On the Behavior of α,β-Unsaturated Thioaldehydes and Thioketones in the Diels−Alder Reaction

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α,β-Unsaturated thioaldehydes and thioketones, $R_1CH{=}CH{-}C(=S)R_2$, are prepared in situ by the reaction between the corresponding carbonyl compounds and bis(dimethylaluminum) sulfide. These compounds undergo [4 + 2] self-dimerization reactions in which one molecule serves as the heterodiene component and the other as the dienophile to afford different types of dimeric products depending on the R_1 and R_2: 1,2-dithiin and 1,3-dithiin ($R_1 = R_2 = H$), 1,2-dithiin (R_1 = Ph, R_2 = H, CH_3), or dihydrothiopyran ($R_1 = R_2$ = Ph). These differences in selectivity are explained on the basis of the relative energies evaluated by molecular orbital (MO) calculations at the DFT (density functional theory) level. The calculations show that in the dimerization reaction of thioacrolein (**I**), the head-to-tail (S−C−S bonded) dimers are kinetically more stable by about 5 kcal/mol but slightly thermodynamically unstable by about 2 kcal/mol than the head-to-head (S−S bonded) dimers. The calculations on thiocinnamaldehyde (**IV**) indicate that the dimerization reactions of phenyl-substituted α,β-unsaturated thioaldehydes and thioketones are almost equally controlled by thermodynamic and kinetic factors. These unsaturated thiocarbonyl compounds also function as heterodienes (C=C−C=S) in the cycloaddition reaction with norbornadiene and as dienophiles (C=S) in the reaction with cyclopentadiene.

Introduction

The biological importance of the disulfide bridge (S−S) is well-recognized. It is one of the two major covalent linkages between amino acids in polypeptides and proteins and usually stabilizes folded proteins, in part, by restricting the conformational flexibility of the unstable unfolded state. The knowledge and understanding of the structural features and physical and chemical properties of S−S bonding molecules are expected to be useful in the alteration or protection of the functional properties of enzymatic complexes and proteins.

The hetero Diels−Alder reaction is a very useful method for the preparation of six-member heterocyclic (including S−S bonding) compounds and has been applied to natural product synthesis.[1] As of now, many dienes and dienophiles involving heteroatoms such as phosphorus, silicon, oxygen, sulfur, and selenium have been investigated. Since the 1980s, carbon−chalcogen double bonds (C=E, E is S, Se, or Te) have been well-recognized as reactive heterodienophiles.[2] During the course of our studies of carbon−chalcogen doubly bonded compounds, we have reported the direct conversion of a carbonyl function to thio-, seleno-, and tellurocarbonyl groups with the use of bis(dimethylaluminum) chalcogenides, $(Me_2Al)_2E$, where E is S, Se, or Te.[3] Using this procedure, we have successfully synthesized α,β-unsaturated selenocarbonyl compounds and have elucidated their behavior as heterodienes and dienophiles.[4] A few more reports on selenadienes have appeared in the literature.[5] In the present work we have investigated the synthesis of α,β-unsaturated thioaldehydes and thioketones and

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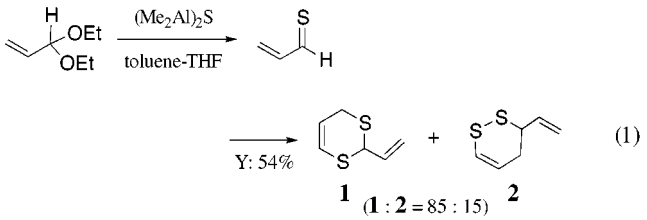
their behavior in the Diels−Alder reaction. These sulfur compounds, $R_1CH{=}CH{-}C(=S)R_2$, function as heterodienes and/or dienophiles in [4 + 2] dimerization reactions to afford different types of dimeric products depending on R_1 and R_2. As expected, they also function as heterodienes (C=C−C=S) in the cycloaddition reaction with norbornadiene and as dienophiles (C=S) in the reaction with cyclopentadiene. Theoretical calculations have been carried out at the DFT level in order to explain the selectivity observed experimentally in the dimerization reactions. For α,β-unsaturated aldehydes and ketones, it is well-recognized that their [4 + 2] dimerization reaction takes place only between the C=C 2π dienophiles and C=C−C=O 4π heterodienes.[6] In contrast, α,β-unsaturated selenoaldehydes and selenoketones[4,5] and most of the sulfur analogues[7] undergo [4 + 2] dimerization reaction in which C=Se or C=S serves as the 2π dienophiles. Yet, no example of α,β-unsaturated telluroaldehydes or telluroketones has appeared. In this paper we report a general understanding and an underlying theory for the behavior of α,β-unsaturated thioaldehydes and thioketones, though some of these compounds have been studied previously.[1,7]

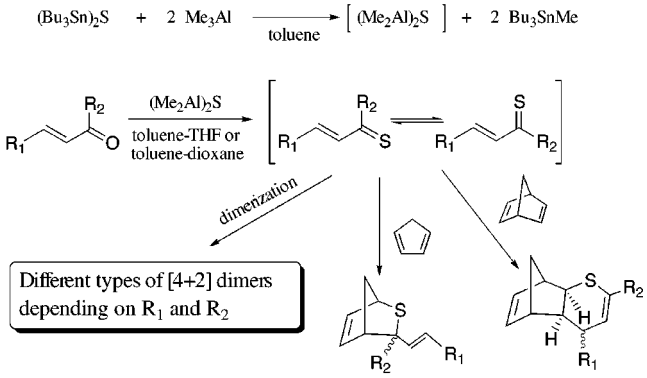
Results and Discussion

Most of α,β-unsaturated thioaldehydes and thioketones were prepared in situ by the reaction between the corresponding α,β-unsaturated carbonyl compounds and bis(dimethylaluminum) sulfide ($Me_2AlSAlMe_2$) and simultaneously subjected to [4 + 2] dimerization or cycloaddition reactions with norbornadiene or cyclopentadiene (Scheme 1). In the case of thioacrolein (eq 1),



(1)

Scheme 1



acrolein diethyl acetal was used instead of acrolein (volatile) in order to improve the yields of products. We have already utilized acetal derivatives including acrolein diethyl acetal as starting material in the preparation of selenocarbonyl compounds.[3d,4b] Bis(dimethylaluminum) sulfide was prepared by the Sn−Al transmetalation reaction, a similar manner as that used for the preparation of selenium analogue.[3f,4] Ishii et al. reported a related compound, bis(diethylaluminum) sulfide ($Et_2AlSAlEt_2$), prepared from the reaction of triethylaluminum with hydrogen sulfide, to be useful in the conversion of carbonyl compounds to thiocarbonyls.[8]

[4 + 2] Dimerization of α,β-Unsaturated Thioaldehydes and Thioketones. α,β-Unsaturated thioaldehydes and thioketones underwent [4 + 2] dimerization reactions with one molecule as the diene partner (4π) and the other as the dienophile (2π). The structures of all products were characterized by NMR (^1H, ^{13}C) and mass spectra (also by elemental analysis and single-crystal X-ray diffraction when necessary). Different substances have shown different selectivities in their dimerization reactions. Thioacrolein gave a mixture of "head-to-tail" dimer **1** (2-vinyl-4*H*-1,3-dithiin) and "head-to-head" dimer **2** (3-vinyl-3,4-dihydro-1,2-dithiin) in the ratio of **1**:**2** = 85:15 (eq 1). In the literature,[7i−l] it has been reported that thioacrolein undergoes [4 + 2] dimerization to give a mixture of these two type dimers. Both **1** and **2** have been isolated from garlic and are known as biologically important compounds which display antithrombotic activity.[9] The dimerizations of thiocinnamaldehyde and 4-phenyl-3-buten-2-thione took place in the head-to-head orientation to give only S−S bonded dimers (eqs 2 and 3). This regioselectivity is the same as that observed for selenium analogues.[4] In the case of thiochalcon (eq 4), however, the C=C bond acted as the 2π dienophile to yield a different type of dimer (**5**) in which a C=S bond was not involved in the reaction. Our explanation is that, in thiochalcon [PhCH=CH−C(=S)Ph], the C=S is greatly stabilized by the resonance effect and steric hindrance of the Ph group. Also the C=C bond is activated by the PhC=S group, so that *not* C=S *but* C=C underwent reaction as the 2π dienophile. This type of dimerization has been described previously.[7c,e] In addition to the formation of dimer **5**, thiochalcon also underwent reaction

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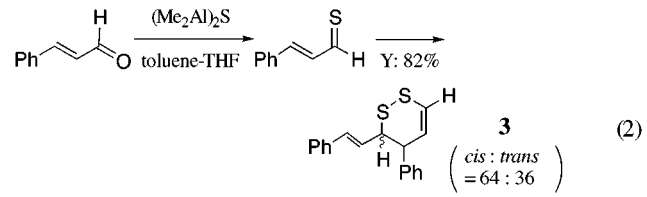
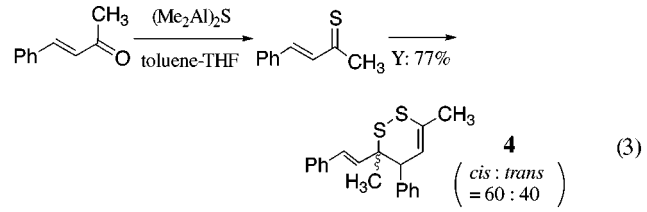
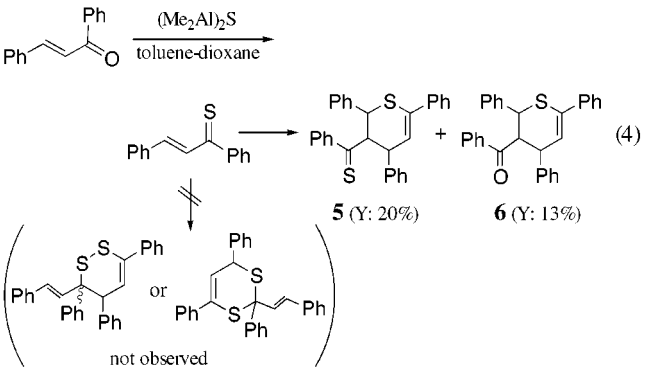
Table 1. NMR Data and Melting Points of Compounds 5 and 6

