Conformations of Chiral α,*β*-Unsaturated Sulfoxides and Their Complexes with Lewis Acids. An ab Initio Study

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Received January 6, 1998. Revised Manuscript Received May 20, 1998

Abstract: The rotational potential energy surface (PES) of methyl vinyl sulfoxide (**1**) was calculated at MP2/6-31+G*, B3LYP/6-311+G*, B3LYP/3-21G$^{(*)}$, MP2/3-21G$^{(*)}$, PM3, and AM1. All ab initio methods gave two conformations: one with the S−O bond (**a**) syncoplanar to the carbon−carbon double bond and one with the lone pair in plane (**b**); the first one is preferred by 1.7 kcal mol^{-1}. The energy difference is strongly basis set dependent: B3LYP/6-311+G* offers the best compromise. Semiempirical methods give a qualitatively different rotational PES. Whereas the effect methyl group in the *E*-position is small, *Z*-substitution leads to destabilization of conformation **a** through sterical interaction, so that conformation **b** is preferred by 0.4 kcal mol^{-1}. Electron-withdrawing substituents such as ester or keto groups in the α-position destabilize conformations **c** and **d** where the lone pair is syncoplanar to the C═C double bond, so that the syncoplanar orientation of the S−O bond is favored by ca. 5 kcal mol^{-1}, depending on the substituent. The structures of the chelate complexes **12** of α-(methanesulfinyl)acrylic acid methyl ester (**6**) with Me$_2$AlCl were also optimized with B3LYP/6-311+G*. The complex **12c** with the aluminum bonded to the carboxylic and the sulfoxide oxygen was calculated to be the most stable. The solvation energies of the complexes were calculated using the SCIPCM model, which allowed an approximation of the upper limit of the energy needed for the formation of the complexes.

Introduction

Chiral sulfoxides can be utilized as powerful chiral auxiliaries[1] because they can easily be prepared in high enantiopurity.[2] Pericyclic transformations, such as ene[3] or Diels−Alder reactions,[4] with chiral alkenyl sulfoxides give particularly high diastereomeric excess. For the understanding of the mechanisms of the asymmetric induction in these reactions, it is important to know the conformations of α,*β*-unsaturated sulfoxides, and how these conformations can be “held in place” (importance of rotational barriers). In this respect, it is one of the most important achievements of modern synthetic chemistry to control the stereochemistry by using various Lewis acids, allowing highly sophisticated stereodivergent transformations starting from a single substrate but giving either enantiomer by choice.[5] Little is known about the structures of Lewis acid complexes of organic substrates,[6] and the differences in the behavior of various Lewis acids are not well understood. Therefore, we were highly interested in the structures and properties of Lewis acid−sulfoxide complexes. In the present paper, we describe semiempirical, ab initio, and density functional (DFT) calculations on substituted sulfoxides and their Lewis acid complexes. We have focused on Me$_2$AlCl as the Lewis acid which is both commonly used and computationally feasible.

Methods

With the exception of the complexes, all starting geometries for the DFT calculations were generated with PC-Model, using the MMX force field.[7] These geometries were preoptimized with the semiempirical PM3 method, employing the MOPAC[8] program on a PC or an IBM RS/6000 workstation for the larger structures. For the DFT calculations, Becke’s three parameter hybrid functional (B3)[9] together with the correlation functional of Lee, Yang, and Parr (LYP) [10] were employed as implemented in Gaussian 94.[11] For the interpretation of wave functions, we utilized the natural bond population analysis (NBO).[12,13] Standardized 3-21G,[14] 6-31G,[15] and 6-311G[16] basis sets were used together with polarization (*)[17] and diffuse (+)[18] functions. For the calculation of solvent effects the SCIPCM[19] model, a polarized continuum model included in Gaussian 94, was employed.

Calculations of Alkenyl Sulfoxides

Methyl vinyl sulfoxide as the simplest model compound for an α,*β*-unsaturated sulfoxide was computed by Kahn and

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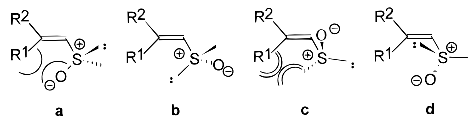
Scheme 1



	R^1	R^2
1	H	H
2	H	CH_3
3	CH_3	H

Table 1: B3LYP/6-311+G* Results for Compounds **1**−**3**

compound	**1**	**2**	**3**
C═C−S−O dihedral angle of **a**	9°	9°	12°
rel energy of **b** [kcal mol^{-1}]	1.7	1.2	−0.4
C═C−S−O dihedral angle of **b**	133°	129°	134°
rel energy of **c** (TS) [kcal mol^{-1}]	5.9	5.4	7.3
C═C−S−O dihedral angle of **c**	−74°	−78°	−98°
rel energy of **d** (TS) [kcal mol^{-1}]	4.4	3.9	1.5
C═C−S−O dihedral angle of **d**	70°	68°	68°

Hehre[20] who showed that conformation **1a** ($R^1 = R^2 =$ H) with an C═C−S−O dihedral angle of approximately 0° represents the global minimum on the RHF/6-31G*//RHF/3-21G* rotational potential energy surface (PES). The local minimum **1b** ($R^1 = R^2 =$ H) is 1.6 kcal mol^{-1} higher in energy (Scheme 1).

