this energy preference by varying electronic or steric factors. When the barrier of the concerted pathway increases (decreases) the barrier of the diradical pathway also increases (decreases) so that the energy of concert remains nearly constant. For the sterically hindered case, an increase in the barrier of the concerted pathway is somewhat greater than that for the diradical path. Thus, the energy of concert decreases slightly but still remains significant. Even for the reaction of selenoformaldehyde and sterically hindered *cis,trans*-2,4-hexadiene, the energy of concert only decreases to 5.9 kcal/mol. Thus, for the sterically hindered case another ion-radical stepwise mechanism may be operative in experiment[11] due to stabilization effects of solvent.

A decrease in the $\mathrm{HOMO_{diene}}-\mathrm{LUMO_{dienophile}}$ gap can modify the concerted mechanism. A pre-reaction charge-transfer complex may precede the cyclic transition structure. This reaction mechanism proceeds almost without an activation barrier.

Acknowledgment. Financial support of this research by the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged.

JO010280G