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Competition between Hetero-Diels−Alder and Cheletropic Addition of Sulfur Dioxide. Theoretical and Experimental Substituent Effects on the Relative Stability of 3,6-Dihydro-1,2-oxathiin-2-oxides (Sultines) and 2,5-Dihydrothiophene-1,1-dioxides (Sulfolenes). Anomeric Effects in Sultine and 6-Substituted Derivatives

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At low temperature and in the presence of CF_3COOH, SO_2 undergoes Diels−Alder additions with (*E*)-1-acetoxybutadiene (**8d**) giving a 1:10 mixture of diastereomeric 6-acetoxysultines (**9d** + **10d**). The Van't Hoff plot for equilibria **8d** + $SO_2 \rightleftarrows$ **9d** + **10d** led to $\Delta H_r = -7.0 \pm 0.3$ kcal/mol, $\Delta S_r = -42 \pm 3$ cal·mol^{-1}·K^{-1}. At 20 °C, **8d** underwent a slow cheletropic addition with SO_2 giving 2-acetoxysulfolene (**11d**, $\Delta H_r \cong -11.5$ kcal/mol), the structure of which was established by single-crystal X-ray diffraction studies. (*E*)-Chloro (**8e**) and (*E*)-bromobutadiene (**8f**) did not undergo Diels−Alder additions with SO_2, even in the presence of protic or Lewis acid promoters. Low yields of 2-chloro- (**11e**) and 2-bromosulfolene (**11f**) were obtained at 20 °C. The structure of **11e** was confirmed by single-crystal X-ray diffraction. The potential energy hypersurfaces of the Diels−Alder and cheletropic additions of SO_2 to butadiene (**8a**), (*E*)-piperilene (**8b**), (*E*)-1-methoxy- (**8c**), (*E*)-1-acetoxy- (**8d**), and (*E*)-1-chlorobutadiene (**8e**) were studied by ab initio quantum calculations at the MP2/6-31G* level. In agreement with the experiment, 6-substituted sultines **9X** and **10X** were less stable than the corresponding 2-substituted sulfolenes **11X** for X = Me, OAc, Cl. With X = OMe, the two diastereomeric 6-methoxysultines (**9c**, **10c**) and 2-methoxysulfolene (**11c**) were calculated to have similar stabilities. This is attributed to a stabilizing thermodynamic anomeric effect or *gem*-sulfinate/methoxy disubstitution effect in **9c**, **10c**. Such effects were not detected for sulfinate/acetoxy (**9d**, **10d**) and sulfinate/chloro (**9e**, **10e**) disubstitutions. The relative instability of 2-acetoxy- (**11d**) and 2-chlorosulfolene (**11e**) compared with their cycloaddents is attributed to repulsive interactions between the SO_2 moieties and the 2-substituents. The Alder *endo* mode of [4 + 2] cycloaddition of SO_2 is predicted to be faster than the "anti-Alder mode" of additions for dienes **8X**, X = Me, OMe, OAc, Cl. The resulting diastereomeric sultines **9X** and **10X**, respectively, exist as equilibria (energy barrier: ca. 5−6 kcal/mol) of two conformers **9X** $\rightleftarrows$ **9′X**, **10X** $\rightleftarrows$ **10′X**. In general, the conformers **9X**, **10X** with pseudoaxial S═O group are preferred (conformational anomeric effect of the sulfinate moiety). Repulsive interactions between pseudoaxial S═O and polar *cis*-6-substituents (e.g.: X = OMe, OAc) in **9X** may render conformers **9′X** (with the S═O and 6-X groups in pseudoequatorial positions) as stable as conformers **9X**. The calculations predict the existence of conformational anomeric effects of 2−3 kcal/mol for the *gem*-sulfinate/methoxy (**9c**, **10′c**) and *gem*-sulfinate/acetoxy disubstitution (**9d**, **10′d**).

Introduction

At low temperature and in the presence of a suitable protic or Lewis acid catalyst, simple 1,3-dienes add reversibly to SO_2 via a hetero-Diels−Alder reaction giving the corresponding 3,6-dihydro-1,2-oxathiin-2-oxides (sultines).[1,2] Above −50 °C the sultines undergo fast cycloreversion liberating the starting diene and SO_2 that can undergo cheletropic additions[3] above −40 °C giving the corresponding 2,5-dihydrothiophene-1,1-dioxide (sulfolenes).[4] With (*E*)-1-methoxybutadiene,[5,6] (*E*)-2-methyl-1-silyloxybutadiene, and (*E*,*E*)-2-methyl-1-silyloxypenta-1,3-diene (e.g., **1**),[7] SO_2 gives at −78 °C adducts that decompose above −20 °C into polymeric material. In the presence of a Lewis acid, they (e.g., **2**) engender zwitterionic species (e.g., **3**) that react with enoxysilanes (e.g., **4**), giving silyl sulfinates (e.g., **5**), the hydrolyses of which generate the corresponding β,γ-unsaturated sulfinic acids

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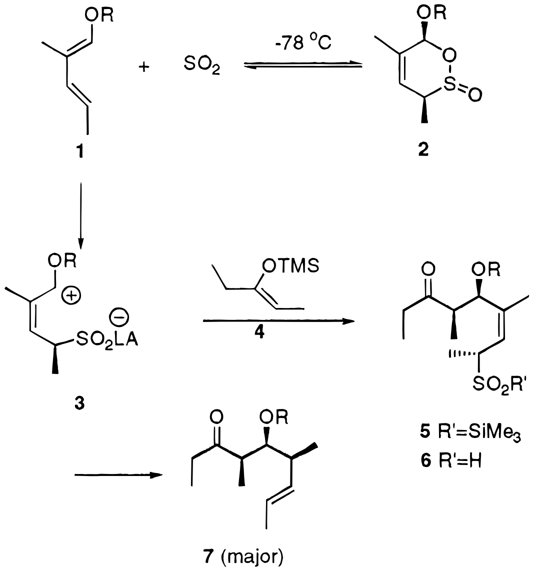
Scheme 1



(e.g., **6**) undergoing fast retro-ene elimination of SO_2 at 20 °C. This led us to propose a new carbon−carbon-bond forming procedure that can generate three contiguous stereogenic centers in a one-pot procedure (Scheme 1) and one (*E*)-alkene unit as shown with **1** + **4** → **7**.[7]

To make progress with the chemistry of sultines, we need to understand the substituent effects on activation energies and on the thermodynamical parameters of the hetero-Diels−Alder additions (reaction I) and of the cheletropic additions (reaction II) of sulfur dioxide to (*Z*)-1-substituted butadienes **8X**.

This report presents experimental studies for the reactions of SO_2 with (*E*)-1-acetoxy- (**8d**), (*E*)-1-chloro- (**8e**), and (*E*)-1-bromobutadiene (**8f**), as well as ab initio quantum calculations for systems with X = H, Me, MeO, OAc, Cl (Scheme 2). In a preliminary work,[5] we had assumed that 6-methoxy substitution should stabilize sultine **9c** more than sulfolene **11c** because of a geminal dioxy substitution effect (thermodynamic anomeric effect[8]). Our calculations supported this hypothesis. Nevertheless, and contrary to expectation, no stabilizing *gem*-sulfinate/acetoxy and *gem*-sulfinate/chloro substituent effects have been found.

The structures of the 6-alkylsultines have been inferred from their ^1H and ^{13}C NMR spectra (dilute solutions in SO_2/CD_2Cl_2, low temperature).[1,5] The data allowed recognition of the diastereomeric sultines but were not sufficient to decide whether the S→O bond prefers the pseudoequatorial (steric effect) or the pseudoaxial positions (conformational anomeric effect[9]). This question will be examined by quantum calculations for the parent sultine **9a** ⇄ **9′a** for which no experimental data are available. If butadiene undergoes the hetero-Diels−Alder addition with SO_2 under protic acid- or Lewis acid-catalyzed conditions, it does so very slowly. Calculations also were carried out for the conformational analysis of the diastereomeric 6-substituted sultines **9X** ⇄ **9′X** and **10X** ⇄ **10′X** with X = Me, MeO, and AcO.

In what follows, the axial or equatorial nature of the S=O bond and of the 6-substituent X in sultines is designated by means of A or B, respectively, in parentheses (the first letter refers to the S=O bond, the second to the substituent X).