However, this model compound is too simple in many cases since substituents at the carbon−carbon double bond should greatly influence the conformational barriers, as it is commonly observed in allylic systems.[21] Especially in the case of α,β-unsaturated sulfoxides in intramolecular reactions, where the carbon−carbon double bond is part of a chain, alkyl substitution in the β-position should have a great effect.

We studied the β-methyl-substituted vinyl sulfoxides **2** as well as **3** and compared them with **1**. The B3LYP/6-311+G* results are given in Table 1. To find an appropriate computational level for further investigations, we calculated the rotational profile of **1** with MP2/6-31+G*, B3LYP/6-311+G*, B3LYP/3-21G$^{(*)}$, MP2/3-21G$^{(*)}$, PM3, and AM1; we compared these results with the earlier findings by Kahn and Hehre (Figure 1).

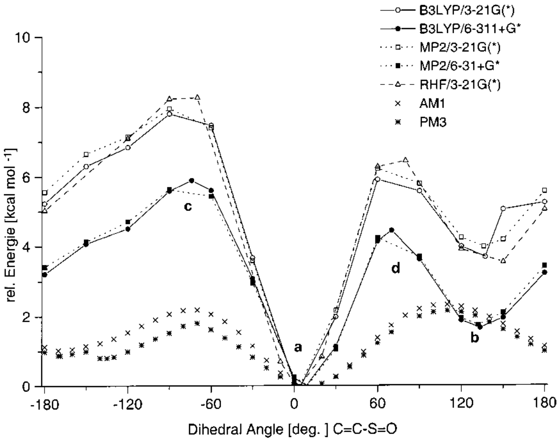


Figure 1. Comparison of the rotational PES of **1** at different levels of theory.

With the exception of AM1 and PM3, we found **1a** to be the global and **1b** a local minimum on the rotational potential energy surface (PES). The energy difference between the minima and the height of the rotational barrier strongly depends on the basis set. The 3-21G$^{(*)}$ basis gives rather large relative energy differences between **1a** and **1b** (3.4, 3.7, and 4.0 kcal mol^{-1} with RHF/3-21G$^{(*)}$, MP2/3-21G$^{(*)}$, and B3LYP/3-21G$^{(*)}$, respectively), whereas B3LYP/6-311+G* and MP2/6-31+G* give 1.7 kcal mol^{-1}. Structure **1c** has an C═C−S−O dihedral angle of −74° and a relative energy of 5.9 kcal mol^{-1}, whereas **1d** has a torsion angle of 70° and a relative energy of 4.4 kcal mol^{-1} at B3LYP/6-311+G*. The differences between the methods are small when the same basis set is used. Since the geometries found with 3-21G$^{(*)}$ do not differ much from those found with a larger basis, the RHF/6-31G*// RHF/3-21G$^{(*)}$ results of Kahn and Hehre[20] compare well with our findings.

Completely different rotational PES are found with AM1 and PM3. With these methods there are two local minima with C═C−S−O dihedral angles of about 0° and 180°, separated by very low rotational barriers. This shows that AM1 and PM3 calculations on vinyl sulfoxides are not even suitable for qualitative purposes.

As the B3LYP/6-311+G* zero-point energies of **1a**, **1b**, **1c,** and **1d** are nearly identical (52.9, 52.8, 52.7, and 52.6 kcal mol^{-1}, respectively), we decided to omit the time-consuming frequency calculations for the structures of substituted derivatives of **1**.

From a stereochemical point of view, one would expect **1b** to be most stable, since there is no substituent in the synperiplanar position relative to the vinylic double bond. As this is not the case, electronic effects must be operative. The NBO charge (B3LYP/6-311+G*) of the vinylic hydrogen in the *Z*-position to the sulfoxide in **1a** is +0.22, whereas in **1b** this charge is +0.19, indicating an electrostatic stabilization of **1a** through the interaction of the oxygen and the *Z*-hydrogen. The Wiberg bond index between these atoms in **1a** is 0.01. However, this value is rather small, so that the conformational preference must be determined mainly by other factors. In the second-order perturbation theory analysis of Fock matrix in the NBO basis for **1a**, an interaction between the C═C π orbital and the S−CH_3 σ* orbital (Scheme 2) as well as an interaction between the C═C π orbital and a Rydberg orbital of the sulfur can be found. Similarly, the C═C π* orbital interacts with the S−CH_3 σ-orbital and the sulfur lone pair. The S−O σ-orbital does not interact with the C═C π-orbital due to orthogonality. According to the NBO analysis there is no S−O π-orbital, i.e., there is no dπ−pπ bonding. Significant interaction between an oxygen lone pair and the C═C π-orbital is also absent. Rather, the O-lone pairs donate electron density in the S−C bonds. For structure **1b** an interaction between the C═C π- and the S−CH_3 σ*-orbitals as well as between the C═C π*- and the S−CH_3 σ-orbitals can also be identified. In addition, there is an interaction between the C═C π- and the S−O σ*-orbitals and,