	5	6
^{1}H NMR (ppm; Hz)	6.90–8.00 (m, 20H, 4xPh), 6.34 (d, $J_{4,5}$= 6.7, 1H, H_5), 5.28 (dd, $J_{2,3}$ = 11.2, $J_{3,4}$ = 4.0, 1H, H_3), 5.06 (d, $J_{2,3}$ = 11.2, 1H, H_2), 4.04 (dd, $J_{4,5}$ = 6.7, $J_{3,4}$ = 4.0, 1H, H_4)	6.90–8.00 (m, 20H, 4xPh), 6.31 (d, $J_{4,5}$ = 6.5, 1H, H_5), 4.84 (d, $J_{2,3}$ = 11.2, 1H, H_2), 4.68 (dd, $J_{2,3}$ = 11.2, $J_{3,4}$ = 4.3, 1H, H_3), 4.21 (dd, $J_{4,5}$ = 6.5, $J_{3,4}$ = 4.3, 1H, H_4)
^{13}C NMR (ppm)	222.4 (C=S), 59.3, 46.6, 45.9 (Ph and C=C carbons are not listed.)	198.2 (C=O), 139.5, 139.3, 138.8, 137.2, 136.0, 133.2, 129.5, 128.9, 128.6, 128.5, 128.4, 128.1, 128.0, 127.6, 127.5, 126.3, 119.8, 50.7, 44.8, 42.7
mp (°C)	130.0–133.0 (blue solid)	187.5–188.5 (light yellow solid)







with the C=C bond of chalcon (the starting material) to give compound **6** as the byproduct. It was observed that the ^{1}H NMR spectra of compounds **5** and **6** are very similar, each proton in the same position of these two compounds resonates with almost the same coupling constants, but their chemical shifts are slightly different (Table 1). This can be explained in that they have the same dihydrothiopyran structure with the only difference being that either PhC=S or PhC=O is the substituent on C_3. The coupling constants of $J_{2,3}$ = 11.2 Hz and $J_{3,4}$ = 4.0 or 4.3 Hz indicate that proton H_3 is in the trans relationship with H_2 and in cis with H_4 in both compounds **5** and **6** (Figure 1). The similarity in the NMR data of **5** and **6** suggests that they have similar structures as shown in Figure 1. When the mixture of dimer **5** and chalcon was heated in benzene as described in the literature,[7f] both compound **6** and its regioisomer **7** (the latter as the major product) were obtained (eq 5). However, under the conditions shown in eq 4, only compound **6** was formed as the cycloaddition product between thiochalcon and chalcon. This is supported by the ^{1}H NMR measurement for the reaction mixture before separation and purification in which the resonance of **7** was not observed. At this point, it is unclear what causes these differences. To establish completely the

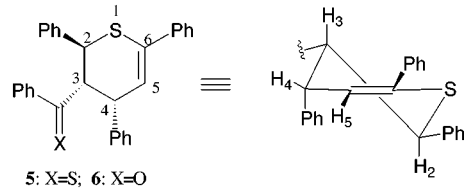
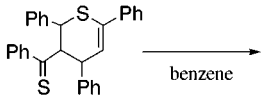
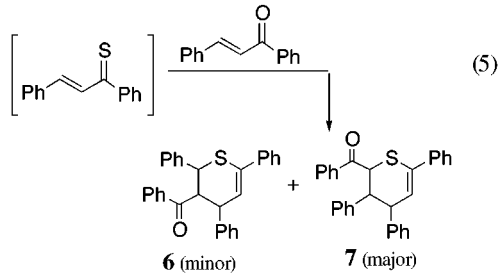


Figure 1. Conformation of compounds **5** and **6**.

structure of compound **6**, a single-crystal structure determination was carried out.





Crystal Structure of Compound 6.[10] The ORTEP drawing is shown in Figure 2, and the selected bond lengths and bond angles are listed in Table 2. As can be seen in Figure 2, the dihydrothiopyran moiety in compound **6** adopts a half-chair conformation, and the benzoyl group on C(2) is in a cis relationship with the phenyl on C(3) and both are trans relative to the phenyl on C(1).

In the reaction of 2-furaldehyde with bis(dimethylaluminum) sulfide, no identifiable product was obtained (Scheme 2). However, the reaction mixture was clear blue in color (a typical character of thiocarbonyl group), which indicates the formation of 2-thioformylfuran. This was confirmed experimentally as follows. To the reaction mixture (a clear blue solution), the addition of norbornadiene gave the corresponding adduct (**8**), where 2-thioformylfuran behaved as a heterodiene (C=C–C=S). On the other hand, the addition of cyclopentadiene resulted in the formation of the Diels–Alder adduct (**9**) in which the thiocarbonyl (C=S) functioned as a dienophile. The

(10) Crystal data for **6**: $C_{30}H_{24}OS$, MW = 432.55, a colorless plate, monoclinic, space group $P2_1/c$, a = 18.265(4) Å, b = 12.308(3) Å, c = 10.377(2) Å, β = 97.76(3)°, V = 2311.4(8) Å^3, Z = 4, D_{calcd} = 1.243 g/cm^3, R1 [$I > 2\theta(I)$] = 0.0701, wR2 [$I > 2\theta(I)$] = 0.1463, R1 (all data) = 0.1177, wR2 (all data) = 0.1724. Preliminary examination and data collection were performed on a Siemens P4 single-crystal diffractometer (oriented graphite monochromator; Mo Kα radiation, wavelength 0.71073 Å) at 298(2) K. The structure was solved by direct methods[11] and refined by full-matrix least-squares methods.[12]

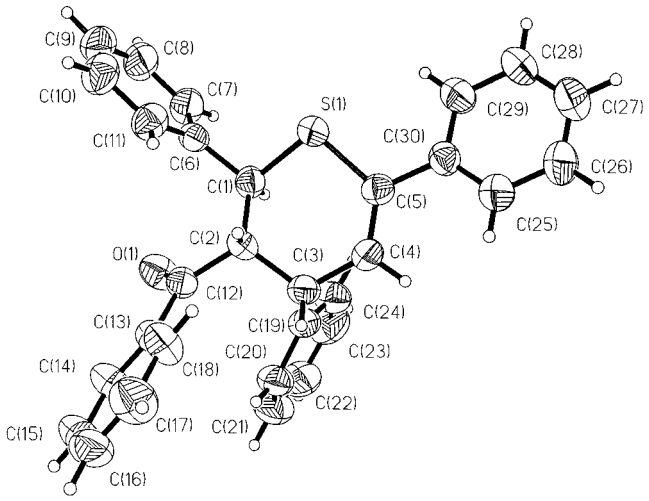
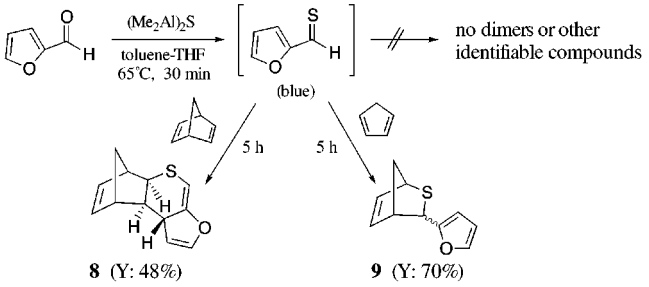


Figure 2. Crystal structure of **6**.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 6

S(1)−C(1)	1.828(4)	C(4)−C(5)	1.338(5)
S(1)−C(5)	1.766(4)	C(1)−C(6)	1.509(5)
C(1)−C(2)	1.525(5)	C(2)−C(12)	1.529(5)
C(2)−C(3)	1.563(5)	C(3)−C(19)	1.525(5)
C(3)−C(4)	1.499(5)	C(5)−C(30)	1.487(5)
C(1)−S(1)−C(5)	101.42(17)	C(4)−C(3)−C(19)	111.1(3)
C(6)−C(1)−C(2)	119.0(3)	C(4)−C(3)−C(2)	112.8(3)
C(6)C(1)−S(1)	103.8(2)	C(2)−C(3)−C(19)	113.3(3)
C(2)−C(1)−S(1)	108.6(2)	C(4)−C(5)−S(1)	122.5(3)
C(1)−C(2)−C(3)	111.3(3)	C(4)−C(5)−C(30)	124.0(3)
C(1)−C(2)−C(12)	111.8(3)	S(1)−C(5)−C(30)	113.5(3)
C(3)−C(2)−C(12)	109.9(3)	C(3)−C(4)−C(5)	128.5(3)

Scheme 2



isolation and characterization of compound **9** have been reported previously.[13]

Calculations. To elucidate the regio- and stereoselectivity of [4 + 2] dimerization of α,β-unsaturated thioaldehydes and thioketones, theoretical calculations were performed on the model compounds, thioacrolein (**I**, CH_2=CH−CH=S) and thiocinnamaldehyde (**IV**, PhCH=CH−CH=S). Density functional theory (DFT),[14] specifically the Becke three-parameter hybrid exchange functional[15] and the Lee−Yang−Parr correlation functional (B3LYP),[16] was used to carry out geometric optimizations of the reactants, transition states, and products along the possible reaction paths as shown in Scheme 3. It can be seen that *trans*-**I** or *trans*-**IV** (here, representing *s-trans*-**I** or *s-trans*-**IV**, respectively) initially rotates through the transition state ($\mathbf{TS_I}$ or $\mathbf{TS_{IV}}$) to the respective cis (*s-cis*) form (*cis*-**I** or *cis*-**IV**). Then [4 + 2] dimerization occurs via head-to-head and head-to-tail orientations to give the dimers *cis*-**II**, *trans*-**II**, *cis*-**V**, *trans*-**V**, *cis*-**III**, *trans*-**III**, *cis*-**VI**, and *trans*-**VI**. Although **II** and **III** are monosubstituted, because the methylene protons (CH_2, originally from *cis*-**I**) on the six-membered ring are different in both transition state and products, we still use *cis*-**II**, *trans*-**II**, *cis*-**III**, and *trans*-**III** in order to be consistent with other compounds such as **V** and **VI**.