Theoretical Methods

Reactants, products, and transition structures corresponding to reactions I and II (Scheme 2) were fully optimized at the MP2/6-31G* level of theory. All the structures located on the potential energy hypersurface were characterized (Hessian matrix) at the HF/6-31G* level by means of vibrational frequency calculations. The G2(MP2, SVP) theory introduced recently by Curtiss and co-workers[10] was used to improve the energetic results. In this method, a basis set extension correction, $\Delta_{\mathrm{MP2,SV}}$, is defined as

$$\Delta_{\mathrm{MP2,SV}} = E[\mathrm{MP2/6\text{-}311+G(3df, 2p)}] - E(\mathrm{MP2/6\text{-}31G^*}) \quad (1)$$

and the total G2(MP2, SVP) energy, E_0, is given by

$$E_0 = E[\mathrm{QCISD(T)/6\text{-}31G^*}] + \Delta_{\mathrm{MP2,SV}} + E(\mathrm{ZPE}) + \mathrm{HCL} \quad (2)$$

where *E*(ZPE) is the zero-point vibrational energy, and HCL (higher-level correction) is an empirical parameter to account for remaining basis set deficiencies that have no effect on the energy differences ΔE_0 computed in the present work.

Because the use of the quadratic configuration interaction to compute the first term in eq 2 exceeded our computer availabilities for X = OMe and OAc (155 and 185 basis functions involved, respectively), the G2(MP2, SVP) values were estimated in such cases by assuming averaged values of the difference $\{\Delta E[\mathrm{QCISD(T)/6\text{-}31G^*}] - \Delta E(\mathrm{MP2/6\text{-}31G^*})\}$obtained from calculations on X = H, CH_3, and Cl. Calculations show that, because of the rather small variances involved, the approach should work quite well (see Table 12 in the Supporting Information).

The electrostatic solvent effects were estimated by performing single-point calculations using a general self-consistent reaction field (SCRF) model proposed for quantum chemical computations on solvated molecules,[11] where the solvent is represented by a dielectric continuum characterized by its relative static dielectric permittivity ϵ_0.

All calculations were carried out using the Gaussian 94 packages of programs.[12] $\Delta H°$ values were computed within the ideal gas, rigid-rotor, and harmonic oscillator

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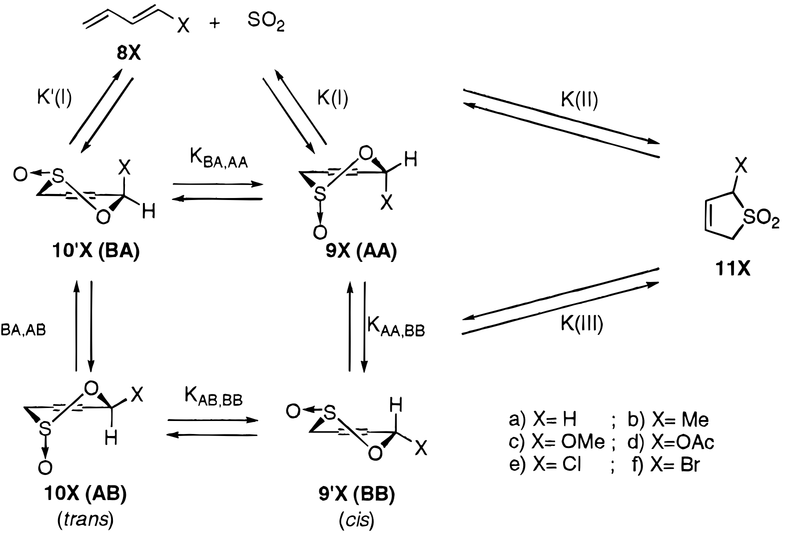
Scheme 2



approximations,[13] as implemented in Gaussian 94. A temperature of 298.15 K and a pressure of 1 atm were assumed in the calculations.

Results

Experimental thermochemical data gave ΔH_r° (**8a** + $SO_2 \rightleftarrows$ **11a**) = −16.4 ± 1.0 kcal/mol,[14] ΔH_r° (**8b** + $SO_2 \rightleftarrows$ **11b**) = −14.9 kcal/mol,[15] and ΔH_r° (isoprene + $SO_2 \rightleftarrows$ 3-methyl-2,5-dihydrothiophen-1,1-oxide) = −16.9 ± 1.1 kcal/mol in the gas phase. For the latter equilibrium in benzene, Isaacs and Laila[16] reported $\Delta H_r = -15.6$ kcal/mol. For the hetero-Diels−Alder addition isoprene + $SO_2 \rightleftarrows$ 4-methyl-3,6-dihydro-1,2-oxathiin-2-oxide, we measured an equilibrium constant K(I) = 0.03 mol^{-1} dm^3 at −60 °C. Assuming ΔS_r(I) = −42 e.u. (see below),[17] one calculates $\Delta H_r(I) = -7.5$ kcal/mol for this equilibrium. Similar values of ΔH_r(I) and ΔS_r(I) can be retained for **8a** + $SO_2 \rightleftarrows$ **9a**. One thus can propose a first estimate of ΔH_r (**9a** $\rightleftarrows$ **11a**) ≅ −9 kcal/mol for the difference in stability between the parent sulfolene **11a** and sultine **9a**.[18] For equilibrium **8b** + $SO_2 \rightleftarrows$ **10b** (most stable diastereomer), K(I) = 0.004 $mol^{-1}dm^3$ was measured at −60 °C, allowing one to estimate ΔH_r (**8b** + $SO_2 \rightleftarrows$ **10b**) = −6.6 kcal/mol with ΔS_r(I) = −42 e.u. This leads to an estimate of ΔH_r (**10b** $\rightleftarrows$ **11b**) ≅ −8.3 kcal/mol. No equilibrium constant could be measured for reaction **8c** + $SO_2 \rightleftarrows$ **9c** (or **10c**), because **8c** was polymerized concurrently with the formation of the adduct when equimolar amounts of SO_2 were used instead of large excesses.

The reactions of SO_2 with (E)-1-acetoxybutadiene (**8d**) were better behaved. In the presence of CF_3COOH, **8d** added to SO_2 gave a 1:10 mixture (thermodynamic ratio) of two diastereomeric sultines **9d**/**10d**, the structures of which were assigned from their ^1H NMR characteristics. Irradiation of the H-6 signal ($\delta_H = 6.69$ ppm) of the *cis*-6-acetoxysultine **9d** led to a positive NOE on H-3 ($\delta_H =$ 3.36 ppm) and not on H′-3 ($\delta_H = 3.84$ ppm). The fact that H′-3 is more deshielded than H-3 by 0.48 ppm is consistent with an axial S═O bond *syn* with respect to H′-3.[19] This suggests therefore that conformer **9d** is favored over **9′d**, as predicted by our calculations. Irradiation of the H-6 signal ($\delta_H = 6.48$ ppm) of the major *trans*-6-acetoxysultine **10d** led to a positive NOE on the signal assigned to H′-3 ($\delta_H = 3.61$ ppm) and not on H-3 ($\delta_H = 3.56$ ppm). In this case, the small chemical shift difference observed for H-3 and H′-3 ($\Delta\delta = 0.05$ ppm) is consistent with an equilibrium of conformers **10d** $\rightleftarrows$ **10′d** in which both conformers are populated similarly, in agreement with our calculations. Van't Hoff plots (−70 to −30 °C) afforded $\Delta H_r(I) = -7.0 \pm 0.3$ kcal/mol and $\Delta S_r(I) = -42 \pm 3$ e.u. for equilibrium **8d** + $SO_2 \rightleftarrows$ **9d** + **10d**. The structure of **11d** was established unambiguously by single-crystal X-ray diffraction studies. At 25 °C, an equilibrium constant K (**8d** + $SO_2 \rightleftarrows$ **11d**) = 0.19 mol^{-1} dm^3 was measured. Assuming ΔS_r(II) = −42 e.u. for this equilibrium, we estimate that ΔH_r (**8d** + $SO_2 \rightleftarrows$ **11d**) ≅ −11.5 kcal/mol. This gives an estimate of 4.5 kcal/mol for the stability difference between sultines **9d** + **10d** and sulfolene **11d**, a value significantly smaller than that found for the unsubstituted and alkyl-substituted analogues (Table 2).

The (E)-1-chloro (**8e**) and (E)-1-bromobutadiene (**8f**) had been reported not to add SO_2.[20] In our hands, no

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[17] Similar value measured for the hetero-Diels−Alder addition of 1,2-dimethylidenecyclohexane to SO_2: Monnat, F.; Vogel, P. in preparation.

[18] Acyclic sulfones $RS(O)_2R'$ have been evaluated to be −7 to −15 kcal/mol more stable than their isomeric sulfinates RS(O)OR′: Liebman, J. F.; Crawford, K. S. K. In *Supplements: The Chemistry of Sulphur-Containing Functional Groups*, Patai, S.; Rapoport, Z., Eds., J. Wiley & Sons Ltd: New York, 1993; p 197.

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[20] Klebanskii, A. L.; Sorokina, R. M.; Khavin, Y. Z. *J. Gen. Chem. USSR* (Engl. Transl.) **1947**, *17*, 235; *Chem. Abstr.* **1948**, *42*, 514.