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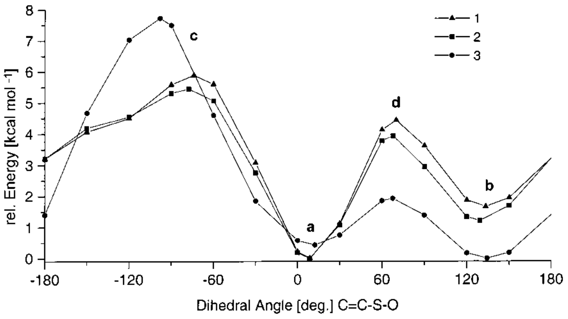

Figure 2. B3LYP/6-311+G* rotational PES of **1**−**3**.

vice versa, between the C=C π^*- and the S−O σ-orbitals. Due to orthogonality there is no interaction between the sulfur lone pair and the C=C π^*-orbital. In summary, structures are favored where the stabilization between the C=C double bond and the substituents at the sulfur are maximized, as in **1a**.

As expected, a methyl group at C-2 in the *E*-position of the carbon−carbon double bond (**2**) has only a small effect on the rotational energy profile around the carbon−sulfur bond. Conformer **2b** ($\angle_{\mathrm{C=C-S-O}} = 129°$, Scheme 1) is 1.4 kcal mol^{-1} higher in energy than **2a** ($\angle_{\mathrm{C=C-S-O}} = 9°$), the global minimum.

The *Z*-isomer **3** displays a different energy profile, where **3b** ($\angle_{\mathrm{C=C-S-O}} = 134°$) is the global minimum and **3a** ($\angle_{\mathrm{C=C-S-O}} = 12°$) is 0.4 kcal mol^{-1} higher in energy (Figure 2). This is a consequence of the repulsion between the oxygen and the methyl group at C-2. Conformation **3c** ($\angle_{\mathrm{C=C-S-O}} = -98°$) experiences the highest H···H repulsion due to the syncoplanar orientation of the methyl group at C-2 and at sulfur (Scheme 1).

Effect of an Electron-Withdrawing Group in the α-Position

Although the sulfoxide function already is electron withdrawing which activates the carbon−carbon double bond, further activation is often needed for reasonable reaction rates under mild conditions in Diels−Alder or ene reactions. Whereas the Diels−Alder reaction of *p*-toloyl vinyl sulfoxide with cyclopentadiene requires heating to 150 °C in a sealed tube over 15 h,[22] reaction of 2-(toluene-4-sulfinyl)acrylic acid ethyl ester gives quantitative conversion at room temperature within 6 h.[23] Therefore, compounds carrying a second electron-withdrawing group, e.g., cyano, carboxyl, or keto group in the α-position are commonly used to increase the reactivity of sulfoxides.

In cyano-substituted vinyl sulfoxide **4** (Scheme 3), only one rotational degree of freedom has to be considered for the rotational PES due to the inherent symmetry of the cyano group. Although the B3LYP/6-311+G* rotational energy profile of **4** and **1** are qualitatively similar (Figure 3), the minimum conformers **4a** vs **4b** (Table 2) differ more in energy than **1a** versus **1b**. Conformation **4b** and even more so the conformation of **4** with a C=C−S−O dihedral angle of about 180° is destabilized compared to the corresponding conformation of **1**. This is due to electrostatic repulsion between the oxygen (NBO charge = −0.91e for C=C−S=O = 180°) and the nitrogen of the cyano group (NBO charge of the nitrogen = −0.26e for C=C−S−O = 180°). The reactivity of a dieno- or enophile is increased with a decrease of the electron density at the carbon−carbon double bond. Although electrostatic interactions are not decisive for pericyclic reactions, the charges at carbon help to understand the polarization and activation effect at least in a qualitative manner. Compared to **1a** (charge = −0.34e at β-C, −0.41e at α-C) a smaller negative NBO charge was found at both carbon atoms of the C=C double bond in **4a** (−0.26e at β-C, −0.36e at the α-C). Thus, the cyano-substituted dienophile (the vinyl sulfoxide) double bond is more electron deficient and allows a faster reaction.

For vinyl sulfoxides containing a carboxylic acid, carboxylic ester, or a keto group in the α-position (**5**−**9**), three rotational degrees of freedom have to be considered due to the rotation of these groups (Scheme 4) as well as the rotation about the carbon−oxygen single bond of the hydroxy or alkoxy group. The conformations of carboxylic acids and esters have been widely discussed in the literature[24] saying that the *s-cis* conformation is preferred. Thus, *s-cis* conformations of the COOH and the COOMe groups of the sulfinyl acrylic acid **5** and the methyl esters **6**−**8**, respectively, were assumed in our computations, leaving the C=C−S−O and S−C−C=O dihedral angles as rotational parameters. Four minimum conformations **5a**−**d** were located at RHF/3-21G$^{(*)}$; these were further optimized with B3LYP/6-311+G* (Scheme 4, Table 3).