The DFT-calculated stationary points and energy profiles of [4 + 2] dimerization of **I** are shown in Figures 3 and 4. DFT relative energies of the reactions are summarized in Table 3. The rotation from the *s-trans*-thioacrolein to the *s-cis* form is endothermic by 3.0 kcal/mol with a barrier of 9.3 kcal/mol. The rotational transition state $\mathbf{TS_I}$ has a twist of 85.3° with respect to planar *trans*-**I** or *cis*-**I**. Since both the C=S and C=C orbitals of *trans*-**I** can act as a 2π dienophile to react with *cis*-**I**, it is necessary to investigate the regioselectivity. Generally, the regioselectivity of [4 + 2] dimerization can be accounted for by the corresponding natural bond orbital (NBO) π electron density and π orbital energy of *trans*-**I** and *cis*-**I**, which are illustrated in Table 4.[17] For both *trans*-**I** and *cis*-**I**, the π_{S1-C2} orbital has larger π electron density than the π_{C3-C4} orbital, and the π_{S1-C2} orbital is higher lying than the π_{C3-C4} orbital, whereas the π^*_{S1-C2} orbital is lower lying than the π^*_{C3-C4} orbital. Thus, the C=S orbital of *trans*-**I** is favored to act as the 2π dienophile over the C=C orbital in [4 + 2] Diels−Alder reaction with a 4π diene. The major contribution to the stabilization of the dimer compounds arises from the interactions between the occupied $\pi_{S1'-C2'}$ orbital of *cis*-**I** and the unoccupied π^*_{S1-C2} orbital of *trans*-**I** and between the occupied π_{S1-C2} orbital of *trans*-**I** and the unoccupied $\pi^*_{S1'-C2'}$ orbital of *cis*-**I** as shown in Scheme 4.

The B3LYP-optimized geometries for dimerization of CH_2=CH−CH=S show that, among the head-to-head and head-to-tail type dimeric products, *cis*-**II**, *cis*-**III**, and *trans*-**III** prefer the "half-chair" (puckered) conformation, while *trans*-**II** favors the "boat" conformation (Figure 3). The $S_1-S_{1'}$ distances in head-to-head dimers *cis*-**II** and *trans*-**II** are shortened by 17−20% as compared to the values in transition states ($\mathbf{TS}_{cis-II}$ and $\mathbf{TS}_{trans-III}$). This is much smaller than the $C_2-C_{4'}$ distance change (34%). Clearly, the S−S bond forms in the early stage of the head-to-head dimerization, while the C−C bond forms in the later stage. Also, the $S_1-C_{4'}$ distances in the head-to-tail dimers *cis*-**III** and *trans*-**III** are shortened by 24−25% as compared to the values in transition states ($\mathbf{TS}_{cis-III}$ and $\mathbf{TS}_{trans-III}$), while the $S_{1'}-C_2$ distances are shortened by 33−36%. Thus, the formations of the two new bonds in the dimerization reactions are not completely synchronous. As shown in Figure 4, the head-to-head dimerization reactions between *trans*-**I** and *cis*-**I**, which give dimers *cis*-**II** and *trans*-**II** through transition

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(12) Sheldrick, G. M. SHELXS-93 Program for Crystal Structure Refinement; Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Gottingen, Germany, 1993.

(13) Segi, M.; Nakajima, T.; Suga, S.; Murai, S.; Ryu, I.; Ogawa, A.; Sonoda, N. *J. Am. Chem. Soc.* **1988**, *110*, 1976.

(14) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, U.K., 1989.

(15) (a) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(16) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785.

(17) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

Scheme 3

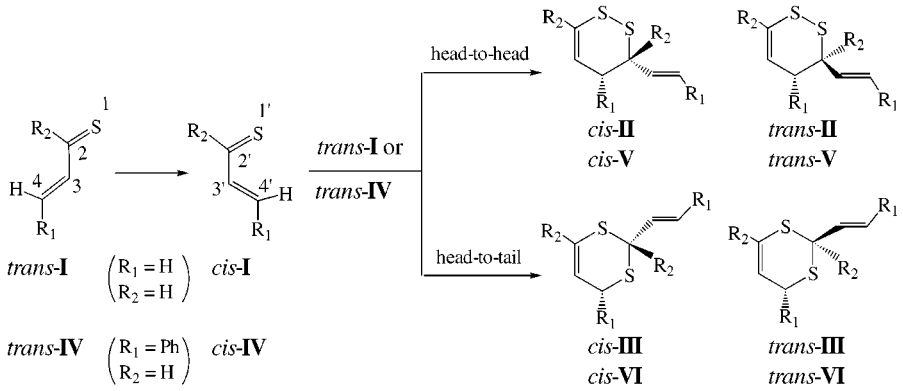


Table 3. Relative Energies (Δ*E*) of [4 + 2] Dimerization of Thioacrolein Calculated Using B3LYP

structure	Δ*E* (kcal/mol)[a]	structure	Δ*E* (kcal/mol)[a]
TS$_{\mathbf{I}}$ + *trans*−**I**	9.25	*trans*-**I** + *cis*-**I**	2.95
TS$_{cis-\mathbf{II}}$	14.98	*cis*-**II**	−16.58
TS$_{trans-\mathbf{II}}$	14.20	*trans*-**II**	−14.86
TS$_{cis-\mathbf{III}}$	9.34	*cis*-**III**	−14.29
TS$_{trans-\mathbf{III}}$	8.92	*trans*-**III**	−13.17

[a] All energies are relative to *trans*-**I** + *trans*-**I** (0.00 kcal/mol), and the BSSE and ZPVE corrections are included.

Table 4. The NBO π Electron Density (e) and π Orbital Energy (a.u.) Of *trans*-I, *cis*-I, *trans*-IV, and *cis*-IV

	π electron density (e)			
	S_1	C_2	C_3	C_4
trans-**I**	1.205	0.760	1.006	0.881
cis-**I**	1.219	0.755	1.060	0.833
trans-**IV**	1.234	0.728	1.000	0.820
cis-**IV**	1.257	0.715	1.059	0.763

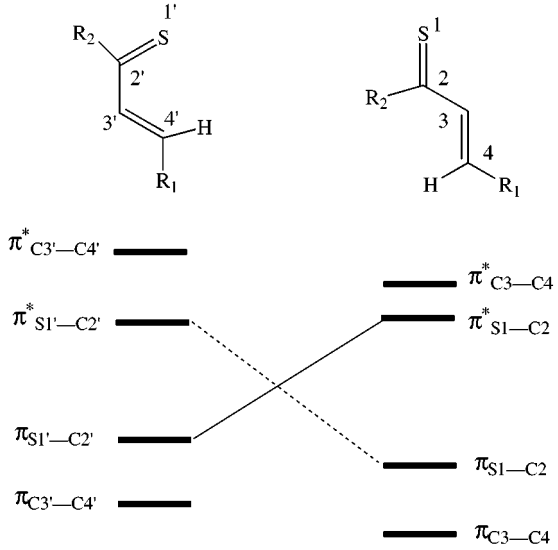
	π orbital energy (a.u.)[a]			
	π_{S1-C2}	π_{C3-C4}	π^*_{S1-C2}	π^*_{C3-C4}
trans-**I**	−0.42401	−0.44879	0.13219	0.22832
cis-**I**	−0.41945	−0.44398	0.13381	0.23079
trans-**IV**	−0.41227	−0.47164	0.13485	0.23719
cis-**IV**	−0.40707	−0.46595	0.13632	0.24299

[a] Second-order perturbation energy is included.

states **TS**$_{cis-\mathbf{II}}$ and **TS**$_{trans-\mathbf{II}}$, are exothermic by 19.6 and 17.9 kcal/mol with the barriers of 12.0 and 11.2 kcal/mol, respectively. The formations of head-to-tail type dimers *cis*-**III** and *trans*-**III**, through the transition states **TS**$_{cis-\mathbf{III}}$ and **TS**$_{trans-\mathbf{III}}$, are exothermic by 17.3 and 16.2 kcal/mol with the barriers of 6.3 and 5.9 kcal/mol, respectively. Thermodynamically, the head-to-head dimerization is slightly favored over the head-to-tail dimerization by about 2 kcal/mol. However, the latter is more kinetically favorable than the former by about 5 kcal/mol. These results suggest that at least the [4 + 2] dimerization of thioacrolein is a kinetically controlled process to give head-to-tail oriented dimer selectively. This is consistent with the experimental observations that the head-to-tail type dimer is major product despite its lesser thermodynamic stability.