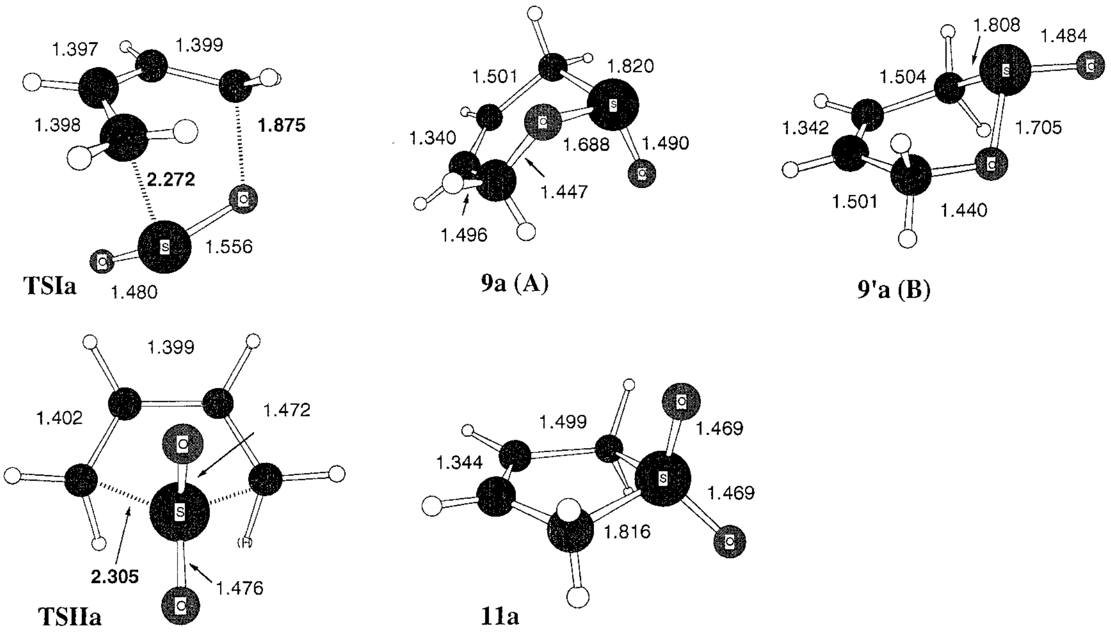

Figure 1. Structures located on the MP2/6-31G* potential energy hypersurface for the cycloaddition reactions of 1,3-butadiene and SO_2 (see text and Scheme 2 for notation).

products resulting from hetero-Diels−Alder additions were observed with these dienes between −100 and +40 °C, in the absence or in the presence of acid promoters. Together with their polymerization, mediocre yield of sulfolenes **11e** (13%) and **11f** (12%) were obtained after long reaction times at 50 °C. This suggests that 1-chloro and 1-bromo substitutions of butadiene render the hetero-Diels−Alder additions too slow or that they destabilize the corresponding sultines, making them invisible under our conditions. The structure of **11e** was confirmed by chemical correlation with 2-chlorosulfolane[21] and by X-ray diffraction studies (see Supporting Information). The structure of **11f** was confirmed by catalytical hydrogenation (H_2, 30 atm) that gave 2-bromosulfolane, a compound identical with that obtained by bromination (Br_2/Ph-H) of sulfolane treated with 1.2 equiv of EtMgBr.

Calculations And Discussion

Figures 1−5 show the structures located (transition structures and products) computed at the MP2/6-31G* level for reactions I and II in Scheme 2, including the most relevant geometrical parameters (in X = AcO, Figure 4 includes, besides the four sultines depicted in Scheme 2, four additional conformers arising as a consequence of the greater complexity of this substituent). Comparison between the calculated and experimental (X-ray diffraction) geometries of sulfolenes **11d** and **11e** generally showed good agreement, except for dihedral angles that, as expected,[22] were slightly less reliable (both theoretical and experimental geometrical parameters are provided as Supporting Information). Table 1 collects the energetic results for all the transition structures, sulfolenes, and the most stable sultine conformers obtained by pathways I and II in Scheme 2.

From the kinetic viewpoint, data in Table 1 show that, according to expectations for Diels−Alder additions with electron-deficient dienophiles, (*E*)-1-methoxybutadiene (**8c**) is calculated to react significantly faster than all other dienes **9X** toward SO_2 via **TSIc** (see Scheme 2). We also find that the cheletropic addition **8c** + $SO_2 \rightleftarrows$ **11c** is easier than for the other dienes. Consistently with the experiment, dienes **8a** and **8e** are very slow in both reactions I and II. In (*E*)-1-acetoxybutadiene, the computed energy barriers adopt intermediate values. It must be pointed out that direct interconversions between sultine **9X** and corresponding sulfolenes **11X** (reaction III) can be discarded from the ab initio calculations.[23] As discussed elsewhere,[24] the symmetries of diene and SO_2 molecular orbitals allow for both HOMO(diene) → LUMO(SO_2) and HOMO(SO_2) → LUMO(diene) interactions during formation of the two C−S bonds of sulfolenes, but only the HOMO(diene) → LUMO(SO_2) interaction contributes predominantly in the formation of the C−S and C−O bonds of sultines. In agreement with other experiments[1,2,6] previous calculations predicted[25] that Lewis acids would catalyze the hetero-Diels−Alder additions better than the corresponding cheletropic addition of SO_2 (reaction II).[24] The notable increase in net charge transfer from (HOMO) diene to (LUMO) dienophile causes an important reduction in the activation energy, thus favoring the formation of sultines at low temperatures. On the other hand, as expected,[26] our calculations show somewhat lower energy barriers for reactions in a solution than in a vacuum.

From the thermodynamic viewpoint, we learn from Table 1 that for **8c** and **8d** the exothermicities of reactions I and II are rather similar, whereas for **8a**, **8b**, and **8e** the cheletropic additions of SO_2 are more exo-

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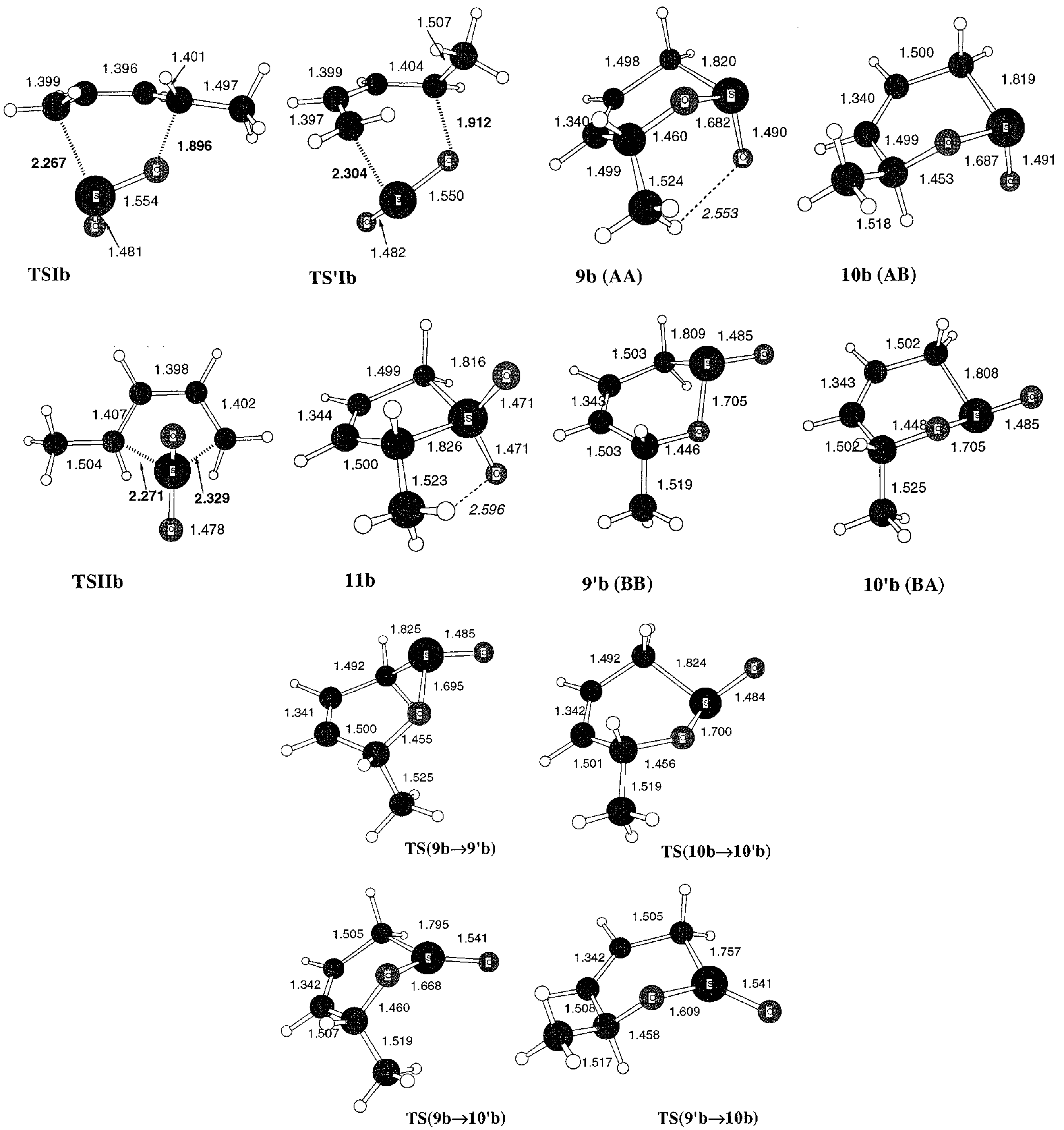
[26] Suárez, D.; Assfeld, X.; González, J.; Ruiz-López, M. F.; Sordo, T. L.; Sordo, J. A. *J. Chem. Soc. Chem. Commun.* **1994**, 1683.



