Cyclic Vinyl *p*-Tolyl Sulfilimines as Chiral Dienophiles: Diels−Alder Reactions with Furan and Acyclic Dienes

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Received October 4, 2001

The dienophilic behavior of the sulfilimine **2**, synthesized from (*Z*)-3-*p*-tolylsulfinylacrylonitrile **1**, in its Diels−Alder reactions with furan and acyclic dienes has been investigated. A complete π-facial selectivity for **2**, opposite to that observed from its precursor **1**, is the main feature of all these cycloadditions. Moreover, the high *exo* selectivity observed in reactions of **2** with furan (not observed for **1**) contrasts with the almost complete *endo* selectivity with other cyclic and acyclic dienes. Additionally, the opposite regioselectivities obtained for **2** with Dane's diene and 1-substituted butadienes (not observed for **1**) are also noteworthy. This behavior allows dienophiles **1** and **2** to be considered as complementary precursors from a synthetic point of view.

Introduction

The sulfinyl group has been shown to be one of the most efficient chiral auxiliaries in asymmetric Diels−Alder reactions,[1] as a result of its ability to differentiate the diastereotopic faces of the double bond of substituted vinyl sulfoxides. Nevertheless, the reactions of vinyl *p*-tolyl sulfoxide with cyclopentadiene exhibited a moderate π-facial selectivity as well as a scarce *endo* selectivity,[2] which indicated that the ability of the sulfinyl group to control the stereochemical course of these reactions is only apparent in the presence of other functional groups that increase the dienophilic reactivity and restrict the conformational equilibrium around the C−S bond. In this sense, a large number of vinyl sulfoxides bearing electron-withdrawing groups have been studied,[1a] alkyl (*Z*)-3-arylsulfinylacrylates being the most widely used in asymmetric synthesis.[3] The alkoxycarbonyl group in these compounds shifts the conformational equilibrium around the C−S bond toward the rotamer with the sulfinyl oxygen in an *s-trans* arrangement (thus controlling the π-facial selectivity) and enhances the weak *endo* orientating character of the sulfinyl group.

In the course of our studies on the behavior of substituted activated vinyl sulfoxides as chiral dienophiles in asymmetric Diels−Alder reactions,[4,1a] we have recently demonstrated that (*Z*)-3-*p*-tolylsulfinylacrylonitriles (**1**) exhibit a complete π-facial selectivity and a very high *endo* selectivity, both higher than those of their corresponding acrylates, when they react with cyclopentadiene.[5] Moreover, the reactivity of the nitriles is clearly higher than that of the esters, which could be demonstrated in reactions with furan and acyclic dienes.[6] As compared with sulfinylacrylates, the higher reactivity and *endo* selectivity of sulfinylacrylonitriles were attributed to the linear structure of the nitrile, which avoids any steric repulsion between CO_2R and SOTol groups distorting the planarity in the case of the ester and hence decreasing both the reactivity and the *endo* selectivity. The interest in asymmetric Diels−Alder reactions of these sulfinylacrylonitriles, with better dienophilic features than their esters counterparts, increased because of the fact that the π-facial selectivity of their reactions with cyclopentadiene can be completely reversed in the presence of $BF_3{\cdot}OEt_2$ (Scheme 1).[5] However, we did not succeed in making use of this inversion with acyclic dienes, because of their fast polymerization in the presence of the catalytic $BF_3{\cdot}OEt_2$.

Fortunately, we found another way to invert the π-facial selectivity of the reaction with cyclopentadiene, consisting of the transformation of the starting nitrile into the cyclic vinyl-*p*-tolylsulfilimine (**2**).[7] As we can see in Scheme 1, the spatial arrangement of the *p*-tolyl group in compound **2** is identical to that of the intermediate generated in the presence of $BF_3{\cdot}OEt_2$ and opposite to that adopted by such a group in the most stable *s-trans*

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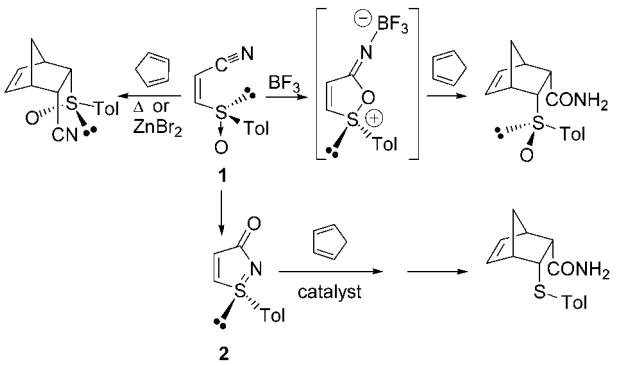
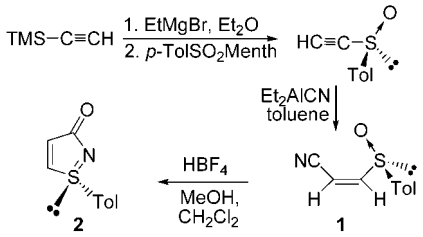
10.1021/jo016174w CCC: $22.00
Published on Web 03/28/2002

Scheme 1



Scheme 2



conformation of the starting nitrile, which justifies the stereochemical evolution of these new dienophiles.

On this assumption we reasoned that sulfilimines **2** could be used as a complementary dienophile to the sulfinyl nitriles for the preparation of adducts derived from furan and acyclic dienes exhibiting the opposite configuration in all the chiral centers created in the cycloaddition. Therefore, in this paper we report the results obtained in these reactions conducted under different conditions in order to expand the scope of applicability of these new dienophiles, which are interesting both from a synthetic and a theoretical point of view.

Results and Discussion

The synthesis of the optically pure vinyl-*p*-tolylsulfilimine **2** can be readily achieved in a short three-step sequence involving sulfinylation of commercially available terminal alkynes,[8] stereoselective conjugated addition of Et_2AlCN to the resulting alkynyl sulfoxides,[5] and treatment of the obtained (*Z*)-sulfinylacrylonitrile **1** with HBF_4 and then quenching with methanol[7] (Scheme 2).