Natural bond orbital (NBO) π electron density and π orbital energy of *trans*-**IV** and *cis*-**IV** are shown in Table 4. One can find that the phenyl substitution leads to an increase of electron density on the S atom and raises the energy of both π_{S1-C2} and $\pi_{S1'-C2'}$ orbitals by nearly 3% in comparison with the value for thioacrolein (**I**). This should enhance the reactivity of [4 + 2] dimerization of

Scheme 4



IV relative to **I**. The DFT-calculated stationary points and energy profiles of [4 + 2] dimerization of **IV** are shown in Figures 5 and 6. DFT relative energies of the reactions are summarized in Table 5. Since no head-to-tail dimers are obtained experimentally, only one isomer (*trans*-**VI**) is involved in calculations for comparison with head-to-head dimers (*cis*-**V**, *trans*-**V**).

As shown in Figures 5 and 6, the rotation from *trans*-**IV** through **TS**$_{\mathbf{IV}}$ to *cis*-**IV** is endothermic by 2.8 kcal/mol with a barrier of 12.6 kcal/mol. The rotational transition state **TS**$_{\mathbf{IV}}$ has a twist of 86.9° with respect to planar *trans*-**IV** or *cis*-**IV**. In comparison with the rotation of *trans*-**I** to *cis*-**I**, the rotation barrier of *trans*-**IV** to *cis*-**IV** is higher by about 3 kcal/mol because of the stronger aromaticity of thiocinnamaldehyde. The shorter distances of $S_1-S_{1'}$ (in **TS**$_{cis-\mathbf{V}}$) and $S_1-C_{4'}$ (in **TS**$_{trans-\mathbf{VI}}$) reveal that the [4 + 2] dimerization of **IV** is more synchronous than that of thioacrolein (**I**). In comparison with the case of **I**, the head-to-head dimerization reaction barriers from **IV** to *cis*-**V** and *trans*-**V** slightly decrease, whereas the head-to-tail dimerization reaction barrier from **IV** to *trans*-**VI** slightly increases. Although the phenyl substitution should enhance the reactivity of **IV** relative to **I**, the [4 + 2] dimerization between *trans*-**IV** and *cis*-**IV** is less exothermic by about 10 kcal/mol than that of *trans*-**I** and *cis*-**I**. Clearly, the steric hindrance in the diene (*cis*-**IV**) actually reduces the reactivity of **IV** in the [4 + 2] dimerization. As shown in Figure 6, the head-to-head dimerization reactions between *trans*-**IV** and *cis*-**IV**,

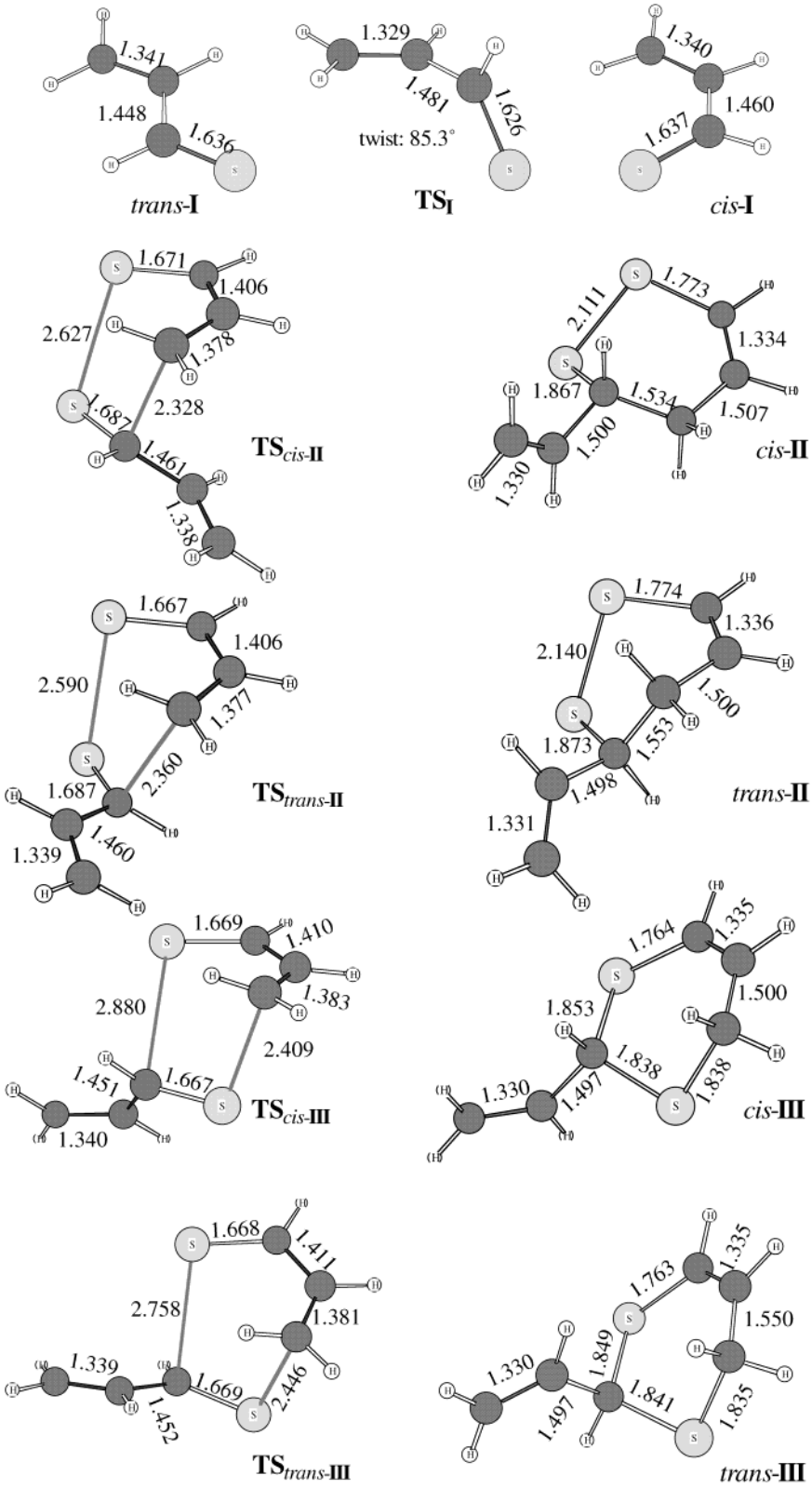


Figure 3. The B3LYP-optimized geometries along the reaction pathways of [4 + 2] dimerization of thioacrolein through intermediates (*trans*-**I** and *cis*-**I**) and transition states (**TS$_{I}$**, **TS$_{cis-II}$**, **TS$_{trans-II}$**, **TS$_{cis-III}$**, and **TS$_{trans-III}$**) to products (*cis*-**II**, *trans*-**II**, *cis*-**III**, and *trans*-**III**).

which give dimers (*cis*-**V**, *trans*-**V**) through transition states **TS$_{cis-V}$** and **TS$_{trans-V}$**, are exothermic by 9.1 and 7.3 kcal/mol with the barriers of 11.3 and 11.0 kcal/mol, respectively. The formation of head-to-tail type dimer (*trans*-**VI**), through the transition state **TS$_{trans-VI}$**, is exothermic by 7.1 kcal/mol with the barrier of 7.9 kcal/mol. The route from **IV** to *cis*-**V** is more exothermic by about 2 kcal/mol than that to *trans*-**V** and *trans*-**VI**. But the reaction barrier of head-to-tail pathway to *trans*-**VI** is lower by about 3 kcal/mol than that of head-to-head pathway to *cis*-**V** and *trans*-**V**. The calculations indicate that the [4 + 2] dimerization of phenyl-substituted α,β-