Generally, C=O and C=C conjugated in-plane conformations of **5** are favored. The preferred orientation of the S−O group of the sulfoxide moiety is syncoplanar with the carbon−carbon double bond (**5a** and **5b**). Conformers **5c** and **5d** with an C=C−S−O dihedral angle of ca. 130° are 5.6 and 5.5 kcal mol^{-1} higher in energy than **5a**, much higher than the corresponding conformers of **1** and **4**. This can be rationalized as being a consequence of the electrostatic repulsion between the sulfoxide oxygen and the carboxylic acid moiety in conformers **5c** (NBO charge of S−O = −0.93e, C=O = −0.58e) and **5d** (NBO charge of S−O = −0.93e, O−H = −0.67e) as noted for **4**. The effect is more pronounced for **5** than for **4** because the carboxy group is larger and more electron demanding than the cyano group. Whereas the carboxylic groups in **5a** and **5b** have nearly planar conformations, **5c** (∠C=C−C=O = 156°) and **5d** (∠C=C−C−OH = 166°) are nonplanar resulting in longer separations between the carboxylic and the sulfoxide oxygen to minimize the electrostatic repulsion. In addition to conformers **5a**−**d** with the generally preferred *s-cis* conformation of the carboxylic acid group, *s-trans* conformer **5e** is also low-lying (1.0 kcal mol^{-1}) due to an intramolecular hydrogen bond. Similarly to the cyano group in **4**, the carboxylic group activates the carbon−carbon double bond in **5**; the α-C (−0.35e) and the β-C (−0.26e) charges in **5a** are comparable to the local charges in **4a** (vide supra).

The rotational profile of the sulfinyl acrylic acid ester **6** is dominated by the same effects found for the free acid, with the exception that there is no stable conformer with an internal hydrogen bond (Scheme 4). Thus, the dihedral angles and relative energies in conformers **6a**−**d** are only slightly different from those for the corresponding conformers of **5**. As found for **5**, both conformations with a syncoplanar sulfoxide moiety (**6a** and **6b**) are close in relative energy ($\Delta E_{\mathrm{rel}} = 0.5$ kcal mol^{-1}). The relative energies of **6c** versus **6d** are only slightly lower than those of **5c** versus **5d**. The activation of the C=C double bond in **6a** is similar to that in **5a** (NBO charge at the α-C = −0.34e, at the β-C = −0.26e).

The effect of a methyl group at C-3 in the *E*-position (**7**) is minimal. The energy difference between conformers **7c** and **7d** (C=C−S−O dihedral angle of about 130°) and **7a** and **7b** (C=C−S−O dihedral angle about 0°) is lower than found for

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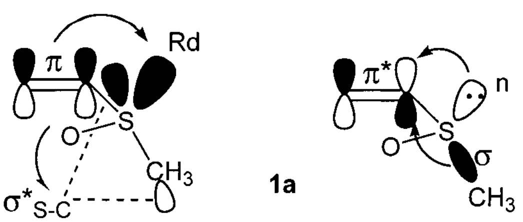
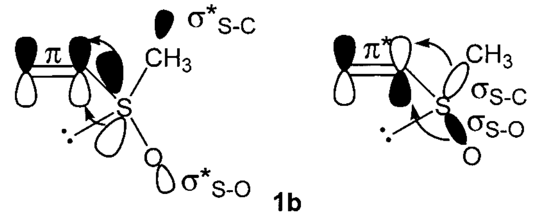
Scheme 2



1a

Interaction	$E^{(2)}$ [kcal mol^{-1}]
π-$\sigma^*_{S\text{-}C}$	1.9
π-Rd	1.5
π^*-$\sigma_{S\text{-}C}$	2.6
π^*-n	2.4
Σ	8.4



1b

Interaction	$E^{(2)}$ [kcal mol^{-1}]
π-$\sigma^*_{S\text{-}C}$	1.5
π-$\sigma^*_{S\text{-}O}$	1.9
π^*-$\sigma_{S\text{-}C}$	1.9
π^*-$\sigma_{S\text{-}O}$	0.7
Σ	6.0

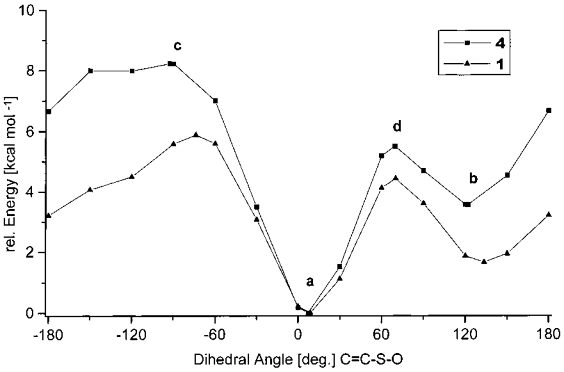


Figure 3. B3LYP/6-311+G* rotational PES of **1** and **4**.