TSIb **TS′Ib** **9b (AA)** **10b (AB)**

TSIIb **11b** **9′b (BB)** **10′b (BA)**

TS(9b→9′b) **TS(10b→10′b)**

TS(9b→10′b) **TS(9′b→10b)**

Figure 2. Structures located on the MP2/6-31G* potential energy hypersurface for the cycloaddition reactions of (*E*)-1-methylbutadiene and SO_2 (see text and Scheme 2 for notation).

thermic than the corresponding hetero-Diels–Alder additions. Experimental data (Table 1) confirm that the stability of the sulfolene relative to the sultine for diene **8d** is considerably smaller than in dienes **8a**, **8b**. The theoretical predictions reproduce the experimental data available for the reactions studied (I, II, and III). The accuracy of the computed reaction energies correspond to what should be expected when using the G2(MP2, SPV) theory in calculations involving hypervalent molecules such as SO_2.[27] Especially satisfactory are experimental and theoretical data collected for equilibrium III.

For the parent sultine **9a** (see Figure 1), the S=O bond is predicted to occupy a pseudoaxial position; its conformer **9′a** with a pseudoequatorial S=O bond is calculated to be ca. 2.6 kcal/mol less stable at the G2(MP2, SVP) level (the MP2/6-31G* value including zero-point energy is 3.4 kcal/mol). We shall use this latter theoretical level in the conformational analysis of sultines **9X** $\rightleftarrows$ **9′X** and **10X** $\rightleftarrows$ **10′X** for X = Me, MeO, AcO (Scheme 3 and Table 2). The axial preference for the S=O bond in **9a** is consistent with the conformational anomeric effect

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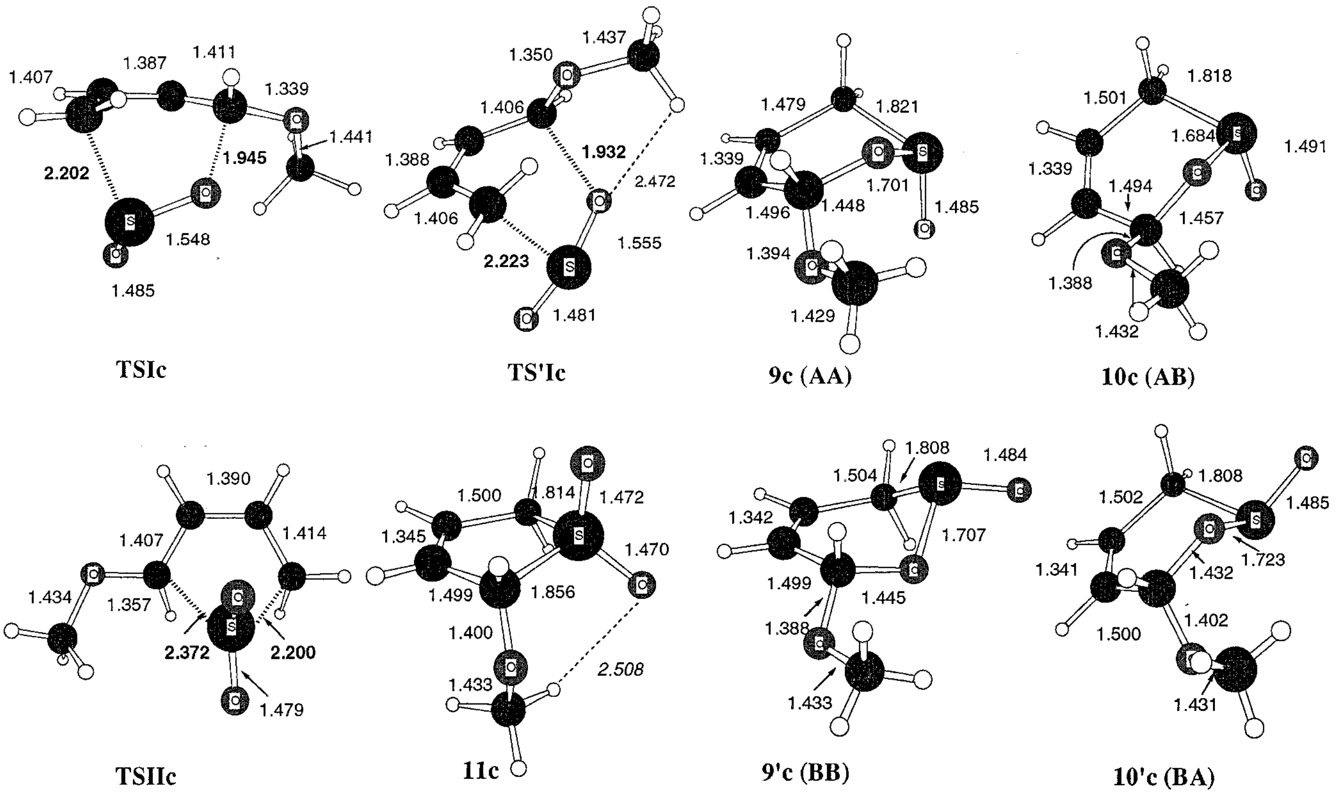
TSIc **TS'Ic** **9c (AA)** **10c (AB)**

TSIIc **11c** **9'c (BB)** **10'c (BA)**

Figure 3. Structures located on the MP2/6-31G* potential energy hypersurface for the cycloaddition reactions of (*E*)-1-methoxybutadiene and SO_2 (see text and Scheme 2 for notation).

(3.5 kcal/mol preference for axial S=O vs equatorial S=O) reported for 1,2-oxathian-2-oxide, the dihydro analogue of **9a**.[28]

Experiments show that 6-methylsultine **10b** is the most stable diastereomeric adduct (pseudoequatorial methyl group).[1] Our calculations provide the mechanistic details (see Scheme 3). Conformer **9b** is formed through the lower energy transition structure **TSIb**. An alternative path via **TS′Ib** leads to the formation of the most stable conformer **10b**. Therefore, **9b** is the kinetically favored conformer, whereas **10b** is formed when the thermodynamic control is established, in full agreement with experimental data.[1] The formation of **10b** through the interconversions **9b** ⇄ **10′b** ⇄ **10b** or **9b** ⇄ **9′b** ⇄ **10b** implies barriers of ca. 70 kcal/mol [see Scheme 3; transition structures **TS**(**9b** → **9′b**), **TS**(**10b** → **10′b**), **TS**(**9b** → **10′b**), and **TS**(**9′b** → **10b**) connecting all conformers are depicted in Figure 2]; they confirm the hypothesis that the isomerization **9b** ⇄ **10b** occurs via [4 + 2] cycloreversion and cycloadditions.

The experimental stability difference between anomeric 2-methoxytetrahydropyran amounts to 0.78 kcal/mol in favor of the conformer with an axial OMe group.[9] Our calculations for the 6-methoxysultines suggest that a similar stabilizing conformational anomeric effect exists for the *gem*-sulfinate/methoxy disubstitution but it must compete with a destabilizing electrostatic interaction when both the S=O and MeO moieties occupy *cis*-pseudoaxial positions (Figure 3). Indeed, the MP2/6-31G* calculations (Table 2) predict the diastereomer **9c** is more stable than **10c** by 0.2 kcal/mol only, whereas the more reliable G2 (MP2, SVP) method estimates that **10c** is the most stable diastereomeric 6-methoxysultine (Table 1). Because conformers **10c** and **10′c** are calculated to have the same stability, we can admit that the stabilizing anomeric effect of the S=O and 6-MeO groups are similar. Their cumulative effect (as realized in **9c**) is larger than the S=O...OMe repulsion (in **9c**) by 2.8 kcal/mol, because **9′c** in which the conformational anomeric effects are absent is calculated to be 2.8 kcal/mol less stable than conformer **9c**.