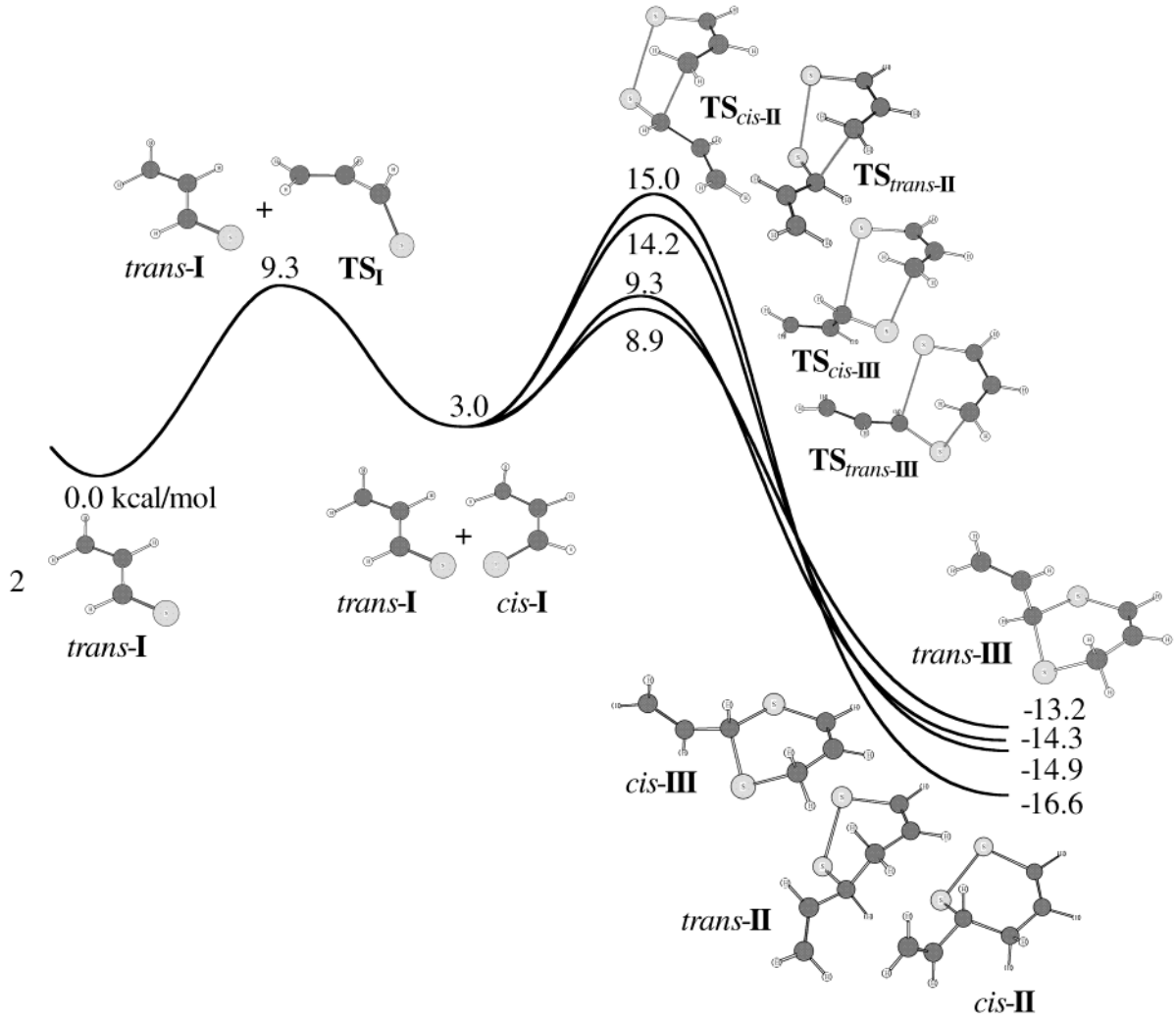


Figure 4. The B3LYP energy profiles along the reaction pathways of [4 + 2] dimerization of thioacrolein through intermediates (*trans*-**I**, *cis*-**I**) and transition states (**TS$_I$**, **TS$_{cis-II}$**, **TS$_{trans-II}$**, **TS$_{cis-III}$**, and **TS$_{trans-III}$**) to products (*cis*-**II**, *trans*-**II**, *cis*-**III**, and *trans*-**III**).

unsaturated thioaldehydes or thioketones is controlled by both thermodynamic and kinetic factors. Because the [4 + 2] dimerization reaction is reversible (Diels−Alder type reaction), there may exist an equilibrium between head-to-head and head-to-tail dimers. The equilibrium finally tends to yield the thermodynamically more stable head-to-head type products under the experimental conditions. This is consistent with the experimental observations that the head-to-head type dimers are major products, and the cis isomer is somewhat favored over the trans isomer.

Cycloaddition Reactions of α,*β*-Unsaturated Thioaldehydes and Thioketones with Norbornadiene or Cyclopentadiene. The results described above have prompted an investigation of the reactions of α,*β*-unsaturated thioaldehydes and thioketones with norbornadiene (a dienophile) and cyclopentadiene (an enophile). In the presence of excess norbornadiene, the reaction of 2-furaldehyde with $(Me_2Al)_2S$ at 65 °C afforded the Diels−Alder adduct (**8**) of 2-thioformylfuran and norbornadiene as the sole isomeric product in 50% yield (Table 6, entry 1). As similarly observed for the selenium analogue,[4b] when the reaction mixture or the isolated product **8** was treated with aqueous HCl (pH 1), the rearomatized compound **11** was obtained (entry 3). In the cases of 2-thioformylthiophene and 2-thioacetylfuran, the cycloaddition products (**10**, **12**) were obtained in moderate yields (entries 2 and 4). When open-chain α,*β*-unsaturated carbonyl compounds were used as the starting material, thioacrolein and thiocinnamaldehyde yielded their [4 + 2] dimers predominantly (entries 5 and 6), while 4-phenyl-3-buten-2-thione gave only its cycloadduct (**15**) with norbornadiene (entry 7). The structures of all these compounds have been determined by NMR, mass spectrometry, and elemental analysis. In the same manner as observed for the selenium analogues,[4] all cycloadducts of α,*β*-unsaturated thiocarbonyls with norbornadiene have the exo configuration. The stereochemistry has been revealed from the NMR spectra. For example (Scheme 5), in the ^{1}H NMR spectrum of compound **8**, the large coupling constant between protons H_9 and H_{10} (J = 10.1 Hz) suggests they are in the trans relationship, and the "W" form long-distance couplings of H_2-H_{14b} (J = 1.8 Hz) and $H_{10}-H_{14b}$ (J = 1.5 Hz) indicate the exo configuration. The exo configuration is also supported by the fact that in its ^{13}C NMR spectrum the resonance of the bridge carbon (C_{14}, δ 43.6) is shifted upfield 5.2 ppm compared with the carbon (δ 48.8) in the same position

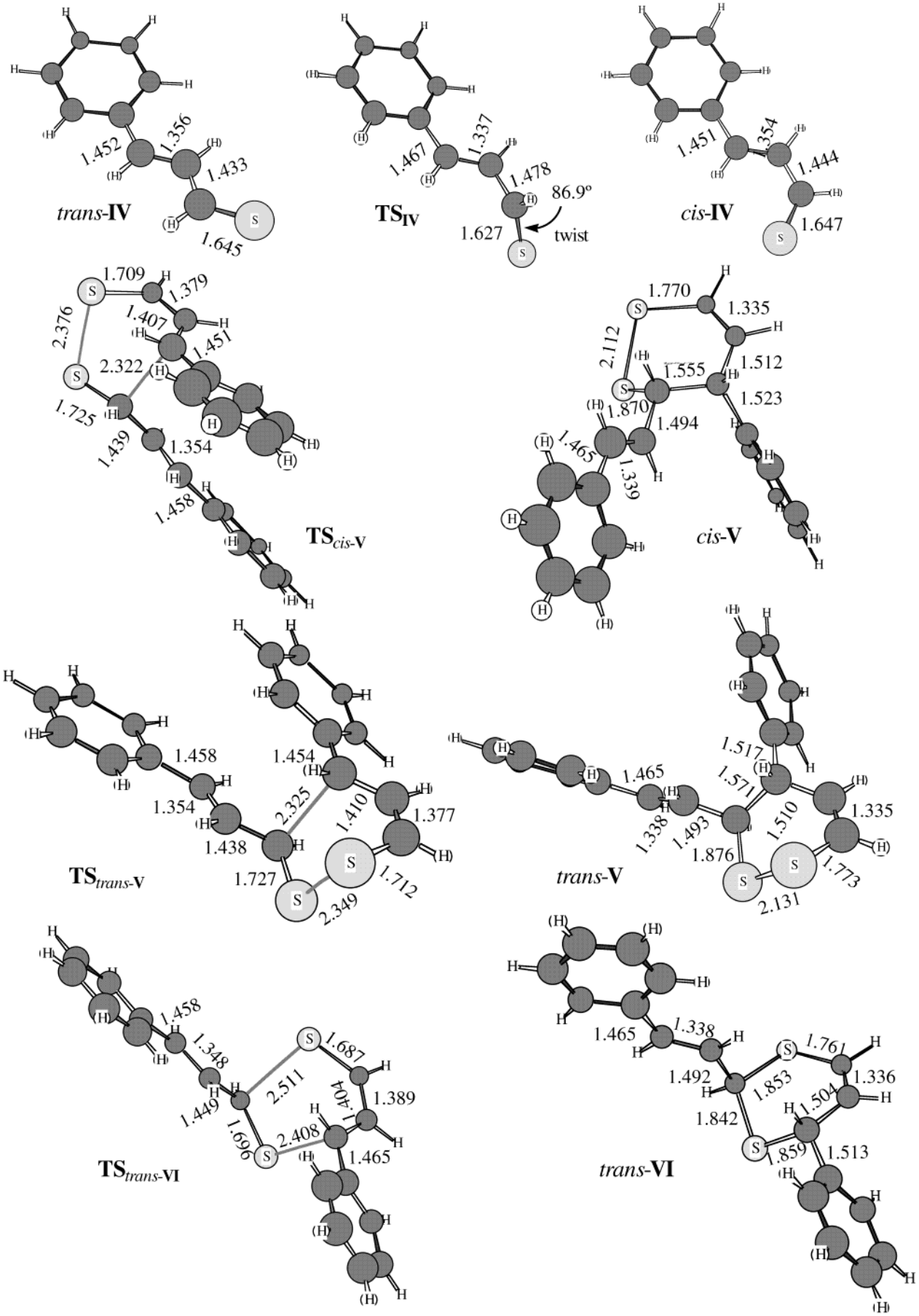


Figure 5. The B3LYP-optimized geometries along the reaction pathways of [4 + 2] dimerization of thiocinnamaldehyde through intermediates (*trans*-**IV**, *cis*-**IV**) and transition states (**TS$_{IV}$**, **TS$_{cis-V}$**, **TS$_{trans-V}$**, and **TS$_{trans-VI}$**) to products (*cis*-**V**, *trans*-**V**, and *trans*-**VI**).