Scheme 3

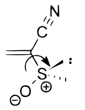


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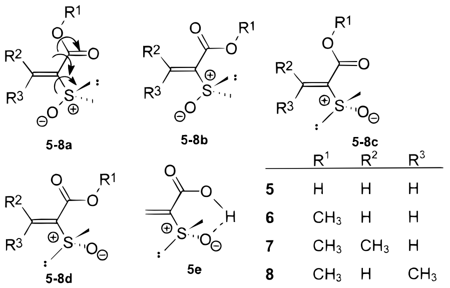
Table 2: Energies [kcal mol^{-1}] and Dihedral Angles of the Rotamers of **4**

	energy	C=C−S−O dihedral angle
4a*	0	7
4b	3.6	122
4c (TS)	8.2	−93
4d (TS)	5.5	70

the corresponding conformers of **6**. *Z*-Substitution of the carbon−carbon double bond has a more distinct influence. The energy difference between **8a** and **8b** with the sulfur−oxygen bond syn-periplanar to the carbon−carbon double bond and **8c** and **8d** (C=C−S−O dihedral angle of about 130°) is reduced to one-half compared to that of the conformers of **6**. As for **3**, there is steric repulsion between the vinylic methyl group and the sulfoxide oxygen destabilizing **8a** and **8b**. However, there is also an even more pronounced destabilizing effect in **8c** and **8d** through interaction between the nonbonding electron pairs of the ester and sulfoxide oxygen. The minimum conformation of **7** is 2.1 kcal mol^{-1} more stable than the minimum conformation of **8**, in accord with the experimental result of Tanikaga et al.,[25] who observed that Knoevenagel condensations of aldehydes and arylsulfinyl acetate only give the thermodynamically more stable *E*-products.

Scheme 4



	R^1	R^2	R^3
5	H	H	H
6	CH_3	H	H
7	CH_3	CH_3	H
8	CH_3	H	CH_3

Table 3: B3LYP/6-311+G* Optimization Results for **5**−**9**

compound	**5**	**6**	**7**	**8**	**9**
a C=C−S−O dihedral angle	5°	5°	3°	1°	5°
C=C−C=O dihedral angle	179°	179°	182°	−175°	179°
b C=C−S−O dihedral angle	4°	3°	3°	3°	0°
C=C−C=O dihedral angle	−4°	−5°	−6°	−1°	−27°
rel energy to **a** [kcal mol^{-1}]	0.6	0.5	0.3	0.2	3.5
c C=C−S−O dihedral angle	127°	130°	130°	130°	could
C=C−C=O dihedral angle	156°	148°	148°	149°	not be
rel energy to **a** [kcal mol^{-1}]	5.6	5.4	4.6	2.8	localized
d C=C−S−O dihedral angle	130°	131°	137°	132°	133°
C=C−C=O dihedral angle	−14°	−15°	−31°	−15°	47°
rel energy to **a** [kcal mol^{-1}]	5.5	5.2	4.4	2.4	5.0

In contrast to **6**, the orientation of the carbonyl group relative to the carbon−carbon double bond has a great influence on the potential energy surface of **9**: the *s-cis* conformer **9b** is 3.5 kcal mol^{-1} higher in energy than the *s-trans* conformer **9a** (Scheme 5). This is a consequence of the steric repulsion between the two methyl groups in **9b**, which is minimized through an out-of-plane distortion of the keto group. Hypothetical **9c**, which would be comparable to **6c**, is not a local minimum; it is highly destabilized by electrostatic repulsion between both oxygen atoms (**9a**'s NBO charge of S−O = −0.95, C=O = −0.55). In contrast to **6d**, there is no destabilizing electrostatic repulsion in **9d**; however, methyl

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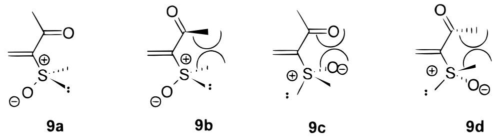
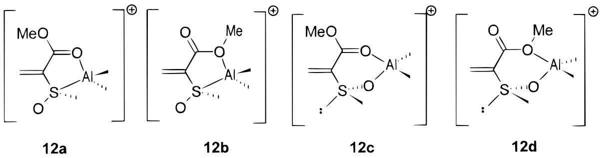
[25] Tanikaga, R.; Konya, N.; Tamura, T.; Kaji, A. *J. Chem. Soc., Perkin. Trans. 1* **1987**, 825.

Scheme 5



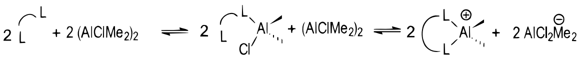
Scheme 6



repulsion disfavors **9d** in the same way as **9b**, leading to a relative energy of 5.0 kcal mol^{-1} and a nonplanar keto group. A similar interaction energy (5.2 kcal mol^{-1}) was obtained by simple addition of the energy difference between **1a** and **1b** (1.7 kcal mol^{-1}) caused by the different orientation of the S−O group and the energetical difference between **9a** and **9b** (3.5 kcal mol^{-1}) (Table 3).

Lewis Acids Complexes of Alkenyl Sulfoxides

Since the S−O group operates as an acceptor site for Lewis acids, the conformations should strongly be influenced by complexation. Although monomeric Me$_2$AlCl has only one coordination site, the formation of chelates is possible if the second coordination site of the chelating ligand replaces the chloride in the modentate complex. The chloride can then be transferred to a second Me$_2$AlCl molecule to give the chelate complex cation and the Me$_2$AlCl$_2$ anion (eq 1).