The results obtained in the Diels−Alder cycloadditions of **2** with furan under different conditions are collected in Table 1. Refluxing **2** in an excess of furan, in the absence of any cosolvent, for several days, afforded the unaltered starting sulfilimine (entry 1). When the reaction was conducted at high pressure, a mixture of two adducts could be detected, but the major component of the reaction mixture was the starting material (entry 2). In the presence of 1.2 equiv of $ZnBr_2$ as a catalyst at room temperature a mixture of *exo*-**3A** (major) and *endo*-**3B** (minor) adducts was obtained, although the reaction was not complete (entry 3). No improvement was achieved with the use of high pressures in the presence of $ZnBr_2$ (entry 4), because the conversion was similar and the stereoselectivity decreased. The best results were obtained working at low temperature (−20 °C) when the process was catalyzed by $BF_3{\cdot}OEt_2$ (entry 5). Under these conditions, an almost complete conversion was observed, as well as the formation of *exo*-**3A** as the major product, which could be easily isolated diastereomerically pure in 85% yield. However, the stereoselectivity under these catalytic conditions was lost on increasing the temperature (entry 6). Contrary to the cycloadditions of (*Z*)-sulfinylacrylonitriles,[6] the use of Me_3AlCl in the reactions of vinyl sulfilimines led to decomposition mixtures.

The behavior of vinyl-*p*-tolylsulfilimine **2** with acyclic dienes such as (*E*)-1-methoxy-1,3-butadiene (**4**) and piperylene (**5**) was also investigated. These dienes had afforded high stereoselectivities and regioselectivities in reactions with (*Z*)-sulfinylacrylonitrile **1**,[6] although in the presence of $BF_3{\cdot}OEt_2$ as the catalyst no transformation had been achieved (see above). The results are summarized in Table 2.

The low solubility of **2** in both dienes made necessary the use of CH_2Cl_2 as a solvent. All assays were performed with 2 equiv of diene, although higher ammounts of diene (up to 8 equiv) were also tried with identical results. When the reactions were performed at atmospheric pressure, even at high temperature (entry 4) or in the presence of $ZnBr_2$ as a catalyst (entries 1 and 6), the degree of transformation was small in the best of the cases, with substantial amounts of unaltered starting material being recovered. The best results were achieved by combining the use of high pressure and a catalyst (entries 3 and 7). With (*E*)-1-methoxy-1,3-butadiene (**4**) in the presence of $ZnBr_2$ at 4 kbar the reaction evolved with complete regio-, *endo*, and π-facial selectivities, affording just one adduct *endo*-**6A**. Under the same conditions, the reaction with piperylene (**5**) gave a mixture of two regioisomers **7** (regioisomer **7A** being predominant), but once again the π-facial and the *endo* selectivities of the process were complete.

Finally, reactions with 3,4-dihydro-6-methoxy-1-vinyl naphthalene (**8**) (Dane's diene)[9] were also studied (Table 3). The interest of this diene, one of the most frequently used in the construction of steroidal skeletons,[10] is related to the regioselectivity of their reactions, mainly with the role of Lewis acid catalysts, which are able to invert it in many cases.[11] These reactions only take place at high pressure (4 kbar), affording mixtures of two stereoisomers, *endo*-**9A** and *exo*-**9A**, the former being clearly

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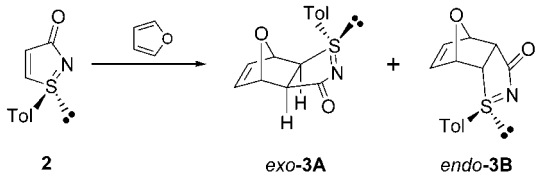
Table 1. Diels–Alder Reactions of 2 and Furan

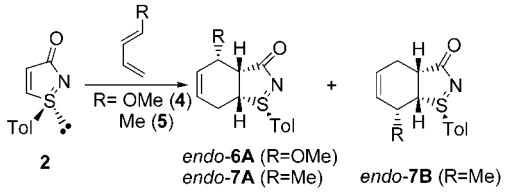


2 *exo*-**3A** *endo*-**3B**

					isolated yield (%)	
entry	Lewis acid	conditions	pressure	ratio[a] **2**:*exo*-**3**:*endo*-**3**	*exo*-**3A**	*endo*-**3B**
1		reflux, 4 d	1 bar	100: 0:0		
2		rt, 6 d	4 kbar	80:17:3		
3	$ZnBr_2$[b]	rt, 4 d	1 bar	19:74:7	69	<7
4	$ZnBr_2$[b]	rt, 3 d	4 kbar	22:55:23		
5	$BF_3{\cdot}OEt_2$[c]	−20 °C, 5 d	1 bar	2:94:4	85	<4
6	$BF_3{\cdot}OEt_2$[c]	reflux, 5 d	1 bar	4:49:47		

[a] From integration of well separated signals of the ^{1}H NMR spectrum of the crude mixture. [b] 1.2 equiv. [c] 2 equiv.

Table 2. Diels–Alder Reactions of 2 with Acyclic Dienes 4 and 5

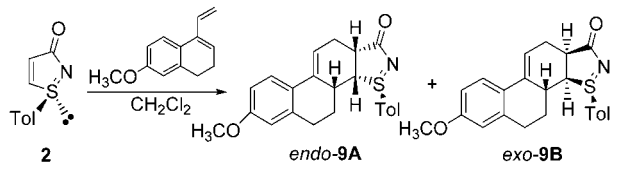


2 *endo*-**6A** (R=OMe) *endo*-**7A** (R=Me) *endo*-**7B** (R=Me)

							isolated yield (%)	
entry	diene	Lewis acid[a]	conditions	pressure	product	ratio[b] **2**:**A**:**B**	**A**	**B**
1	**4**	$ZnBr_2$	rt, 14 d	1 bar	**6A**	90:10:0		
2	**4**		rt, 10 d	4 kbar	**6A**	32:68:0	*c*	
3	**4**	$ZnBr_2$	rt, 3 d	4 kbar	**6A**	0:100: 0	89	
4	**5**		reflux, 10 d	1 bar	**7A/7B**	100: 0:0		
5	**5**		rt, 6 d	4 kbar	**7A/7B**	95:5:0		
6	**5**	$ZnBr_2$	rt, 28 d	1 bar	**7A/7B**	43:50:7	*b*	
7	**5**	$ZnBr_2$	rt, 3 d	4 kbar	**7A/7B**	0:87:13	84	11

[a] 1.2 equiv. [b] From integration of well separated signals of the ^{1}H NMR spectrum of the crude mixture [c] Not determined.