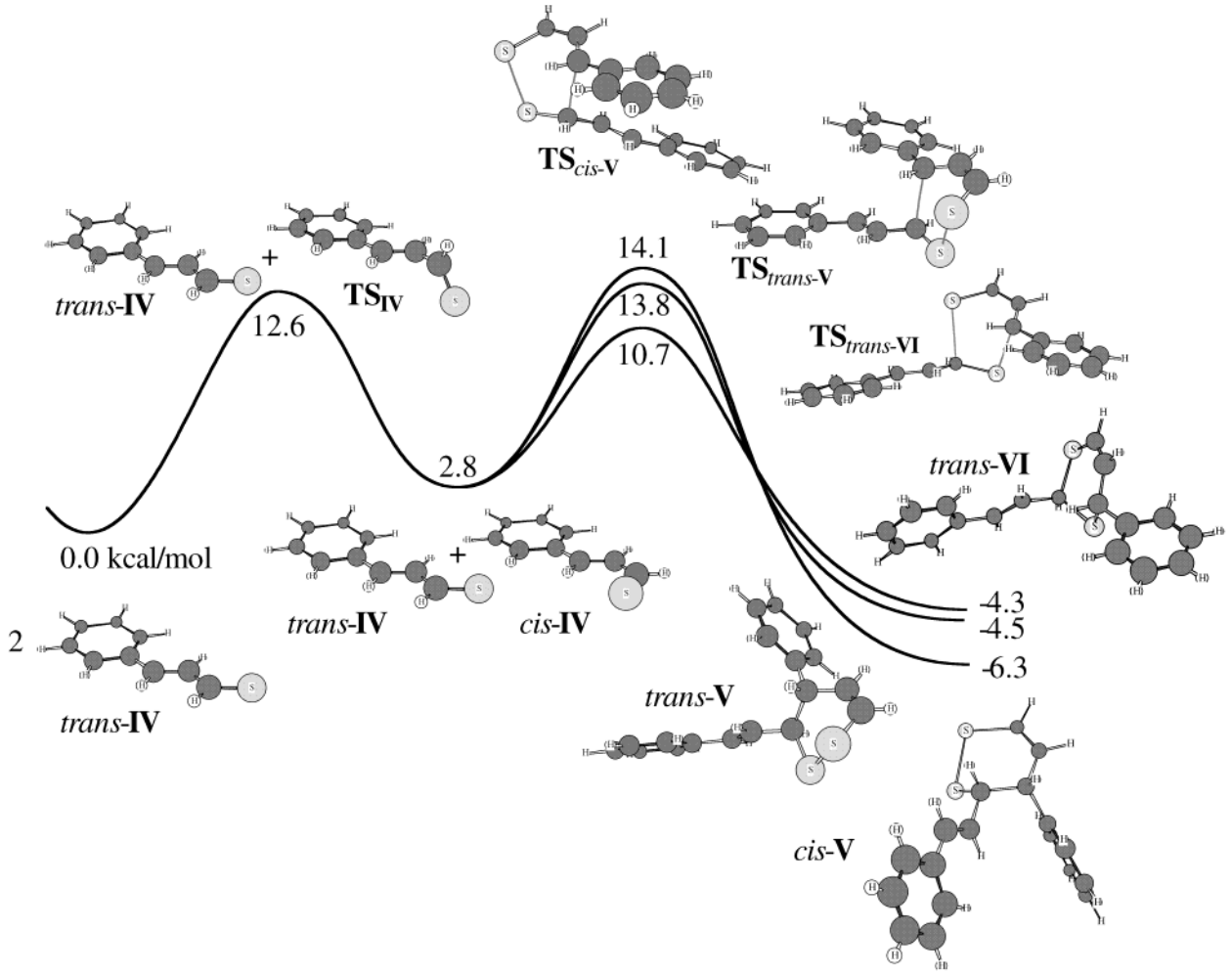


Figure 6. The B3LYP energy profiles along the reaction pathways of [4 + 2] dimerization of thiocinnamaldehyde through intermediates (*trans*-**IV**, *cis*-**IV**) and transition states (**TS$_{IV}$**, **TS$_{cis-V}$**, **TS$_{trans-V}$**, and **TS$_{trans-VI}$**) to products (*cis*-**V**, *trans*-**V**, and *trans*-**VI**).

Table 5. Relative Energies (Δ*E*) of [4 + 2] Dimerization of Thiocinnamaldehyde Calculated Using B3LYP

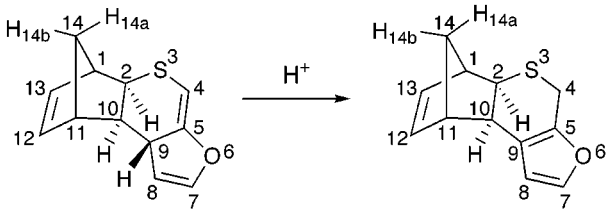
structure	Δ*E* (kcal/mol)[a]	structure	Δ*E* (kcal/mol)[a]
TS$_{IV}$ + *trans*−**IV**	12.62	*trans*-**IV** + *cis*-**IV**	2.78
TS$_{cis-V}$	14.06	*cis*-**V**	−6.26
TS$_{trans-V}$	13.77	*trans*-**V**	−4.51
TS$_{trans-VI}$	10.70	*trans*-**VI**	−4.26

[a] All energies are relative to *trans*-**IV** + *trans*-**IV** (0.00 kcal/mol), and the BSSE and ZPVE corrections are included.

of norbornene.[18] Ohmura and Motoki have reported the same type of reaction between aromatic thioketones and norbornene in which exo configuration products were obtained as well.[7g] For the rearomatized compound **11**, in the ^{1}H NMR spectrum, protons H_7 (δ 7.25) and H_8 (δ 6.32) appeared as a doublet due to the disappearance of H_9. Two doublets at δ3.63 and 3.55 with a large coupling of J = 15.6 Hz arise from the methylene protons (CH_2) adjacent to the sulfur atom. Also, significant changes in the chemical shifts of some protons were observed in response to the structural change from **8** to **11**. For instance, due to the formation of the furan ring

(18) Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*; 3rd ed.; VCH: 1987; p195.

Scheme 5

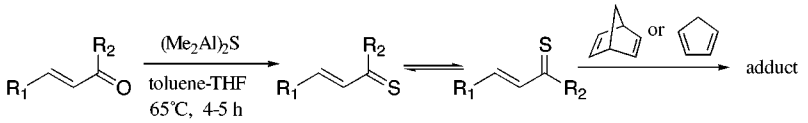


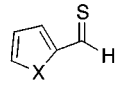
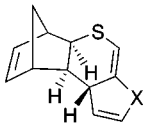
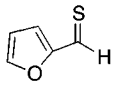
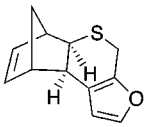
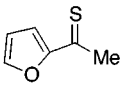
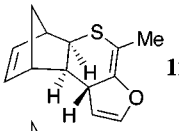
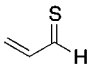
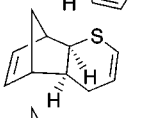
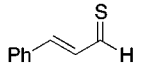
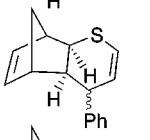
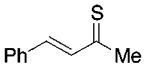
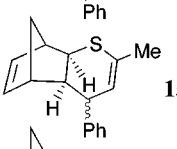
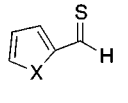
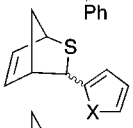
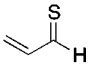
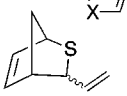
8 **11**

in **11**, proton H_{10} (δ 1.84 in **8** to δ 2.74 in **11**) shifted to a lower field while H_{14a} (δ 2.43 in **8** to δ 1.51 in **11**) shifted to a higher field. The observations in the reactions of α,β-unsaturated thioaldehydes and thioketones with norbornadiene are very similar to those observed for their selenium analogues.[4]

On the other hand, in their reactions with cyclopentadiene, α,β-unsaturated thiocarbonyl compounds behaved as 2π dienophiles (C=S) to afford the Diels−Alder cycloadducts with a little stereoselectivity (entries 8−10). In the reaction with cyclopentadiene, unlike seleno-acrolein, which only acted as a 4π diene (C=C−C=Se),[4b] thioacrolein served as a 2π dienophile (C=S) to afford cycloadduct **17**.

Table 6. Cycloaddition Reaction of α,β-Unsaturated Thioaldehydes and Thioketones with Norbornadiene or Cyclopentadiene



entry	trapping agent	adduct structure			yield (%)[a]	
1			**8**	X = O	50	
2			**10**	S	53	
3[b]			**11**		60	
4			**12**		63	
5[c]			**13**	14	**1 + 2**	27
6			**14**	18 (88 : 12)[d]	**3**	62 (34 : 66)[d]
7			**15**		63 (87 : 13)[d]	
8			**9**	X = O	90 (62 : 38)[e]	
9			**16**	S	93 (60 : 40)[e]	
10[c]			**17**		37 (53 : 47)[e]	

[a] Isolated yeilds. [b] The reaction mixture or the isolated compound **8** was treated with aqueous HCl (pH = 1). [c] Acrolein diethyl acetal was used as the starting material. [d] trans:cis determined by ^{1}H NMR. [e] endo:exo determined by ^{1}H NMR.