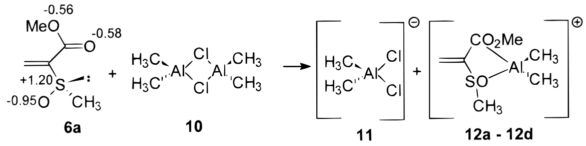
(1)

Experimental evidence for the ligand exchange at aluminum in the case of excess Lewis acid was first reported by Lehmkuhl and Kobs.[26] Chelate complexes with Et$_2$AlCl were also described by Evans et al.[27] and Castellino[28] in their mechanistic studies on *N*-acyloxazolidinones. Thus, it is quite reasonable to assume the formation of a chelate complex with the acrylic acid ester derivative **6** at least in the presence of excess of Me$_2$AlCl (eq 1). Structure **6** has two coordination sites in each functional group for the Lewis acid, the two oxygen atoms in the ester function, and the sulfur or the oxygen in the sulfoxide group. Although the oxygen is favored as coordination site through its negative charge and large Al−O binding energy, there are also sulfoxide complexes observed with the metal coordinated to sulfur.[29] In case of **6**, this would allow chelation without changing the ligand's minimum geometry. Thus, there are four complex ions **12a−d**, derived from the four minimum conformers of **6** (Scheme 6). Complex **12c** was found to be most stable, followed by **12a**, **12b**, and **12d** with relative energies of 7.9, 23.1, and 115.4 kcal mol^{-1}, respectively (Table 4). In **12c**, which is derived from a less stable conformer of **6c**, the metal is coordinated to the atoms bearing the highest negative charge in the free ligand (eq 2). Structure **12d** is destabilized due to methyl repulsion, leading to deformation of the ring compared to that in **12c** (Figure 4). The metal bonding at the sulfoxide oxygen weakens the S−O bond, as it can be seen in the bond lengths (1.51 Å in the free ligand **6a**, 1.55 Å in **12c** and 1.72 Å in **12d**); the Wiberg bond indices are 1.24 in the free ligand, 1.04 in **12c**, and 0.98 in **12d**. Bonding at the sulfur increases the S−O bond strength which is also indicated by a shortening of the respective bond length (1.51 Å in the free ligand **6a**, 1.49 Å in **12a**, and 1.45 Å in **12b**); the Wiberg bond indices are 1.24 in the free ligand and 1.28 in **12a** and **12b**. This is in agreement with the 1.48 Å S−O bond length found in the X-ray structure of the complex cation [CpRu(chir)(MeS(O)-*i*-Pr)]$^+$ (chir = 2(*S*),3(*S*)-bis(diphenylphosphino)butane).[29]

Table 4: Energies for the Complexes **12a−12d**

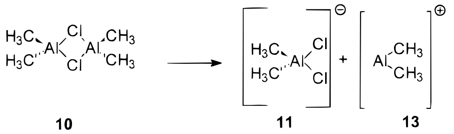
	12a	12b	12c	12d
without Solvation				
energy relative to **12c** [kcal mol^{-1}]	+28.8	+44.1	0	+136.4
Δ*H* of eq **2** [kcal mol^{-1}]	+91.6	+106.9	+62.8	+199.2
Δ*H* of eq **4** [kcal mol^{-1}]	−51.4	−36.3	−80.3	+56.1
with SCIPCM Solvation Model[a]				
energy rel to **12c**	+28.3	+43.6	0	+22.6
complex formation enthalpy Δ*H* of eq **2**	+16.8	+32.0	−11.6	+11.0

[a] SCIPCM single point energy calculated with dielectric constant of $\epsilon = 9.1$ (CH$_2$Cl$_2$) and cavity boundary at the isodensity value of 0.0004.

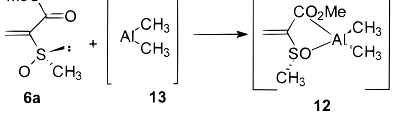


(2)

Since all four chelate complexes have a positive enthalpy of formation, one would conclude that the chelate complexes **12a−d** do not form. Most of this energy is needed for charge separation involved in the formation of **12a−d** via eq 1. The formation of the complexes can be divided into two parts: the dissociation of (Me$_2$AlCl)$_2$, which involves charge separation, and the binding of AlMe$_2$$^+$ to the ligand **6a**. Equation 4 is favorable (ΔH < 0) for the complexes **12a−c**, whereas **12d** is less stable than the separated AlMe$_2$$^+$ and the ligand **6a**.