In the 6-acetoxysultines (Figure 4; more conformers than pairs **9d** ⇄ **9′d** and **10d** ⇄ **10′d** are found on the energy hypersurface of this system due to rotamers about the O−COMe bond of the acetoxy substituent; only the most stable rotamers are shown) our calculations (Tables 1 and 2) predict that sultine **10d** is more stable than its diastereomer **9d** in agreement with our experiments. Thus, in the 6-methyl-(**9b**, **10b**) and 6-ethylsultines,[5] the *trans*-6-substituted sultine **10d** is more stable than the cis-isomer **9d**. As in the case of the 6-methoxysultines **10c** ⇄ **10′c** one calculates that conformers **10d** and **10′d** have the same stability,[29] in agreement with our ^1H NMR data for this system (see above). In this case one also can invoke a conformational anomeric effect of the S=O bond of the sulfinate moiety to be similar to that of the *gem*-sulfinate/methoxy system. **9d** is calculated to be 3 kcal/mol less stable than its diastereomer **10d**. Conformer **9′d** is estimated to be only 0.5 kcal/mol more stable than **9d**, consistent with our ^1H NMR data. One can thus admit that the repulsive interaction between the two *cis*-pseudoaxial S=O and AcO groups in **9d** overwhelms the cumulative conformational anomeric effects of these

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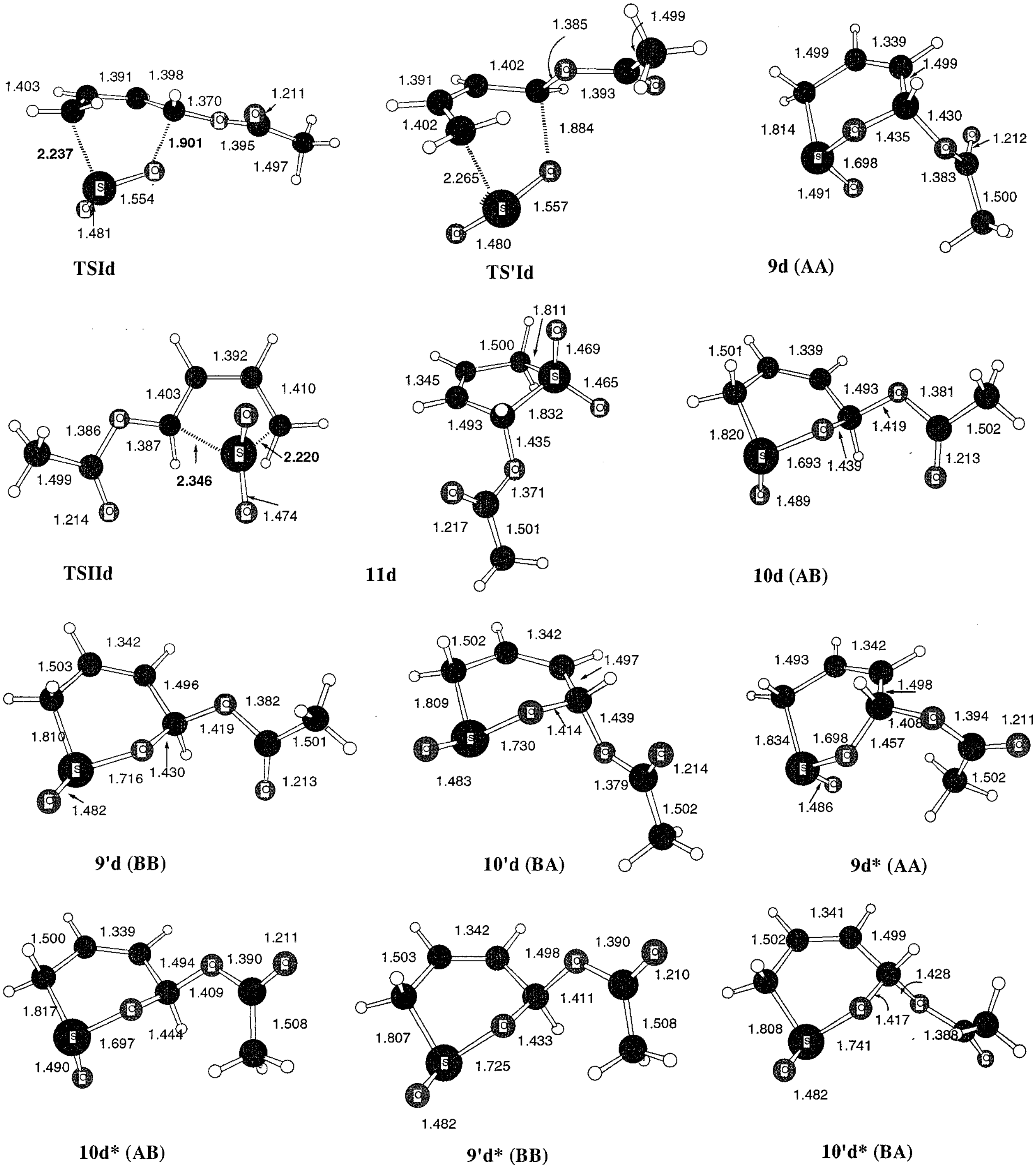
[28] Harp, D. N.; Gleason, J. G. *J. Org. Chem.* **1971**, *36*, 1314 and references cited therein.

[29] Attempts to slow the interconversions of conformer pairs **9d** ⇄ **9′d** and **10d** ⇄ **10′d** failed because no significant line broadening could be detected at −110 °C, the temperature at which two phases start to form.



TSId **TS'Id** **9d** (AA)

TSIId **11d** **10d** (AB)

9'd (BB) **10'd** (BA) **9d*** (AA)

10d* (AB) **9'd*** (BB) **10'd*** (BA)

Figure 4. Structures located on the MP2/6-31G* potential energy hypersurface for the cycloaddition reactions of (*E*)-1-acetoxybutadiene and SO_2 (see text and Scheme 2 for notation).

groups by 3 kcal/mol (**9′d** does not benefit from any conformational anomeric effect). Our calculations seem to exaggerate the stability difference between **9d** and **10d**, because our experimental data give $\Delta G = 0.9$ kcal/mol at 198 K for equilibrium **10d** $\rightleftarrows$ **9d** in $SO_2/CD_2Cl_2/CF_3COOH$.

In the 6-chlorosultines, the MP2/6-31G* calculations (Table 2) favor **9e** over its diastereomer **10e** by 0.2 kcal/mol, whereas the G2(MP2, SVP) methods predict **10e** to be more stable than **9e** by 1.2 kcal/mol (Table 1). We thus must admit that repulsive S=O...Cl interactions in **9e** compete with the hypothetical conformational anomeric effect of the *gem*-sulfinate/chloro system, or that the latter does not exist.

The most striking outcome of our studies is the observation that the *gem*-sulfinate/methoxy substitution is accompanied by a thermodynamic anomeric effect[8] that is significantly larger than those of the *gem*-sulfinate/acetoxy and *gem*-sulfinate/chloro systems. To confirm this phenomenon further we have calculated the energies of