Table 3. Diels–Alder Reactions of 2 and Dane's Diene (8)



2 *endo*-**9A** *exo*-**9B**

					isolated yield (%)	
entry	Lewis acid[a]	conditions	pressure	ratio[b] **2**:**9A**:**9B**	*endo*-**9A**	*exo*-**9B**
1		rt, 7 d	1 bar	100: 0:0		
2	$ZnBr_2$	rt, 7 d	4 kbar	0:73:27	70	5
3		rt, 14 d	4 kbar	0:86:14	84	7

[a] 1.2 equiv. [b] From integration of well separated signals of the ^{1}H NMR spectrum of the crude mixture.

predominant. In this reaction, the presence of the catalyst decreased the stereoselectivity (compare entries 2 and 3 in Table 3), but the regioselectivity remained unaltered and the yields were very high in any case. These results demonstrate that the reactions of sulfilimine **2** with Dane's diene are completely regio- and π-facial selective, and their *endo* selectivity is very high although not complete. Concerning the regioselectivity, it seems to be controlled by the sulfur function at the dienophile and the substituent at C-1 at the diene whereas in reactions with 1-substituted dienes the amide moiety at the dienophile **2**, instead of the sulfur function, was mainly responsible for the regioselectivity (see Table 2).

The stereochemistry of the adducts resulting from all of these reactions was unequivocally established by chemical correlation with compounds of known configuration (Scheme 3). Thus, the major adducts obtained in reactions with acyclic alkenes (*endo*-**6A** and *endo*-**7A**) were correlated with the major adducts, *endo*-**12** and *endo*-**13**, obtained from sulfinylacrylonitrile **1**, whose optical purities were determined by NMR using $Eu(hfc)_3$ as the LSR.[6] Treatment of the adducts obtained from sulfilimine with $LiAlH_4$ in THF yielded the corresponding sulfenyl carboxamides **10A** and **11A**. The same compounds could be obtained from *endo*-**12** and *endo*-**13** by hydrolysis of the cyano group with anchimeric assistance of the sulfinyl oxygen.[12] Specific rotation of the compounds derived from both routes are identical but with the opposite sign, thus demonstrating that they are enantiomers. The stereochemistry of the minor regioisomer **7B** was assigned by asuming that the π-facial selectivity and the *endo* selectivity are identical in both regioisomeric approaches.

The *endo* or *exo* character of the resulting adducts (*exo*-**3A** was isolated by chromatography, whereas diastereomerically pure *endo*-**3B** could not be isolated) was determined by ^{1}H NMR. The absolute configuration of

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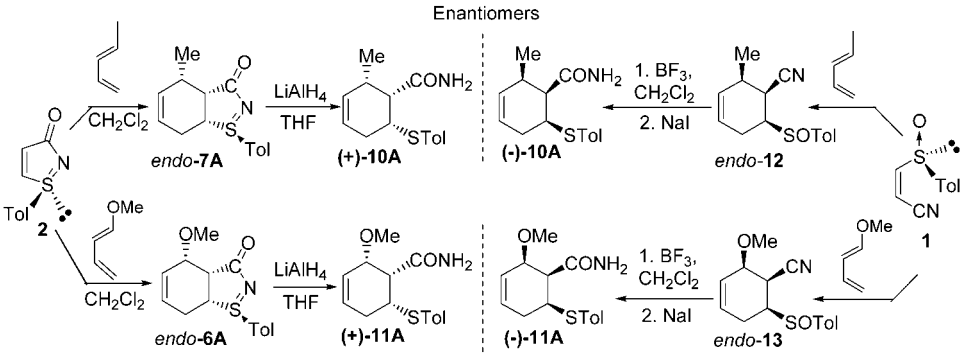
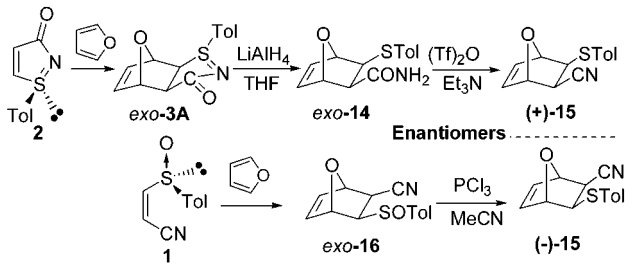
Scheme 3



Scheme 4



compound *exo*-**3A** obtained as the major product from these reactions was unequivocally assigned by chemical correlation with the *exo*-adduct (*exo*-**16**) obtained as the minor product from Diels−Alder reaction of (*Z*)-sulfinylacrylonitrile with furan, which had been previously described.[6] In this case, the correlation was made by using a slightly different sequence (Scheme 4). Thus, adduct *exo*-**3A** was treated with $LiAlH_4$−THF affording *exo*-**14**, which was transformed into sulfenylnitrile **15** with the dehydrating reagent $(Tf)_2O-NEt_3$.[13] The enantiomer of this compound resulted from reduction with PCl_3-CH_3CN of the adduct *exo*-**16**, one of the minor ones obtained from (*Z*)-sulfinylacrylonitrile **1** (Scheme 4). The configuration of the minor adduct *endo*-**3A** was assigned by assuming that the π-facial selectivity is identical for the *endo* and *exo* approaches.

Finally, the configurational assignment of the adducts *endo*-**9A** and *exo*-**9B** also required their transformation into the corresponding diastereomeric sulfenylcarboxamides *endo*-**17A** and *exo*-**17B** with $LiAlH_4$ (Scheme 5). The reaction of the adduct **18**, obtained from compound **1** with the Dane's diene,[6] with $BF_3{\cdot}OEt_2$ and NaI yielded the carboxamide *endo*-**19**, whose ^1H NMR spectrum is different from those of **17A** and **17B**, as it must be expected for regioisomers.[14]

The configuration of the major adduct **9A**, resulting from the *endo* approach of the diene to the less hindered face of the dienophile, was unequivocally assigned by ^1H NMR analysis (NOE)[15] (Figure 1). Configuration of minor **9B**, obtained in less than a 5% yield, was tentatively assigned as the *exo* isomer of **9A**, resulting from cycloaddition with the same π-facial selectivity.[14]

Upon establishing the configurational assignment of all obtained adducts, we can summarize the main differences between the dienophiles **1** and **2** in their reactions with furan and acyclic dienes. The main difference is that both dienophiles evolve with the opposite π-facial selectivity. In this sense, the control of this type of selectivity is very efficient for both dienophiles but even better for **2**.[16] This could be easily explained taking into account that the relative spatial arrangement of the *p*-tolyl group is opposite for both dienophiles (Scheme 6). In this sense compounds **1** and **2** can be considered as complementary.