Conclusions

α,β-Unsaturated thioaldehydes and thioketones function as both 4π and 2π components in the [4 + 2] dimerization reactions to afford six-membered dimeric products with different selectivities depending on the substituent groups. On the other hand, these compounds served as 4π dienes (C═C−C═S) in reactions with norbornadiene to give the Diels−Alder adducts. In reactions with cyclopentadiene, they acted as 2π dienophiles (C═S), as expected. The calculations at the DFT level show that, in the [4 + 2] dimerization of α,β-unsaturated thiocarbonyl compounds, there is not much energy difference between head-to-head and head-to-tail pathways. Therefore, an equilibrium may exist between these two pathways. Under the experimental conditions, the equilibrium finally tends to yield either a mixture of head-to-head and head-to-tail dimers or only the former (thermodynamically more stable). The theoretical calculations on thioacrolein are in good agreement with the experimental results as the kinetically favored head-to-tail dimer has been obtained as major product.

Experimental Section

General Considerations. Toluene, THF, and 1,4-dioxane were carefully refluxed over sodium or potassium metal and distilled under argon prior to use. Reactions were carried out under an atmosphere of dry argon. The ^{1}H and ^{13}C NMR spectra were recorded on a 200 or 400 MHz FT-NMR spectrometer in $CDCl_3$ with TMS as the internal standard. Mass spectra were run at 70 eV in the EI mode. Melting points were determined on a capillary tube apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc. and Canadian Microanalytical Service, Ltd. Bis(tributyltin) sulfide, $(Bu_3Sn)_2S$, was prepared according to the literature.[19]

Theoretical Details. All DFT calculations were performed using GAUSSIAN94 and GAUSSIAN98 programs,[20] at the Supercomputer Center and the Department of Chemistry of Texas A&M University on Silicon

(19) Harpp, D. N.; Gingras, M.; Aida, T.; Chan, T. H. *Synthesis* **1987**, 1122.

Graphics Power Challenge, Origin 2000, and the Cray J90 servers. The transition states (TS) were optimized using a quasi-Newton method,[21] in which the final updated Hessian shows only one negative eigenvalue, and were characterized by one and only one imaginary frequency for every unique TS in a separate calculation.[22] The triple-ζ basis sets 6-311G with polarization functions (6-311G**) were used for sulfur and carbon atoms of heterodiene,[23] the double-ζ basis set 6-31G was used for hydrogen atoms of heterodiene,[24] and the double-ζ basis set 3-21G was used for carbon and hydrogen atoms of the phenyl substituent.[20] The relative energies have been corrected for the basis-set superposition error (BSSE)[25] and the zero-point vibrational energy (ZPVE).

General Procedure for Dimerization of α,β-Unsaturated Thioaldehydes and Thioketones. Under a dry argon atmosphere, 1.58 g (2.58 mmol) of $(Bu_3Sn)_2S$, 5.6 mL (2.8 mmol) of Me_3Al (2 M toluene solution), and 20 mL of toluene were stirred in a 100 mL three-necked, round-bottom flask at 60−70 °C for 2 h. This produces $(Me_2Al)_2S$ as a white suspension in toluene. The addition of THF or dioxane (10 mL) converted the suspension to a clear solution. To the latter was added 3.26 mmol of an α,β-unsaturated aldehyde or ketone. The mixture was stirred at 65 °C for 4−5 h and then poured into ice−water (40 mL) and extracted with CH_2Cl_2 (30 mL × 3). The organic extract was dried over $MgSO_4$ and evaporated. The residue was separated through chromatography on silica gel (230−400 mesh) using hexane followed by hexane−CH_2Cl_2 (5:1) as the solvents. Evaporation of the eluate gave the dimer of the respective α,β-unsaturated thioaldehyde or thioketone.

2-Vinyl-4*H*-1,3-dithiin (1) and 3-vinyl-3,4-dihydro-1,2-dithiin (2): yellow oil, yield 54%, **1**:**2** = 85:15; the spectral and analytical data have been reported in the literature.[7i−l]

4-Phenyl-3-(*E*-2-phenylvinyl)-3,4-dihydro-1,2-dithiin (3): yellow oil, yield 82%, cis:trans = 64:36; the spectral data are the same as those reported in the literature.[7m]

4-Phenyl-3,6-dimethyl-3-(*E*-2-phenylvinyl)-3,4-dihydro-1,2-dithiin (4): yellow oil, yield 77%, cis:trans = 60:40. ^{1}H NMR ($CDCl_3$, δ) *cis*: 7.40−7.16 (m, 10H), 6.51 (d, *J* = 16.2 Hz, 1H), 6.34 (d, *J* = 16.2 Hz, 1H), 5.83 (dq, *J* = 4.3, 1.5 Hz, 1H), 3.83 (dd, *J* = 4.3, 1.8 Hz, 1H), 2.04 (dq, *J* = 1.8, 1.5 Hz, 3H), 1.30 (s, 3H). ^{1}H NMR ($CDCl_3$, δ) *trans*: 7.40−7.16 (m, 10H), 6.37 (d, *J* = 16.2 Hz, 1H), 6.16 (d, *J* = 16.2 Hz, 1H), 5.79 (dq, *J* = 4.3, 1.5 Hz, 1H), 3.60 (dd, *J* = 4.3, 1.8 Hz, 1H), 2.06 (dq, *J* = 1.8, 1.5 Hz, 3H), 1.67 (s, 3H). IR (NaCl, cm^{-1}): 3050, 2950, 1750, 1630, 1570, 1490. MS (*m*/*z*): 324 (M^+), 162 ([(1/2)M]$^+$). Anal. Calcd for $C_{20}H_{20}S_2$: C, 74.02; H, 6.21. Found: C, 73.91; H, 6.21.

3-Thiobenzoyl-2,4,6-triphenyl-3,4-dihydro-2*H*-thiopyran (5): The spectral data are reported in the literature.[7e]

3-Benzoyl-2,4,6-triphenyl-3,4-dihydro-2*H*-thiopyran (6): See Table 1 (^{1}H NMR data and melting point have been reported previously.[7f])

General Procedure for Cycloaddition Reactions of α,β-Unsaturated Thioaldehydes and Thioketones with Norbornadiene or Cyclopentadiene. Under a dry argon atmosphere, to a white suspension of $(Me_2Al)_2S$ in toluene (20 mL), prepared in situ from 1.58 g (2.58 mmol) of $(Bu_3Sn)_2S$ and 5.6 mL (2.8 mmol) of Me_3Al (2 M toluene solution) as described above, was added THF (10 mL) followed by 15 mmol of norbornadiene (or cyclopentadiene) and 3.26 mmol of an α,β-unsaturated aldehyde or ketone. The mixture was stirred at 65 °C for 4−5 h and then treated in the same manner as described for the dimerization reaction. The Diels−Alder cycloaddition products of α,β-unsaturated thioaldehyde or thioketone with norbornadiene (or cyclopentadiene) were isolated by column chromatography on silica gel (230−400 mesh) with hexane followed by hexane−CH_2Cl_2 (5:1) as the solvents.

***exo*-9,10-*trans*-6-Oxa-3-thiatetracyclo[9.2.1.0^{2,10}.0^{5,9}]-tetradeca-4,7,12-triene (8):** yellow oil, yield 50%. ^{1}H NMR ($CDCl_3$, δ): 6.61 (dd, *J* = 2.8, 1.8 Hz, 1H), 6.22 (dd, *J* = 5.5, 3.0 Hz, 1H), 6.12 (dd, *J* = 5.5, 3.0 Hz, 1H), 5.67 (dd, *J* = 3.1, 1.2 Hz, 1H), 5.52 (ddd, *J* = 2.8, 2.8, 1.2 Hz, 1H), 3.24 (dq, *J* = 10.1, 2.5 Hz, 1H), 2.86 (dd, *J* = 7.9, 1.8 Hz, 1H), 2.83 (brs, 1H), 2.74 (brs, 1H), 2.43 (d, *J* = 8.9 Hz, 1H), 1.84 (ddd, *J* = 10.1, 7.9, 1.5 Hz, 1H), 1.63 (m, *J* = 8.9, 1.8, 1.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, δ): 162.2, 145.2, 138.7, 137.0, 107.6, 90.3, 57.0, 48.2, 47.1, 47.0, 46.0, 43.6. IR (NaCl, cm^{-1}): 3075, 2975, 1660, 1570, 1475. MS (*m*/*z*): 204 (M^+), 138 ([M − cyclopentadiene]$^+$).

***exo*-9,10-*trans*-3,6-Dithiatetracyclo[9.2.1.0^{2,10}.0^{5,9}]-tetradeca-4,7,12-triene (10):** yellow oil, yield 53%. ^{1}H NMR ($CDCl_3$, δ): 6.35 (dd, *J* = 6.1, 1.8 Hz, 1H), 6.24 (dd, *J* = 5.5, 3.0 Hz, 1H), 6.23−6.21 (m, 1H), 6.11 (dd, *J* = 5.5, 3.0 Hz, 1H), 5.93 (ddd, *J* = 6.1, 2.7, 1.2 Hz, 1H), 3.43 (dq, *J* = 10.7, 2.7 Hz, 1H), 2.92 (brs, 1H), 2.80 (brs, 1H), 2.76 (dd, *J* = 7.9, 1.8 Hz, 1H), 2.50 (d, *J* = 9.1 Hz, 1H), 1.82 (ddd, *J* = 10.7, 7.9, 1.5 Hz, 1H), 1.63 (m, *J* = 9.1, 1.8, 1.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, δ): 144.8, 139.0, 136.6, 125.6, 124.3, 109.6, 57.3, 55.9, 47.4, 47.3, 45.1, 43.4. IR (NaCl, cm^{-1}): 3050, 2950, 1660, 1580, 1450. MS (*m*/*z*): 220 (M^+), 154 ([M − cyclopentadiene]$^+$).