(3)



(4)

The energy required for the formation of the ions is more difficult to calculate, since it is not correct to assume a complete separation of the ion pairs of **12a−d** and **11**; the interaction with the solvent may stabilize the charged chelate complexes substantially. However, complete separation of the ions in a solvent, for which a polarizable continuum is used as model, can be used to approximate the upper limit for the energy needed for the formation of the chelate complexes **12a−d** in solution. Any interaction between the ions **12a−d** and **11** in solution can

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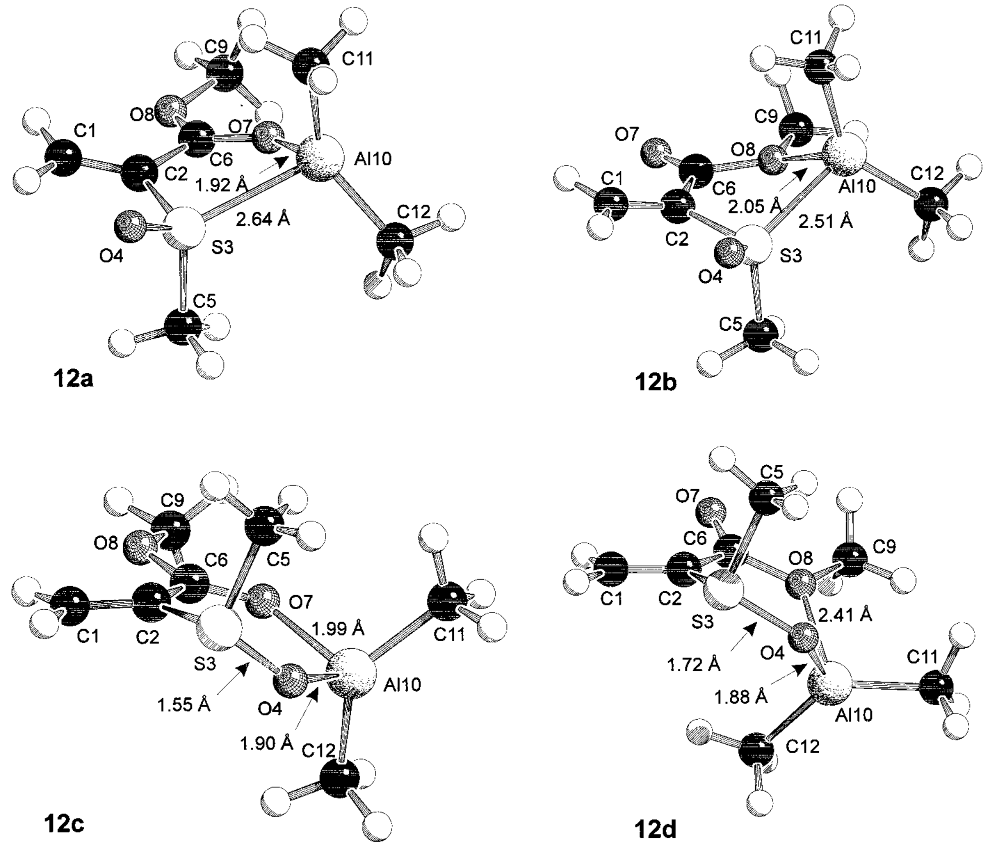
(26) Lehmkuhl, A.; Kobs, H. D. *Liebigs Ann. Chem.* **1968**, *719*, 11.

(27) Evans, A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1988**, *110*, 1238.

(28) Castellino, S.; Dwight, W. J. *J. Am. Chem. Soc.* **1993**, *115*, 2986.

(29) Schenk, W. A.; Frisch, J.; Dürr, M.; Burzlaff, N.; Stalke, D.; Fleischer, R.; Adam, W.; Prechtl, F.; Smerz, A. K. *Inorg. Chem.* **1997**, *36*, 2372.



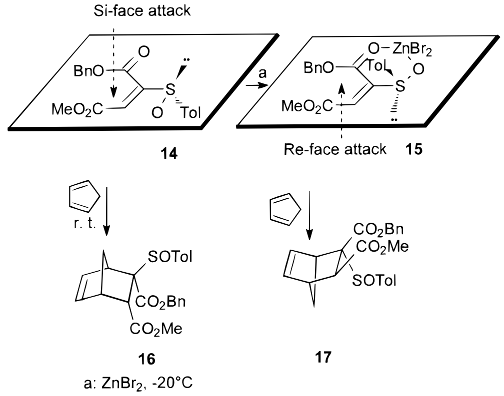
12a **12b** **12c** **12d**

Figure 4. B3LYP/6-311+G*-optimized geometries of **12a**−**d**.

lead to further stabilization and to a lower reaction enthalpy for the formation reaction of **12a**−**d**. Therefore, we decided to calculate the energies of **6a**, **10**, **11**, and **12a**−**d** using the SCIPCM solvation model. Including solvation the most stable complex **12c** has a negative reaction enthalpy of eq 2 (−11.6 kcal mol^{-1}), whereas the ΔH values of the other complexes remain positive, but are also lowered. In the "solvated" complexes the NBO charge at the β-C (−0.17e) is lower than in the free ester **6a** (−0.26e), whereas the NBO charge at the α-C remains nearly unchanged (−0.35e), leading to a stronger polarization of the C=C double bond. The electron density in the C=C double bond is lowered, and the reactivity is raised.