Concerning the regioselectivity, two main differences have been observed. First, the cyclic dienophile **2** exhibits a regioselectivity with 1-substituted dienes **4** and **5**, where the amide function is the main controller, yielding the *ortho*-adduct as predominant, opposite to the regioselectivity obtained with Dane's diene, which only affords the *meta*-adduct (with respect to the substituent at C-1). Second, this change in the regioselectivity was not observed for compound **1**, which reacted with all of the dienes, yielding the *ortho*-adducts.[6] The results obtained with dienes **4** and **5** can be explained by assuming that the electronic influence of the cyano and amide groups in the regiochemistry must be higher than that of the sulfur function, hence favoring the formation of the *ortho*-adducts with respect to the former ones. As this situation is analogous to reactions with Dane's diene, other factors, such as the steric interactions of Dane's diene with the *s-trans* oxygens at dienophiles, must be responsible for the observed differences. As we can see in Figure 2, such interactions of the carbonyl oxygen at the dienophile **2** unstabilize the TS, yielding the *ortho*-adduct (**B** in Figure 2), thus evolving preferentially through the TS, which yields the *meta*-adduct (**A** in Figure 2). On the contrary, in reactions of dienophile **1** the steric grounds reinforce the electronic tendency, since the interactions of the diene with the *s-trans* sulfinyl oxygen determine the higher stability of the transition state favored by electronic grounds (**B′** in Figure 2), where such interactions are absent. As the steric interactions must be less significant in reactions with 1-substituted dienes, they are not able to invert the orientation imposed by the electronic factors. However, the formation of a small amount of the regioisomer **7B** in the reaction

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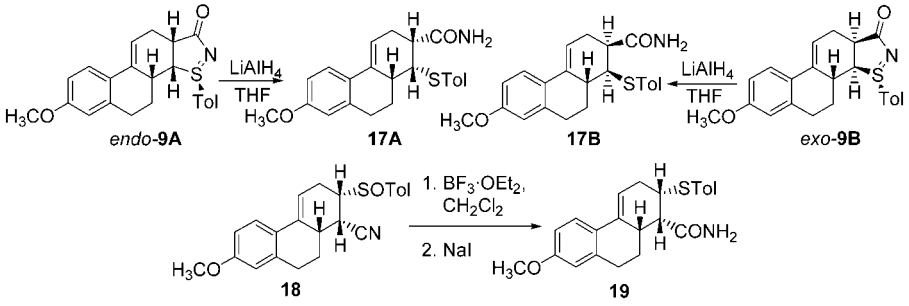
(14) Initially we thought that the minor cycloadduct **9B** should be the regioisomer of **9A** with *endo* stereochemistry, as it happened with piperylene. So, we transformed **9B** and **18** into their corresponding sulfenylcarboxamides, **17B** and **19**, with the hope that they would be enantiomers, such as it had been demonstrated for the adducts derived from furane, piperylene, and 1-methoxybutadiene. However, we could check that the NMR spectra of the obtained carboxamides, **17B** and **19**, were different, proving that they were not enantiomers. This fact suggested to us that **17A** and **17B** should be the adducts resulting from the *endo* and *exo* approaches of Dane's diene to the less hindered face of the dienophile **2**, but with the regiochemistry opposite to that observed in the case of dienophile **1**.

(15) Double pulsed field gradient echo-DPFGS (Bruker DRX-500).

(16) The reaction of **1** with acyclic dienes **4** and **5** yielded mixtures of two *endo*-adducts (see ref 6).

Scheme 5



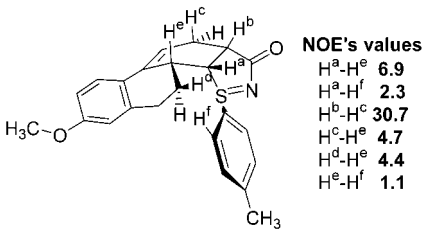


Figure 1. NOE values for adduct **9A**.

Scheme 6

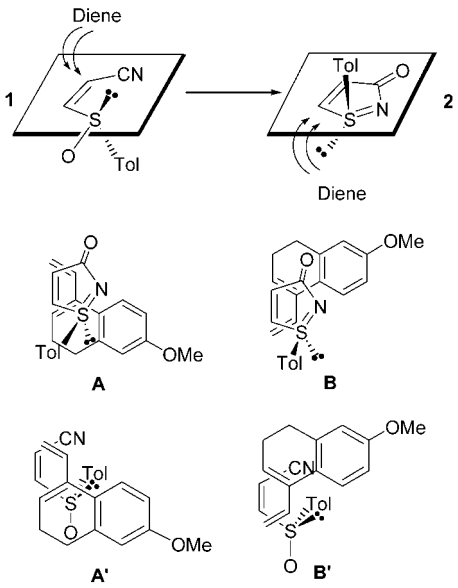


Figure 2. Approaches accounting for the regiochemistry of reactions with Dane's diene.

with piperylene (see Table 2) could be indicative of a small contribution of these steric effects.

The last issue that deserves to be commented is the *exo*-selectivity observed in the reactions of the dienophile **2** with furan. Initially we thought that this result was a consequence of a retro Diels−Alder process, which would determine the formation of a mixture of adducts, the thermodynamically most stable *exo* one being the major component of the equilibrium. However, we could demonstrate that this was not the case. Reactions conducted in refluxing furan, conditions favoring that the thermodynamic equilibrium was reached, afforded a 1:1 mixture of the *endo* and *exo* adducts (entry 6, Table 1), which suggests a similar stability for both. On the other hand, when compounds *exo*-**3A** and *endo*-**3B** were independently treated with furan under the conditions described in entry 5 (Table 1), we could not detect the formation of a mixture of diastereoisomers, which indicates that the retro Diels−Alder reaction does not take place under such conditions.

Dienophiles exhibiting kinetic *exo*-selectivity are not too frequent, and this feature is usually associated with secondary orbital overlap in the *endo* transition structures,[17] solvent effects,[18] or steric effects of the substituents destabilizing the *endo* approach.[19] Nevertheless, in the case of dienophile **2** there do not exist such substituents, which suggests that the electrostatic interactions or the solvent effects must be responsible for the observed behavior. To support some of these issues accounting for the obtained results, some theoretical calculations were performed (see the following article). According to the obtained results, the incorporation of the solvent to the transition state is able to account for the highest stability of the *exo*-TS.

As a conclusion, we can state that sulfilimine **2** exhibits a reactivity that allows its complete reaction with furan as well as with acyclic dienes. The π-facial selectivity is complete in all of the studied reactions and controlled by the orientation of the *p*-tolylsulfinyl group. The *endo* selectivity is almost complete in most of the reactions with acyclic dienes (only Dane's diene affords a small amount of the *exo*-isomer), but reactions with furan evolved with a marked *exo*-selectivity, which is not a consequence of a retro Diels−Alder process. Finally, the regioselectivity is almost complete with all of the studied dienes, but the orientation with 1-substituted butadienes is the opposite to that with Dane's diene. Taking into account that the mentioned behavior is different in many aspects to that found for sulfinylacrylonitrile **1**, dienophiles **1** and **2** can be considered as complementary from stereochemical and regiochemical points of view. Bearing in mind that sulfilimines can be easily obtained from sulfinylnitriles, this behavior is of great synthetic interest.