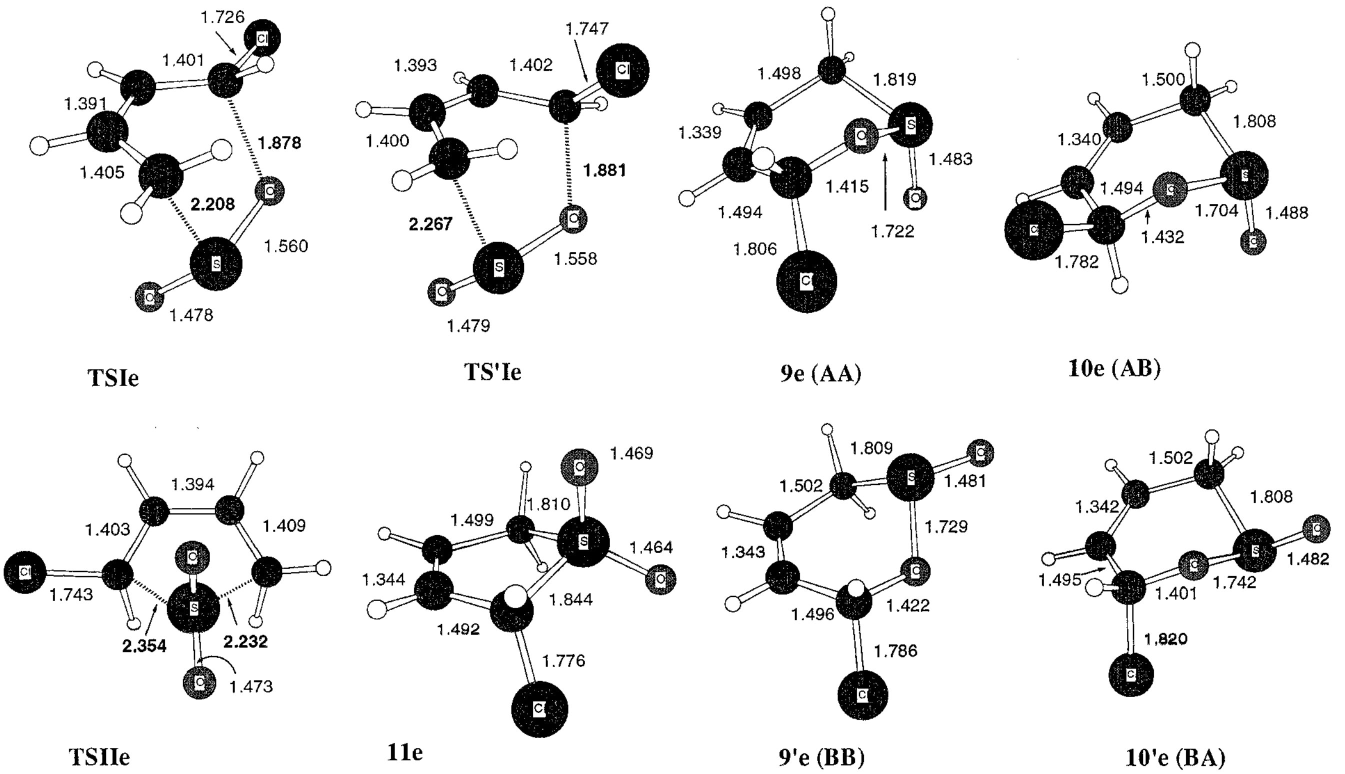


Figure 5. Structures located on the MP2/6-31G* potential energy hypersurface for the cycloaddition reactions of (*E*)-1-chlorobutadiene and SO_2 (see text and Scheme 2 for notation).

Table 1. Calculated Energies (kcal/mol)[a] of the MP2/6-31G* Optimized Transition Structures (TS) and Products Relative to Reactants for the Diels–Alder (I) and Cheletropic (II) Reactions of 1-X-butadiene (X = H, CH_3, OMe, OAc, Cl) with Sulfur Dioxide

reactions	TS	ΔE^{b}	products	$\Delta H_{el}{}^{b}$	$\Delta H_{int}{}^{c}$	$\Delta H_{r}{}^{c,d}$	$\Delta H_{r}(III)^{d,f}$
butadiene + SO_2 (Ia)	**TSIa**	19.2 (−0.6)	**9a**	−5.2 (−1.2)	2.6	−2.6 [−7.6][e]	
butadiene + SO_2 (IIa)	**TSIIa**	19.0 (−1.1)	**11a**	−13.5 (−3.1)	2.5	−10.9 [−16.4]	−8.3 [−9.0]
(*E*)-piperilene + SO_2 (Ib)	**TSIb**	15.7 (−0.4)	**9b**	−5.9 (−0.8)	2.4	−3.5	
(*E*)-piperilene + SO_2 (I′b)	**TS′Ib**	21.3 (−0.2)	**10b**	−7.2 (−0.9)	2.4	−4.8 [−6.6]	
(*E*)-piperilene + SO_2 (IIb)	**TSIIb**	17.3 (−0.9)	**11b**	−14.3 (−2.6)	2.5	−11.8 [−14.9]	−7.0 [−8.3]
(*E*)−1-MeO-butadiene + SO_2 (Ic)	**TSIc**	11.5 (0.2)	**9c**	−7.5 (−1.0)	2.4	−5.1	
(*E*)−1-MeO-butadiene + SO_2 (I′c)	**TS′Ic**	15.2 (−0.3)	**10c**	−8.4 (0.2)	2.5	−5.9	
(*E*)−1-MeO-butadiene + SO_2 (IIc)	**TSIIc**	16.0 (−0.4)	**11c**	−9.0 (−2.5)	2.6	−6.4	−0.5
(*E*)−1-AcO-butadiene + SO_2 (Id)	**TSId**	14.5 (−0.1)	**9d**	−3.0 (0.0)	2.2	−0.8	
(*E*)−1-AcO-butadiene + SO_2 (I′d)	**TS′Id**	18.9 (−1.1)	**10d**	−6.6 (−0.8)	2.3	−4.3 [−7.0]	
(*E*)−1-AcO-butadiene + SO_2 (IId)	**TSIId**	18.5 (−0.9)	**11d**	−9.1 (−1.8)	2.3	−6.8 [−11.5]	−2.5 [−4.5]
(*E*)−1-Cl-butadiene + SO_2 (Ie)	**TSIe**	18.8 (−0.4)	**9e**	−3.6 (−2.0)	2.2	−1.4	
(*E*)−1-Cl-butadiene + SO_2 (I′e)	**TS′Ie**	23.6 (0.1)	**10e**	−4.4 (−0.8)	2.2	−2.2	
(*E*)−1-Cl-butadiene + SO_2 (IIe)	**TSIIe**	19.6 (−0.5)	**11e**	−10.0 (−2.6)	2.3	−7.7	−5.5

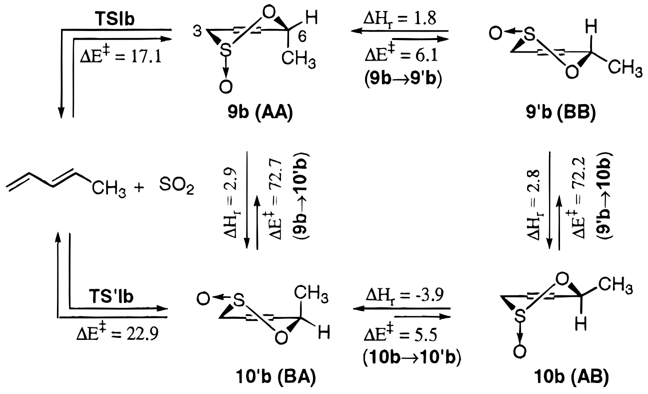
[a] G2(MP2,SVP) energies (see the text for more details). [b] MP2/6-31G* SCRF estimate of the electrostatic solvent effect using a relative permittivity of 13.3 to simulate the experimental conditions in parentheses. [c] Computed using HF/6-31G* ΔH_{vib} contributions scaled by 0.8905 and including ΔH_{rot} and ΔH_{trans}. [d] Values obtained from experimental constants or from thermochemical data in parentheses. [e] Experimental ΔH_r(I) value for isoprene.[1,5] [f] Theoretical data correspond to the most stable conformer of the substituted sultine (see text) in all cases.

Table 2. Relative Energies (MP2/6-31G* Values Including Zero-Point Energy Correction; kcal/mol) of the Different Conformers of 6-Methoxysultines, 6-Acetoxysultines, and 6-Chlorosultines (See Text for Notation)

	diastereomers			
	cis ⇄ *cis*		*trans* ⇄ *trans*	
	9X (AA)	**9′X (BB)**	**10X (AB)**	**10′X (BA)**
6-methoxysultines (*X* = c)	(0.0)	2.8	0.2	0.4
6-acetoxysultines (*X* = d)	3.0	2.5	(0.0)	0.0
6-chlorosultines (*X* = e)	(0.0)	3.1	0.2	0.3

the isodesmic reactions IV and V (Scheme 4). At the MP2/6.31G* level (see Table 3) one confirms that the sultines are stabilized by a thermodynamic anomeric effect (*gem*-disubstitution effect) of the 6-methoxy group in both diastereomeric forms (compare ca.. −13 kcal/mol for OMe with −6 to −7 kcal/mol for Me). Such an effect is not detected for 6-acetoxy substitution of the sultines, whereas a destabilizing *gem*-sulfinate/chloro effect might exist. No stabilizing *gem*-MeO/sulfone effect can be seen with reaction **11a** + $CH_3OMe \rightleftarrows$ **11c** + CH_4 (compare −5.5 kcal/mol for OMe with −6.1 kcal/mol for Me) confirming that the relative stability of 2-methoxysulfolene (**11c**) is similar to that of its isomeric sultines **9c** and **10c** (ΔH_r(III) = −0.5 kcal/mol; see Table 1). The extra stabilization caused by the thermodynamic anomeric effect that stabilizes the 6-methoxysultines (**9c**, **10c**) does not overwhelm the intrinsic greater relative stability of

Scheme 3. (MP2/6-31G*) [ΔH_r, $\Delta E^{\ddagger}$ in kcal/mol]



Scheme 4

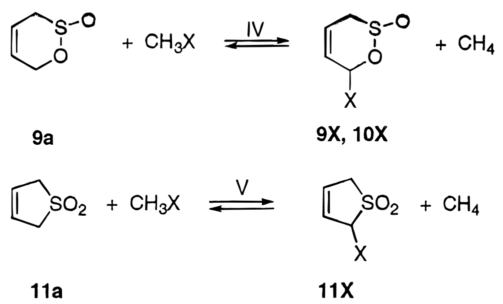


Table 3. MP2/6-31G* Reaction Energies (kcal/mol) for Isodesmic Processes IV and V (See Text) Involving 1-X-Butadiene Sultines and Sulfolenes (X = CH_3, OMe, OAc, Cl)

reactions	X	CH_3 (b)	OMe (c)	OAc (d)	Cl (e)
9a + $CH_3X \rightleftarrows$ **9X** + CH_4	ΔE(IV)	−6.2	−13.4	−5.6	−4.7
9a + $CH_3X \rightleftarrows$ **10X** + CH_4	ΔE(IV)	−7.2	−13.2	−8.6	−4.5
11a + $CH_3X \rightleftarrows$ **11X** + CH_4	ΔE(V)	−6.1	−5.5	−3.0	−1.2

2-methoxysulfolene (**11c**). Why only one adduct of (*E*)-1-methoxybutadiene (**8c**) with SO_2 has been observed so far is still unexplained. Is it a sultine or a sulfolene?