***exo*-6-Oxa-3-thiatetracyclo[9.2.1.0^{2,10}.0^{5,9}]tetradeca-5,7,12-triene (11):** yellow oil, yield 60%. ^{1}H NMR ($CDCl_3$, δ): 7.25 (d, *J* = 2.0 Hz, 1H), 6.32 (d, *J* = 2.0 Hz, 1H), 6.28 (dd, *J* = 5.9, 2.9 Hz, 1H), 6.22 (dd, *J* = 5.9, 2.9 Hz, 1H), 3.63 (d, *J* = 15.6 Hz, 1H), 3.55 (d, *J* = 15.6 Hz, 1H), 3.01 (dd, *J* = 7.8, 2.0 Hz, 1H), 2.89 (brs, 1H), 2.84 (brs, 1H), 2.74 (d, *J* = 7.8 Hz, 1H), 1.51 (brd, *J* = 9.3 Hz, 1H), 1.41 (dt, *J* = 8.8, 2.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, δ): 147.6, 139.7, 137.9, 136.9, 121.0, 110.5, 51.0, 49.7, 44.8, 42.4,

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38.3, 21.9. IR (NaCl, cm^{-1}): 3075, 2975, 1660, 1570, 1475. MS (*m*/*z*): 204 (M^+), 138 ([M − cyclopentadiene]$^+$).

***exo*-9,10-*trans*-4-Methyl-6-oxa-3-thiatetracyclo-[9.2.1.0^{2,10}.0^{5,9}]tetradeca-4,7,12-triene (12):** yellow oil, yield 63%. ^{1}H NMR ($CDCl_3$, δ): 6.61 (dd, J = 2.8, 1.8 Hz, 1H), 6.21 (dd, J = 5.8, 3.0 Hz, 1H), 6.10 (dd, J = 5.8, 3.0 Hz, 1H), 5.45 (dd, J = 2.8, 2.4 Hz, 1H), 3.21 (dq, J = 10.1, 2.4 Hz, 1H), 2.94 (dd, J = 7.9, 1.8 Hz, 1H), 2.80 (brs, 1H), 2.72 (brs, 1H), 2.37 (d, J = 8.9 Hz, 1H), 1.93 (d, J = 2.8 Hz, 3H), 1.79 (ddd, J = 10.1, 7.9, 1.5 Hz, 1H), 1.60 (m, J = 8.9, 1.8, 1.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, δ): 155.2, 145.1, 138.8, 136.7, 107.5, 100.5, 56.7, 48.4, 47.0, 46.9, 46.4, 43.5, 16.4. IR (NaCl, cm^{-1}): 3030, 2950, 1690, 1600, 1450. MS (*m*/*z*): 218 (M^+), 152 ([M − cyclopentadiene]$^+$).

***exo*-3-Thiatricyclo[6.2.1.0^{2,7}]undeca-4,9-diene (13):** yellow oil, yield 14%. ^{1}H NMR ($CDCl_3$, δ): 6.41 (dd, J = 8.6, 2.4 Hz, 1H), 6.29 (ddd, J = 8.6, 7.0, 3.4 Hz, 1H), 6.20 (dd, J = 5.5, 3.1 Hz, 1H), 6.04 (dd, J = 5.5, 3.1 Hz, 1H), 3.00 (dd, J = 7.3, 1.5 Hz, 1H), 2.75 (brs, 1H), 2.61 (brs, 1H), 2.50−2.44 (m, 1H), 2.39 (brd, J = 8.9 Hz, 1H), 1.96−1.80 (m, 2H), 1.53 (ddd, J = 8.9, 1.8, 1.5 Hz, 1H).

***exo*-6-Phenyl-3-thiatricyclo[6.2.1.0^{2,7}]undeca-4,9-diene (14):** white solid, mp 66.0−67.0 °C, yield 18%, trans:cis = 88:12. ^{1}H NMR ($CDCl_3$, δ) *trans*: 7.22 (m, 5H), 6.48 (dd, J = 8.8, 2.9 Hz, 1H), 6.29 (dd, J = 8.8, 3.4 Hz, 1H), 6.07−6.00 (m, 2H), 3.14−3.08 (m, 2H), 2.82 (brs, 1H), 2.56 (brs, 1H), 2.50 (brd, J = 8.8 Hz, 1H), 2.01 (ddd, J = 10.8, 7.8, 1.5 Hz, 1H), 1.56 (dt, J = 8.8, 1.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, δ) *trans*: 145.1, 139.3, 137.3, 136.0, 128.6, 128.5, 126.5, 124.6, 56.0, 49.0, 48.6, 47.8, 46.5, 43.7. IR (NaCl, cm^{-1}): 2950, 2875, 1640, 1580, 1470. MS (*m*/*z*): 240 (M^+), 174 ([M − cyclopentadiene]$^+$). Anal. Calcd for $C_{16}H_{16}S$: C, 79.95; H, 6.71. Found: C, 79.45; H, 6.68.

***exo*-4-Methyl-6-phenyl-3-thiatricyclo[6.2.1.0^{2,7}]-undeca-4,9-diene (15):** white solid, mp 86.5−87.5 °C, yield 63%, trans:cis = 87:13. ^{1}H NMR ($CDCl_3$, δ) *trans*: 7.38−7.20 (m, 5H), 6.09−5.93 (m, 3H), 3.17 (dd, J = 7.9, 1.5 Hz, 1H), 3.09 (dq, J = 11.0, 2.7 Hz, 1H), 2.80 (brs, 1H), 2.53 (brs, 1H), 2.46 (brd, J = 8.9 Hz, 1H), 2.00−1.90 (m, 4H), 1.54 (brd, J = 8.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, δ) *trans*: 145.4, 139.4, 135.9, 134.6, 131.1, 128.5, 128.4, 126.3, 55.1, 49.7, 48.4, 48.3, 46.2, 43.6, 23.6. IR (NaCl, cm^{-1}): 2950, 2820, 1600, 1580, 1470. MS (*m*/*z*): 254 (M^+), 188 ([M − cyclopentadiene]$^+$). Anal. Calcd for $C_{17}H_{18}S$: C, 80.27; H, 7.15. Found: C, 80.26; H, 7.13.

3-(2-Thienyl)-2-thiabicyclo[2.2.1]hept-5-ene (16): yellow oil, yield 93%, endo:exo = 80:20. ^{1}H NMR ($CDCl_3$, δ) endo: 7.11−7.10 (m, 1H), 6.91−6.90 (m, 1H), 6.88−6.86 (m, 1H), 6.56 (dd, J = 5.5, 3.1 Hz, 1H), 5.69 (dd, J = 5.5, 3.4 Hz, 1H), 5.15 (d, J = 3.7 Hz, 1H), 4.12 (brs, 1H), 3.59 (brs, 1H), 1.78 (t, J = 1.8 Hz, 1H). ^{1}H NMR ($CDCl_3$, δ) exo: 7.19−7.18 (m, 1H), 7.07−7.05 (m, 1H), 6.96−6.94 (m, 1H), 6.39 (dd, J = 5.5, 2.7 Hz, 1H), 6.08 (dd, J = 5.5, 3.4 Hz, 1H), 4.19 (s, 1H), 3.30 (brs, 1H), 1.97 (d, J = 9.5 Hz, 1H), 1.70 (dt, J = 9.5, 2.1 Hz, 1H). IR (NaCl, cm^{-1}): 3055, 2930, 1608, 1423, 1400. MS (*m*/*z*): 194 (M^+), 128 ([M − cyclopentadiene]$^+$). Anal. Calcd for $C_{10}H_{10}S_2$: C, 61.81; H, 5.19. Found: C, 61.75; H, 5.13.

3-Vinyl-2-thiabicyclo[2.2.1]hept-5-ene (17): yellow oil, yield 37%, endo:exo = 53:47. ^{1}H NMR ($CDCl_3$, δ) endo: 6.43 (dd, J = 5.5, 3.1 Hz, 1H), 5.79 (dd, J = 5.5, 3.1 Hz, 1H), 5.38 (dt, J = 16.8, 9.8 Hz, 1H), 5.18 (brd, J = 16.8 Hz, 1H), 4.96 (brd, J = 9.8 Hz, 1H), 4.28 (dd, J = 9.8, 3.7 Hz, 1H), 4.01 (brs, 1H), 3.38 (brs, 1H), 1.71−1.58 (m, 2H). ^{1}H NMR ($CDCl_3$, δ) exo: 6.33 (dd, J = 5.5, 3.1 Hz, 1H), 5.95 (dd, J = 5.5, 3.1 Hz, 1H), 5.94 (dt, J = 16.8, 9.5 Hz, 1H), 5.22 (brd, J = 16.8 Hz, 1H), 5.06 (brd, J = 9.5 Hz, 1H), 4.08 (dd, J = 9.8, 3.7 Hz, 1H), 3.38 (d, J = 9.5 Hz, 1H), 3.13 (brs, 1H), 1.71−1.58 (m, 2H).

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **4**, **6**, **8**, **10**, **11**, **12**, **14**, and **15**. Packing diagram, tables of crystal data and structure refinement, atomic coordinates and isotropic and anisotropic displacement parameters, and bond distances and angles for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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