Experimental Section

General Methods. Dienes, except Dane's diene, and Lewis acids are commercially available and were used without further purification. $ZnBr_2$ was flamed-dried in the reaction flask prior to use. Flash chromatography was performed with silica gel 60 (230−400 mesh ASTM), and silica gel F_{254} plates were used for preparative TLC. NMR spectra were determined in $CDCl_3$ solutions at 200 (or 300) and 50.3 (or 75.5) MHz for ^1H and ^{13}C NMR, respectively; *J* values are given in hertz.

(17) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 4388.

(18) Berson, J.; Hamlet, Z.; Mueller, W. J. *J. Am. Chem. Soc.* **1962**, *84*, 297.

(19) (a) Brown, F. K.; Houk, K. N.; Burnell, D. J.; Valenta, Z. *J. Org. Chem.* **1987**, *52*, 3050. (b) Kakushima, M.; Scott, D. *Can. J. Chem.* **1979**, *57*, 1399. (c) Kakushima, M. *Can. J. Chem.* **1979**, *57*, 2564.

Yields are shown in Tables 1−3. All described compounds were over 97% pure by NMR analysis. Compound **1** was synthesized and purified according to the procedure described in ref 5. To verify the optical purity of **1** to be used as the substrate in further reactions, it was necessary to check it by NMR using $Yb(hfc)_3$ as the LSR (substrate−LSR molar ratio 1:0.3). Compound **2** was synthesized and purified according to procedure described in ref 7. Its optical purity could not be determined directly either by HPLC or NMR. However, a >97% ee could be inferred by indirect methods.[7] High-pressure reactions were performed in 1.5 mL polyethylene sample vials.

Diels−Alder Cycloadditions of 2 with Furan. Method i. Thermal Conditions. A solution of **2** (143 mg, 0.75 mmol) in an excess of furan (2 mL, 27.5 mmol) was kept at room temperature at 4 kbar. When the reaction was completed (4 days), the crude mixture was concentrated, and the residue was purified by flash chromatography (acetone).

Method ii. In the Presence of $ZnBr_2$. To a solution of $ZnBr_2$ (270 mg, 1.2 mmol) in THF (0.4 mL), under argon at room temperature, was added a solution of **2** (191 mg, 1.0 mmol) in CH_2Cl_2 (0.5 mL) and the mixture was stirred for 1 h. Then an excess of furan (2 mL, 27.5 mmol) was added. The reaction mixture was stirred at room temperature for 4 days, water (4 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 4 mL). The organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography (acetone).

Method iii. In the Presence of $BF_3{\cdot}OEt_2$. To a solution of **2** (1.0 mmol) in refluxing CH_2Cl_2 (1 mL) under argon was added $BF_3{\cdot}OEt_2$ (225 μL, 2 mmol). The reaction mixture was stirred for 1 h, and then an excess of furan (2 mL, 27.5 mmol) was added. The reaction mixture was stirred at −20 °C for 5 days, then poured into water (4 mL), and extracted with CH_2Cl_2 (3 × 4 mL). The organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography (acetone).

(1*S*)-1-(*p*-Tolyl)-3a,4,7,7a-tetrahydro-3*H*-4,7-epoxy-1λ^4-1,2-benzisothiazol-3-one (*exo*-3A). It was crystallized from CH_2Cl_2−acetone−hexane (white solid): yield 85%; mp 172−173 °C; $[\alpha]^{20}_D$ +133.6 (*c* 0.5, $CHCl_3$); ^{1}H NMR δ 7.51 and 7.36 (AA′BB′ system, 4H), 6.62 (dd, 1H, *J* = 1.6 and 5.9 Hz), 6.35 (dd, 1H, *J* = 1.8 and 5.9 Hz), 5.55 (d, 1H, *J* = 1.7 Hz), 5.42 (d, 1H, *J* = 1.7 Hz), 3.68 (d, 1H, *J* = 6.7 Hz), 3.23 (d, 1H, *J* = 6.7 Hz), 2.36 (s, 3H); ^{13}C NMR δ 185.4, 143.9, 140.2, 134.4 (2C), 131.0 (2C), 125.9 (2C), 83.4, 81.9, 71.0, 51.8, 21.5; HRMS (FAB) 260.0745 $[M + H]^+$ ($C_{14}H_{14}NO_2S$ requires 260.0753).

Diels−Alder Cycloadditions of 2 with Acyclic Dienes. Reactions at High Pressure. Method i: Thermal Conditions. A solution of **2** (191 mg, 1.0 mmol) and 4 mmol of the corresponding diene in CH_2Cl_2 (1 mL) was kept at 4 kbar at room temperature. When the reaction was completed, the crude mixture was concentrated and the residue was purified by flash chromatography.

Method ii: In the Presence of $ZnBr_2$. To a solution of $ZnBr_2$ (270 mg, 1.2 mmol) in THF (0.4 mL), under argon at room temperature, was added a solution of **2** (191 mg, 1.0 mmol) in CH_2Cl_2 (1 mL). The reaction mixture was stirred for 1 h at room temperature. Then the corresponding diene (2 mmol of piperylene or 1-methoxybutadiene) was added, and the mixture was kept at 4 kbar at room temperature. When the reaction was completed, water (4 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 5 mL). The organic layer was dried (Na_2SO_4) and concentrated.

(1*S*,3a*R*,4*S*,7a*R*)-4-Methoxy-1-(*p*-tolyl)-3a,4,7,7a-tetrahydro-3*H*-1,2-benzisothiazol-3-one (6A). Reaction of **2** with methoxybutadiene (method ii) and further flash chromatographic purification (acetone) afforded **6A** as an oil in 89% yield: $[\alpha]^{20}_D$ +127.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR δ 7.48 and 7.25 (AA′BB′ system, 4H), 6.18 (ddt, 1H, *J* = 0.5, 2.4, and 5.1 Hz), 5.89 (ddd, 1H, *J* = 9.6, 3.2, and 5.5 Hz), 4.18 (dd, 1H, *J* = 4.0 and 5.4 Hz), 3.73 (ddd, 1H, *J* = 6.2, 8.6, and 9.8 Hz), 3.25 (s, 3H), 2.98 (dd, 1H, *J* = 4.0 and 10.0 Hz), 2.79 (ddd, 1H, *J* = 3.0, 6.2, and 17.2 Hz), 2.62 (ddd, 1H, *J* = 5.7, 8.6, and 17.2 Hz), 2.31 (s, 3H); ^{13}C NMR δ 184.4, 143.5, 134.1, 130.5 (2C), 129.4, 128.5, 125.5 (2C), 70.8, 63.6, 56.8, 48.0, 24.1, 21.1; HRMS (EI) 275.0972 ($C_{15}H_{18}NOS$ requires 275.0980).