Further experimental studies are now required to confirm our preliminary work.[5] It is possible that sulfolene **11c** has not been observed together with sultine **9c** because the rate of formation of **11c** is significantly smaller than that of **9c** as predicted (Table 2). Because **8c** + $SO_2 \rightleftarrows$ **9c** decomposed quickly above −20 °C, the conditions were not realized that would allow for **11c** to be formed concurrently with the polymerization of diene **8c**. The calculated energy for equilibrium Vd (−3.0 kcal/mol; Table 3) suggests a destabilizing effect of the acetoxy substituent in the 2-acetoxysulfolene **11d**, as found experimentally (ΔHr(IIId) = −11.5 kcal/mol compared with ΔH_r(IIIb) = −14.9 kcal/mol; Table 2). A somewhat larger destabilization effect is calculated for the chloro substituent, in agreement with our experiments. This can be interpreted in terms of repulsive electrostatic interactions between the SO_2 moiety and the AcO, Cl substituents of the sulfolenes (Figures 4 and 5).

Our calculations suggest the existence of hydrogen bondings of the type Me...OSO (see **11b**, Figure 2) and OMe...OSO (see **11c**, Figure 3) for 2-methylsulfolene and 2-methoxysulfolene, respectively.

Conclusion

Experiments and high-level ab initio quantum calculations agree that the diastereomeric 6-substituted sultines **9X** and **10X** resulting from the hetero-Diels−Alder additions of SO_2 to (*E*)-piperilene (**8b**), (*E*)-1-acetoxybutadiene (**8d**), and (*E*)-1-chlorobutadiene (**8e**) are less stable than the corresponding 2-substituted sulfolenes **11X** (X = Me, OAc, Cl) resulting from the cheletropic additions **8X** + SO_2. With (*E*)-1-methoxybutadiene (**8c**), SO_2 is predicted to generate two diastereomeric 6-methoxysultines **9c** and **10c** and 2-methoxysulfolene (**11c**) with similar stabilities. This is attributed to a stabilizing thermodynamic anomeric effect or *gem*-sulfinate/methoxy disubstitution effect in **9c**, **10c**. There is no such effect for the sulfone/methoxy disubstitution in **11c**. In agreement with our experiments, the calculations predict destabilizing interactions in 2-acetoxysulfolene (**11d**) and 2-chlorosulfolene (**11e**) caused by electrostatic repulsions between the SO_2 group and the 2-acetoxy and 2-chloro substituents, respectively. Except for parent butadiene (**8a**), the uncatalyzed hetero-Diels−Alder additions of SO_2 to 1,3-dienes (**8b**−**8e**) are predicted to be faster than the corresponding cheletropic additions. The Alder mode of addition which leads to *cis*-6-substituted sultines (**9X** $\rightleftarrows$ **9′X**) is always predicted to be faster than the “anti-Alder” mode of addition giving the diastereomeric *trans*-6-substituted sultines (**10X** $\rightleftarrows$ **10′X**). Sultines can adopt two pseudo-chair conformations.

In the parent sultine, conformer **9a** with a pseudoaxial S═O bond is preferred over conformer **9′a** with a pseudoequatorial S═O bond by ca. 3 kcal/mol, thus indicating the existence of a conformational anomeric effect for the sultinate moiety of the sultines. In the *cis*-6-methylsultine (**9b**) with pseudoaxial S═O and methyl groups, the barrier energy for the interconversion into its conformer **9′b** (with pseudoequatorial S═O and methyl groups) is estimated to be 5−6 kcal/mol. The steric factor makes the *cis*-6-methylsultine (**9b**) about 1 kcal/mol less stable than the *trans*-6-methylsultine (**10b**). The calculations predict the existence of conformational anomeric effects in 6-methoxy- (**9c**, **10c**) and 6-acetoxysultines (**9d**, **10d**), which amounts to ca. 3 kcal/mol. In the *cis*-diastereomers **9c** and **9d** electrostatic repulsions between the pseudoaxial S═O, OMe, and OAc groups, respectively, are competing with the conformational anomeric effects and render the *trans*-diastereomeric sultine **10c** as stable as **9c**. For the 6-acetoxy-substituted analogue, the *trans*-isomer **10d** is estimated to be more stable than the *cis*-sultine **9d** in agreement with our experiments. The pseudoaxial S═O/pseudoaxial OAc repulsion is evaluated to be somewhat more important than the pseudoaxial S═O/pseudoaxial OMe repulsion. Consequently, conformers **10c** and **10′c** have similar stabilities. Conformer pairs **9d** $\rightleftarrows$ **9′d** and **10d** $\rightleftarrows$ **10′d** are calculated to have similar relative stabilities, in agreement with ^{1}H NMR data.

Experimental Section

NMR Sample preparation and Thermochemical Parameters. CD_2Cl_2 and toluene were distilled over anhyd CaH_2, CF_3COOH over P_2O_5. SO_2 was filtered through a column of alcaline aluminum oxide 90 (activity I, Merck) before use. In a weighed, dry 5-mm NMR Pyrex tube, dienes **8X** (0.05−0.3 mmol), toluene (internal reference, 5−15 mg), CD_2Cl_2 (0.2−0.3 g), and CF_3COOH (0.01−0.2 mmol; catalyst, if any) were mixed under an Ar atmosphere at 20 °C. The solution was degassed by several freeze−thaw cycles at 10^{-2} Torr. Degassed SO_2 (0.1−0.4 mL) was transferred to the above mixture on the vacuum line. The NMR tube was sealed under vacuum. The NMR tube, frozen in liquid N_2, was warmed to −100 °C in liquid EtOH/liquid N_2 and transferred into the Bruker ARX-400 spectrometer probe cooled to −90 °C. Other tubes were left in thermostated EtOH baths at various temperatures until equilibria were reached, then cooled to −100 °C, and transferred into the spectrometer probe cooled to −90 °C. When viscous solutions were obtained at temperatures lower than −70 °C, mixtures of $CD_2Cl_2/CFCl_3$ were used instead of pure CD_2Cl_2. When the equilibrium constant measurements were terminated, the NMR tube was allowed to reach room temperature and was weighed together with the piece of tube left over after sealing: this allowed verification of the exact amount of SO_2 introduced in the diene solution. Spectra were recorded for 90° pulses with a delay of 10−15 s between pulses, same spectral window (16−32 scans). The equilibrium constants at a given temperature were evaluated for at least three different NMR samples and had reproducible values within experimental error, varying the initial cycloaddent ratio. Enthalpies and entropies of reactions were obtained through Van't Hoff plots, the equilibrium constants being determined by using the concentrations of the products and reactants.