In **12c**, the methyl groups, which shielded the α-side in the free ligand **6a**, now shields the β-face. If the reaction is controlled sterically by the substituent at sulfur, one expects a change in the diastereoselectivity of the reaction. Using $ZnBr_2$ as Lewis acid, such a reversal in diastereoselectivity was experimentally observed.[30] Without using a Lewis acid, the Si-face of **14** was preferentially attacked by the cyclopentadiene to give **16** and **17** in a ratio of 73:8. Using $ZnBr_2$, the reaction takes place at the Re-face of the complex **15** and a **16**:**17** ratio of 6:91 was obtained (Scheme 7). Further examples for this change in diastereoselectivty exist.[31]

Scheme 7



14 **15** **16** **17**

a: $ZnBr_2$, -20°C

Conclusions

In methyl vinyl sulfoxide (**1**), the *s-cis* conformation (**1a**) of the S−O bond in α,β-unsaturated sulfoxides is favored. A second conformer (**1b**) with a C=C−S−O dihedral angle is 1.7 kcal mol^{-1} (B3LYP/6-311+G*) less stable. The energy difference between the conformations is strongly basis set dependent; electron correlation is not very important. MP2/6-31+G*, B3LYP/3-21G$^{(*)}$, MP2/3-21G$^{(*)}$, and RHF/3-21G$^{(*)}$ give a qualitatively correct rotational PES for C=C−S−O, whereas AM1 and PM3 are unsuitable.

Structure **1a** is stabilized the interactions of the σ_{S-CH_3}-orbital and the sulfur lone pair with the $\pi_{C=C}$*-orbital as well as the interaction of the $\pi_{C=C}$-orbital with the σ_{S-CH_3}*-orbital and a Rydberg orbital at the sulfur. The $\sigma_{S-CH_3}-\pi_{C=C}$*, $\sigma_{S-O}-\pi_{C=C}$*, $\pi_{C=C}-\sigma^*_{S-CH_3}$, and $\pi_{C=C}-\sigma_{S-O}$* interactions in **1b** lead to a smaller stabilization than in **1a**.

E-Substitution at C-2 (**2**) led to no significant changes in the rotational PES. A methyl group in *Z*-position at C-2 (**3**) destabilizes the *s-cis* conformation (**3a**) so that **3b** (∠C=C−S−O = 134°) is favored by 0.4 kcal mol^{-1}.

Electron-withdrawing groups in the α-position as the cyano, caboxylic, or keto group lead to a destabilization of the

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(30) Alonso, I.; Carretero, J. C.; García Ruano, J. L. *J. Org. Chem.* **1994**, *59*, 1499.

(31) (a) Arai, Y.; Matsui, M.; Fujii, A.; Kontani, T.; Ohno, T.; Koizumi, T.; Shiro, M. *J. Chem. Soc., Perkin Trans. 1*, **1994**, 25. (b) Carreño, M. C.; García Ruano, J. L.; Toledo, M. A.; Urbano, A.; Remor, C. Z.; Stefani, V. *J. Org. Chem.* **1996**, *61*, 503.

conformations with a C═C−S−O dihedral angle of about 130° due to electrostatic repulsion between the sulfoxide oxygen and the oxygen or nitrogen atom in the electron-withdrawing group. In the case of the cyano-substituted **4**, the difference between **4a** (∠C═C−S−O = 7°) and **4b** (∠C═C−S−O = 122°) is 3.6 kcal mol^{-1}. In **5** and **6** with a carboxylic acid or ester group in the α-position, the preferred conformation a has an C═C−S−O dihedral angle of 5° and an C═C−C═O dihedral angle of 179°. Conformations **c** and **d** with a C═C−S−O dihedral angle of ca. 130° are 5.5 kcal mol^{-1} less stable. As already observed for **3**, a methyl group in *Z*-position destabilizes the conformations with *s-cis* orientation of the S−O bond, thus the **8a** is only 2.8 kcal mol^{-1} more stable than **8c**.

The calculation of the four possible chelate complexes of α-(methanesulfinyl)acrylic acid methyl ester (**6**) with Me_2AlCl demonstrated that the complex **12c**, in which the aluminum is bound to the sulfoxide oxygen and the C═O group, is the most stable. This complex cation **12c** is stabilized by 80.3 kcal mol^{-1} compared to the free ligand and the $AlMe_2^+$. The reaction enthalpy ΔH for the reaction of $(Me_2AlCl)_2$ + ligand **6** → complex cations + $Me_2AlCl_2^-$ with the SCIPCM solvation model was estimated to approximate the upper energy limit for formation of the complexes including the energy required for the formation of the ions. Again **12c** is most favorable ($\Delta H = -11.6$ kcal mol^{-1}) whereas the ΔH for the other complexes is positive. Cation **12c** is derived from a less-favored conformation of the ligand. Thus complexation can alter the stereochemical outcome significantly.

Acknowledgment. This work was supported by the Fonds der chemischen Industrie (Liebig Fellowship for P.R.S.) and the Stiftung Volkswagenwerk.

Supporting Information Available: Absolute energies and geometrical data of **1** at different levels of theory, absolute B3LYP/6-311+G* energies for compounds **1**−**13**, and selected geometrical and NBO analysis data for **12a**−**d** (2 pages print/PDF). See any current masthead page for ordering information and Web access instructions.

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