(1*S*,3a*R*,4*S*,7a*R*)-4-Methyl-1-(*p*-tolyl)-3a,4,7,7a-tetrahydro-3*H*-1,2-benzisothiazol-3-one (7A). Reaction of **2** with piperylene (method ii) and further flash chromatographic purification (acetone) afforded **7A** in 84% yield. It was crystallized from 1:1 hexanes−ethyl acetate (white solid): mp 154−155 °C; $[\alpha]^{20}_D$ +84.2 (*c* 0.5, $CHCl_3$); ^{1}H NMR δ 7.46 and 7.30 (AA′BB′ system, 4H), 5.89 (dt, 1H, *J* = 1.9 and 4.0 Hz), 5.75 (ddt, 1H, *J* = 1.9, 3.8, and 8.6 Hz), 3.91 (ddd, 1H, *J* = 4.6, 7.8, and 8.3 Hz), 2.93 (dd, 1H, *J* = 5.6 and 8.6 Hz), 2.72 (dt, 1H, *J* = 4.7 and 17.5 Hz), 2.60 (dq, 1H, *J* = 1.9 and 17.5 Hz), 2.51 (m, 1H), 2.37 (s, 3H), 1.39 (d, 3H, *J* = 7.2 Hz); ^{13}C NMR δ 188.4, 143.1, 135.9, 133.6, 130.5 (2C), 125.4 (2C), 123.0, 64.3, 44.2, 29.8, 25.4, 21.2, 16.0; HRMS (EI) 259.1037 ($C_{15}H_{18}NOS$ requires 259.1030). Anal. Calcd for $C_{15}H_{18}NOS$: C, 69.47; H, 6.61; N, 5.40; S, 12.34. Found: C, 69.19; H, 6.65; N, 5.19; S 12.14.

(1*S*,3a*R*,7*R*,7a*R*)-7-Methyl-1-(*p*-tolyl)-3a,4,7,7a-tetrahydro-3*H*-1,2-benzisothiazol-3-one (7B). Reaction of **2** with piperylene (method ii) and further flash chromatographic purification (acetone) afforded **7B** as a white solid in 11% yield: mp 86−87 °C; $[\alpha]^{20}_D$ +2.2 (*c* 1.49, $CHCl_3$) ^{1}H NMR δ 7.42 and 7.31 (AA′BB′ system, 4H), 6.02 (ddd, 1H, *J* = 3.2, 6.4, and 12.6 Hz), 5.72 (dt, 1H, *J* = 3.2 and 9.4 Hz), 3.96 (ddd, 1H, *J* = 0.8, 5.4, and 9.4 Hz), 3.17 (ddd, 1H, *J* = 1.9, 7.5, and 9.4 Hz), 2.89 (ddd, 1H, *J* = 1.6, 6.7, and 15.3 Hz), 2.65 (m, 1H), 2.39 (s, 3H), 2.10 (m, 1H), 1.45 (d, 3H, *J* = 7.1 Hz); ^{13}C NMR δ 190.7, 143.1, 134.9, 131.3 (2C), 130.7, 130.2, 125.7 (2C), 73.8, 41.9, 30.6, 29.2, 25.8, 21.4, 17.9.

Diels−Alder Cycloadditions of 2 with Dane's Diene. Reactions at High Pressure. Method i: Thermal Conditions. To a solution of **2** (191 mg, 1.0 mmol) in CH_2Cl_2 (1 mL) was added a 1 M solution of Dane's diene (1.6 mL, 3 mmol) in benzene. The mixture was kept at 4 kbar at room temperature for 14 days. When the reaction was completed, the crude mixture was concentrated, and the residue was purified by flash chromatography.

Method ii: In the Presence of $ZnBr_2$. To a solution of $ZnBr_2$ (270 mg, 1.2 mmol) in THF (0.5 mL), under argon at room temperature, was added a solution of **2** (191 mg, 1.0 mmol) in CH_2Cl_2 (1 mL). The reaction mixture was stirred for 1 h at room temperature. Then a 1 M solution of Dane's diene (1.6 mL, 3 mmol) in benzene was added, and the mixture was kept at 4 kbar at room temperature for 7 days. When the reaction was completed, water (4 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 5 mL). The organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography.

(1*S*,1a*R*,3a*R*,11a*R*)-1a,3a,4,10,11,11a-Hexahydro-8-methoxy-1-(*p*-tolyl)-3*H*-1,2-phenanthrene-isothiazol-3-one (*endo*-9A). Reaction of **2** with Dane's diene (method i) afforded *endo*-**9A** in 84% yield. It was crystallized from acetone (white solid): mp 123−124 °C; $[\alpha]^{20}_D$ −141.3 (*c* 0.25, $CHCl_3$); ^{1}H NMR δ 7.49 (d, 1H, *J* = 8.7 Hz), 7.41 and 7.30 (AA′BB′ system, 4H), 6.76 (dd, 1H, *J* = 2.4 and 8.7 Hz), 6.66 (d, 1H, *J* = 2.6 Hz), 6.37 (dt, 1H, *J* = 3.0 and 6.9 Hz), 4.15 (dd, 1H, *J* = 4.7 and 9.7 Hz), 3.80 (s, 3H), 3.33 (t, 1H, *J* 7.5 Hz), 3.11 (dd, 1H, *J* = 7.5 and 15.0 Hz), 2.90−2.70 (m, 3H), 2.40 (s, 3H), 2.30−2.13 (m, 2H), 2.05 (dq, 1H, *J* = 4.5 and 11.9 Hz); ^{13}C NMR δ 190.4, 158.9, 143.2, 137.9, 135.6, 134.5, 130.8 (2C), 126.2, 125.8 (2C), 125.1, 120.4, 113.1, 112.8, 73.8, 55.2, 43.2, 36.8, 29.9, 27.2, 26.9, 21.4; HRMS (FAB) 378.1527 $[M + H]^+$ ($C_{23}H_{23}NO_2S$ requires 378.1539).