Data for 6-Acetoxy-3,6-dihydro-1,2-oxathiin-2-oxides (9d ⇄ 9′d and 10d ⇄ 10′d). In the presence of one equiv, of CF_3COOH, (*E*)-1-acetoxybutadiene (**8d**) reacted with SO_2 at −75 °C to give a 1:10 mixture of two diastereomeric sultines. This ratio was the same at the beginning and at the end of the reaction and at higher temperatures, when cycloreversion was observed. Equilibrium was reached after 10 h. ^1H NMR (400 MHz, CD_2Cl_2/SO_2, 198 K) of the major sultine **10d**: δ_H 2.23 (s, Ac), 3.56 and 3.61 (2m, $H_2C(3)$), 6.14 (m, H−C(5)), 6.26 (m, H−C(4)), 6.48 (m, H−C(6)), ^3J (H-5,H-6) ≅ ^4J (H-4,H-6) = 2.4 ± 0.2 Hz, ^3J (H-4,H-5) = 11.6 ± 0.2 Hz (through homonuclear decoupling); ^{13}C NMR (100.6 MHz, CD_2Cl_2/SO_2, 198 K)δ_C: 20.6 ppm (q, ^1J (C,H) = 131 Hz, Ac), 45.2 (t, 142, C(3)), 84.0 (d, 180, C(6)), 119.5 (d, 176, C(4)), 122.8 (d, 171, C(5)), 172.5 (s, COO); assignments confirmed by $^1H/^{13}C$-correlated two-dimensional spectra HETCOR and HSQC. Equilibrium constant K (298 K) = 0.022 ± 0.006 dm^3mol^{-1}. Data for **9d**: ^1H NMR (400 MHz, CD_2Cl_2/SO_2, 198 K)δ_H 2.36 (s, Me), 3.36 (ddt, H−C(3)), 3.84 (ddt, H′−C(3)), 6.00 (dq, H−C(5)), 6.69 (m, H−C(6)), 6.17 (m, H−C(4), ^2J (H-3,H′-3) = 17.3, ^3J (H-3,H-4) = 4.8, ^3J (H′-3,H-4) = 4.0, ^3J (H-4,H-5) = 11.2, ^3J (H-5,H-6) = 1.9, ^4J (H-3,H-5) = ^4J (H′-3,H-5) = 2, ^4J (H-4,H-6) = 1.3, ^5J (H-3,H-6) = ^5J (H′-3,H-6) = 2.1; ^{13}C NMR (100.6 MHz, CD_2Cl_2/SO_2, 198 K)δ_C 20.6 (q, 131, Ac), 46.7 (d, 142, C(3)), 87.6 (d, 180, C(6)), 122.0 (d, 171, C(4)), 123.7 (d, 171, C(5)), 173.0 (s, COO), assignments confirmed by HETCOR and HSQC. Equilibrium constants for reaction **8d** + SO_2 ⇄ **9d** + **10d**: K = 0.103 ± 0.005 dm^3mol^{-1} (at 183 K), 0.0394 ± 0.004 (193 K), 0.0244 ± 0.004 (198 K), 0.0158 ± 0.004 (203 K), 0.0110 ± 0.0034 (208 K), 0.0080 ± 0.0031 (213 K), 0.0037 ± 0.0006 (223 K), 0.0020 ± 0.00012 (233 K), 0.0009 ± 0.00006 (243 K).

2-Acetoxy-2,5-dihydrothiophene-1,1-dioxide (**11d**). A mixture of (*E*)-1-acetoxybutadiene (1 g, 8.9 mmol) and SO_2 (3.97 g, 62 mmol, 7 equiv) was placed in a Pyrex tube, degassed on the vacuum line. After sealing the tube, the mixture was left at 20 °C for 6 days. After cooling in liquid N_2, the tube was opened and the SO_2 evaporated. The residue was purified by flash chromatography on silica gel (EtOAc/light petroleum 1:1) yielding 671 mg (3.8 mmol, 43%) of a colorless solid that recrystallized from CH_2Cl_2/pentane, yielding colorless needles used for the X-ray diffraction studies. In solution, **11d** is slowly decomposed into (*E*)-1-acetoxybutadiene and SO_2 at 20 °C. It is stable in the crystalline form. mp 65−68 °C. ^1H NMR (400 MHz, $CDCl_3$)δ_H 2.23 (s, 3H, Ac), 3.77 (dddd, 1H, ^2J (H−C(5a),H−C(5b)) = 17.2, ^3J (H−C(4),H−C(5b)) = 3.0, ^4J (H−C(3),H−C(5b)) = 2.4, ^5J (H−C(2),H−C(5b)) = 1.1, H−C(5b)), 3.80 (dddd, 1H, ^2J (H−C(5a),H−C(5b)) = 17.2, ^3J (H−C(4),H−C(5a)) = 2.9, ^4J (H−C(3),H−C(5a)) = 2.6, ^5J (H−C(2),H−C(5a)) = 2.4, H−C(5a)), 5.93 (dddd, 1H, ^3J (H−C(3),H−C(2)) = 2.9, ^5J (H−C(2),H−C(5a)) = 2.4, ^4J (H−C(4),H−C(2)) = 1.2, ^5J (H−C(2),H−C(5b)) = 1.1, H−C(2)), 6.16 (dddd, 1H, ^3J (H−C(3),H−C(4)) = 8.8, ^3J (H−C(3),H−C(2)) = 2.9, ^4J (H−C(3),H−C(5a)) = 2.6, ^4J (H−C(3),H−C(5b)) = 2.4, H−C(3)), 6.43 (dddd, 1H, ^3J (H−C(3),H−C(4)) = 8.8, ^3J (H−C(4),H−C(5b)) = 3.0, ^3J (H−C(4),H−C(5a)) = 2.9, ^4J (H−C(4),H−C(2)) = 1.2, H−C(4)).

2-Chloro-2,5-dihydrothiophene-1,1-dioxide (**11e**). The procedureis the same as for the preparation of **11d**, starting from (*E*)-1-chlorobutadiene[30] (**8e**, 5 g, 0.057 mol) and heating to 50 °C for 12 h. Yield: 1.14 g (13%), yellowish oil that crystallizes from 1:1 Et_2O/pentane: colorless crystals used for the X-ray analysis, mp 40−42 °C. ^1H NMR (400 MHz, $CDCl_3$)δ_H 3.85 (m, H−C(5)), 5.28 (m, H−C(2)), 6.26 (dddd, ^3J (H-3,H-4) = 8.6, ^3J (H-3,H-2) = ^3J (H-3,H-5) = ^4J (H-3,H-5) = 2.0, H−C(3)), 6.29 (dddd, ^3J (H-3,H-4) = 8.6, ^3J (H-4,H-5) = 3.0, ^3J (H-4,H-5) = 2.5, ^4J (H-2,H-4) = 1.1, H−C(4)); ^{13}C NMR (100.6 MHz, $CDCl_3$)δ_C 53.3 (t, 145, C(5)), 69.7 (d, 170, C(2)), 127.4 (d, 176, C(4)), 128.7 (d, 179, C(3)).

2-Bromo-2,5-dihydrothiophene-1,1-dioxide (**11f**). The procedure is the same as for the preparation of **11e**, starting from (*E*)-1-bromobutadiene[30] (**8f**, 1 g, 0.0075 mol). Yield: 0.16 g (11%), yellow oil. ^1H NMR (400 MHz, $CDCl_3$)δ_H 3.83 (*m*, ^2J = 16, ^3J (H−C(5), H−C(4)) = 2.5, ^4J (H−C(5), H−C(2)) = 2.5, ^4J (H−C(5), H−C(3)) = 1.5, H−C(5)); 3.9 (*m*, ^2J = 16, ^3J (H′−C(5), H−C(4)) = 3, ^4J (H′−C(5), H−C(3)) = 2.1, ^5J (H′−C(5), H−C(2)) = 0.9, H′−C(5)); 5.4 (*m*, ^5J (H−C(2), H−C(5)) = 1.6, ^5J (H−C(2), H′−C(5)) = 0.9, H−C(2)); 6.23 (*m*, ^3J (H−C(3), H−C(4)) = 8.6, ^4J (H−C(3), H′−C(5)) = 0.9, ^4J (H−C(3), H−C(5)) = 2.5, H−C(3)); 6.32 (*m*, ^3J (H−C(4), H−C(3)) = 8.6, ^3J (H−C(4), H′−C(5)) = 3, ^3J (H−C(4), H−C(5)) = 2.5, H−C(4)). ^{13}C NMR (100.6 MHz, $CDCl_3$)δ_C 57.7 (t, 145), 58.3 (t, 155), 126.6 & 129.5 (2d, 176).

2-Chlorosulfolane. Sulfolene **11e** (88 mg, 0.6 mmol) in CH_2Cl_2 (3 mL) was pressured with H_2 (1 atm) and stirred at 20 °C for 1 h in the presence of 10% Pd/C (20 mg). After filtration (Celite) and solvent evaporation, flash chromatography on silica gel (CH_2Cl_2) gave 53 mg (60%) of a colorless oil identical (spectral data) with a sample of 2-chlorosulfolane prepared from sulfolane according to Kattenberg.[21]

2-Bromosulfolane. A mixture of sulfolene **11f** (150 mg, 0.09 mmol), MeOH (3 mL), and 10% Pd/C (20 mg) was degassed on the vacuum line and pressurized with H_2 (30 bar). After shaking at 25 °C for 12 h, the catalyst was filtered off, the solvent evaporated, and the residue purified by flash chromatography on silica gel (CH_2Cl_2) giving 40 mg (25%) of yellowish oil identical (spectral data) with the 2-bromosulfolane prepared according to Faith et al.[31]

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Supporting Information Available: Data for **11d**, **11e**, **11f**. Tables of bond lengths, bond angles, and dihedral angles for crystalline (X-ray) and MP2/6-31G* structures **11d**, **11e**. Total energies for all the structures located as computed at the different levels of theory, and ΔE[QCISD(T)/6-31G*] − ΔE[MP2/6-31G*] values corresponding to the MP2/6-31G* optimized transition structures and products for the hetero-Diels−Alder addition and the cheletropic addition of SO_2 to (*E*)-1-X-butadiene (X = H, Me, and Cl) (19 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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