(1*S*,1a*S*,3a*S*,11a*R*)-1a,3a,4,10,11,11a-Hexahydro-8-methoxy-1-(*p*-tolyl)-3*H*-1,2-phenantrene-isothiazol-3-one (*exo*-9B): It was obtained as the minor product (<5%) of the reaction of **2** with Dane's diene (method i) and could not be completely purified. ^{1}H NMR (from a mixture) δ 7.47 and 7.31 (AA′BB′, 4H), 7.41 (d, 1H, *J* = 8.5 Hz), 6.67 (dd, 1H, *J* = 2.6 and 8.7 Hz), 6.59 (d, 1H, *J* = 2.6 Hz), 6.14 (m, 1H), 4.1 (ddd, 1H, *J* = 2.7, 6.2, and 8.1 Hz), 3.70 (s, 3H), 3.14 (dd, 1H, *J* = 5.4 and 8.6 Hz), 2.96 (dd, 1H, *J* = 2.8 and 6.9 Hz), 2.93 (dd, 1H, *J* = 2.6 and 6.5 Hz), 2.88−2.68 (m, 4H), 2.4 (s, 3H), 1.97 (dq, 1H, *J* = 4.0 and 12.5 Hz); ^{13}C NMR δ 188.2, 158.9, 143.2, 139.6, 134.6, 130.7 (2C), 126.6, 125.6 (2C), 125.3, 124.8, 114.0, 112.8, 112.6, 65.4, 55.2, 44.0, 36.9, 30.9, 26.9, 23.5, 21.4.

Reactions of Cycloadducts with $LiAlH_4$. General Procedure. A suspension of the adduct (1 mmol) and $LiAlH_4$ (1

mmol) in THF (2 mL) under argon was stirred for 5 min. Water (2 mL) was added, and the mixture was extracted with AcOEt (3 × 4 mL). The organic layer was dried (Na_2SO_4) and evaporated.

(2*R*,3*S*)-3-[(*p*-Tolyl)sulfenyl]-7-oxabicyclo[2.2.1]hept-5-ene-8-carboxamide (14). Reaction of *exo*-**3A** with $LiAlH_4$ and further flash chromatographic purification (acetone) afforded **14**. It was crystallized from CH_2Cl_2−acetone−hexane (white solid): mp 152−153 °C; $[\alpha]^{20}_D$ +43.0 (*c* 1.78, $CHCl_3$); ^{1}H NMR δ 7.36 and 7.15 (AA′BB′ system, 4H), 6.41 (dd, 1H, *J* = 1.6 and 5.9 Hz), 6.37 (dd, 1H, *J* = 1.6 and 5.9 Hz), 5.47 (bs, 2H), 5.17 (t, 1H, *J* = 1.2 Hz), 4.93 (t, 1H, *J* = 1.2 Hz), 3.33 (d, 1H, *J* = 8.3 Hz), 2.79 (dd, 1H, *J* = 2.4 and 8.3 Hz) and 2.33 (s, 3H); ^{13}C NMR δ 173.5, 139.6, 137.7, 136.5, 135.1, 132.0 (2C), 130.0 (2C), 84.2, 81.8, 50.3, 49.3, 21.1; HRMS (FAB) 262.0902 $[M + H]^+$ ($C_{14}H_{16}NO_2S$ requires 262.0908).

(1*R*,2*S*,6*R*)-2-Methoxy-6-[(*p*-tolyl)sulfenyl]cyclohex-3-ene-1-carboxamide [(+)-11A]. Reaction of **6A** with $LiAlH_4$ and further flash chromatographic purification (1:1 hexanes−ethyl acetate) afforded (+)-**11A**. It was crystallized from 1:1 hexanes−ethyl acetate (white solid): mp 131−132 °C; $[\alpha]^{20}_D$ +85.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR δ 7.36 and 7.09 (AA′BB′ system, 4H), 6.79 (bs, 1H), 6.10 (bs, 1H), 5.83 (bs, 2H), 4.06 (dd, 1H, *J* = 1.2 and 3.4 Hz), 3.44 (ddd, 1H, *J* = 3.4, 5.6 and 8.3 Hz), 3.43 (s, 3H), 3.18 (dd, 1H, *J* = 3.4 and 5.2 Hz), 2.57−2.38 (m, 2H) and 2.3 (s, 3H); ^{13}C NMR δ 172.8, 137.2 (2C), 132.4 (2C), 129.7 (2C), 129.0, 125.9, 75.8, 56.8, 47.9, 44.9, 31.3, 20.9; HRMS (FAB) 278.1215 $[M + H]^+$ ($C_{15}H_{19}NO_2S$ requires 278.1212). Anal. Calcd for $C_{15}H_{19}NO_2S$: C, 64.95; H, 6.90; N, 5.05; S, 11.56. Found: C, 64.71; H, 6.95; N, 5.12; S 11.82.

(1*R*,2*S*,6*R*)-2-Methyl-6-[(*p*-tolyl)sulfenyl]cyclohex-3-ene-1-carboxamide [(+)-10A]. Reaction of **7A** with $LiAlH_4$ and further flash chromatographic purification (1:1 hexanes−ethyl acetate) afforded (+)-**10A** as an oil: $[\alpha]^{20}_D$ +130.4 (*c* 1.25, $CHCl_3$); ^{1}H NMR δ 7.37 and 7.09 (AA′BB′ system, 4H), 6.28 (bs, 1H), 5.83 (bs, 1H), 5.73 (ddd, 1H, *J* = 1.8, 4.8, and 5.4 Hz), 5.49 (dd, 1H, *J* = 1.8 and 10.1 Hz), 3.47 (ddd, 1H, *J* = 4.1, 6.5, and 10.3 Hz), 2.76 (t, 1H, *J* = 4.8 Hz), 2.55−2.46 (m, 1H), 2.46−2.35 (m, 2H), 2.30 (s, 3H), 1.08 (d, 3H, *J* = 7.3 Hz); ^{13}C NMR δ 173.4, 137.2 (2C), 132.8 (2C), 130.0, 129.7 (2C), 125.8, 49.1, 45.4, 32.9, 28.9, 21.0, 17.7; HRMS (FAB) 262.1269 $[M + H]^+$ ($C_{15}H_{19}NOS$ requires 262.1266).

(1*R*,5*R*,6*R*)-5-Methyl-6-[(*p*-tolyl)sulfenyl]cyclohex-3-ene-1-carboxamide (10B). Reaction of **7B** with $LiAlH_4$ and further flash chromatographic purification (1:1 hexanes−ethyl acetate) afforded **10B**. It was crystallized from 1:1 hexanes−ethyl acetate (white solid): mp 162−163 °C; $[\alpha]^{20}_D$ −50.5 (*c* 0.4, $CHCl_3$); ^{1}H NMR δ 7.38 and 7.06 (AA′BB′ system, 4H), 6.05 (bs, 1H), 5.82 (bs, 1H), 5.69 (ddd, 1H, *J* = 2.4, 4.6, and 7.3 Hz), 5.43 (ddq, 1H, *J* = 1.6, 3.8, and 9.9 Hz), 3.82−3.75 (m, 1H), 2.89 (ddd, 1H, *J* = 2.4, 5.6, and 11.0 Hz), 2.82−2.70 (m, 1H), 2.62−2.42 (m, 1H), 2.29 (s, 3H), 2.38−2.21 (m, 1H), 1.14 (d, 3H, *J* = 6.9 Hz); ^{13}C NMR δ 175.8, 137.2, 133.4, 132.3, 131.9 (2C), 130.1 (2C), 124.9, 55.2, 46.7, 37.7, 25.4, 21.4, 18.8; HRMS (EI) 261.1192 $[M + H]^+$ ($C_{15}H_{19}NOS$ requires 261.1187). Anal. Calcd for $C_{15}H_{19}NOS$: C, 68.93; H, 7.33; N, 5.36; S, 12.27. Found: C, 68.81; H, 7.37; N, 5.22; S, 12.27.

(1*R*,2*R*,10a*R*)-1,2,3,9,10,10a-Hexahydro-7-methoxy-1-[(*p*-tolyl)sulfenyl]-phenanthrene-1-carboxamide (17A). Reaction of *endo*-**9A** with $LiAlH_4$ and further flash chromatographic purification (acetone) afforded **17A**. It was crystallized from acetone (white solid): mp 213−214 °C; $[\alpha]^{20}_D$ −78 (*c* 0.15, DMSO-d_6); ^{1}H NMR (DMSO-d_6, 50 °C) δ 7.61 (d, 1H, *J* = 8.9 Hz), 7.35 and 7.07 (AA′BB′ system, 4H), 7.20 (bs, 1H), 6.81 (bs, 1H), 6.71 (dd, 1H, *J* = 2.8 and 8.9 Hz), 6.61 (d, 1H, *J* = 2.0 Hz), 6.29 (t, 1H, *J* = 2.0 Hz), 3.98 (t, 1H, *J* = 2.4 Hz), 3.70 (s, 3H), 2.86−2.74 (m, 2H), 2.73−2.64 (m, 2H), 2.63−2.53 (m, 1H), 2.36−2.28 (m, 1H), 2.26 (s, 3H), 1.95−1.76 (m, 1H), 1.56−1.44 (m, 1H); ^{13}C NMR (DMSO-d_6) δ 173.7, 158.2, 137.9, 135.8, 134.1, 131.9, 131.8 (2C), 129.6 (2C), 126.4, 124.6, 116.4, 113.3, 112.9, 55.2, 54.6, 44.4, 43.4, 29.9, 27.4, 24.9, 20.6; HRMS (FAB) 380.1684 $[M + H]^+$ ($C_{23}H_{25}NO_2S$ requires 380.1677). Anal. Calcd for $C_{23}H_{25}NO_2S$: C, 72.79; H, 6.64; N, 3.69; S, 8.45. Found: C, 72.48; H, 6.71; N, 3.71; S, 8.13.

(1*S*,2*S*,10a*R*)-1,2,3,9,10,10a-Hexahydro-7-methoxy-1-[(*p*-tolyl)sulfenyl]-phenanthrene-1-carboxamide (17B). Reaction of *exo*-**9B** with $LiAlH_4$ and further chromatographic purification (acetone) afforded **17B** as an oil: $[\alpha]^{20}_D$ +89 (*c* 0.1, $CHCl_3$); ^{1}H NMR δ 7.57 (d, 1H, *J* = 8.9 Hz), 7.44 and 7.14 (AA′BB′ system, 4H), 6.72 (dd, 1H, *J* = 2.7 and 8.9 Hz), 6.57 (d, 1H, *J* = 3.0 Hz), 6.37−6.27 (m, 1H), 5.81 (bs, 1H), 5.58 (bs, 1H), 3.55 (dt, 1H, *J* = 8.6 and 4.3 Hz), 3.29 (s, 3H), 2.96 (t, 1H, *J* = 5.1 Hz), 2.86−2.76 (m, 2H), 2.72−2.62 (m, 2H), 2.61−2.50 (m, 1H), 2.34 (s, 3H), 1.97−1.83 (m, 1H), 1.82−1.72 (m, 1H); ^{13}C NMR δ 172.9, 158.7, 137.7, 133.2, 132.8 (2C), 130.5, 129.9 (2C), 125.9, 124.7, 116.4, 113.2, 112.9, 55.2, 49.7, 45.1, 38.9, 32.1, 30.6, 30.1, 26.7, 21.1; HRMS (FAB) 380.1684 $[M + H]^+$ ($C_{23}H_{25}NO_2S$ requires 380.1677).

Reactions of Cycloadducts with BF_3·OEt_2/NaI. General Procedure. To a solution of cycloadduct (1 mmol) in CH_2Cl_2 (2 mL) was added BF_3·OEt_2 (1.2 mmol), and the resulting mixture was stirred at reflux for 1 h. Then it was cooled at room temperature, and NaI (5 equiv) was added. The mixture was stirred overnight. It was quenched with water (4 mL) and extracted with CH_2Cl_2 (3 × 4 mL). The organic layer was washed with Na_2SO_3 (4 mL), dried (Na_2SO_4), and concentrated.

(1*S*,2*R*,6*S*)-2-Methoxy-6-[(*p*-tolyl)sulfenyl]cyclohex-3-ene-1-carboxamide [(−)-11A]. Reaction of (1*R*,2*R*,6*S*)-2-methoxy-6-[(*R*)-(*p*-tolyl)sulfinyl]-3-cyclohexene-1-carbonitrile (*endo*-**13**)[6] with BF_3·OEt_2 and NaI afforded (−)-**11A**. It was purified by flash chromatography (1:1 hexanes−ethyl acetate): $[\alpha]^{20}_D$ −82.4 (*c* 1.0, $CHCl_3$).

(1*S*,2*R*,6*S*)-2-Methyl-6-[(*p*-tolyl)sulfenyl]cyclohex-3-ene-1-carboxamide [(−)-10A). Reaction of (1*S*,2*R*,6*S*)-2-methyl-6-[(*R*)-(*p*-tolyl)sulfinyl]-3-cyclohexene-1-carbonitrile (*endo*-**12**)[6] with BF_3·OEt_2 and NaI afforded **(−)-10A**. It was purified by flash chromatography (1:1 hexanes−ethyl acetate): $[\alpha]^{20}_D$ −125.9 (*c* 1.25, $CHCl_3$).

(1*S*,2*S*,3*S*,4*R*)-3-[(*p*-Tolyl)sulfenyl]-7-oxabicyclo[2.2.1]-hept-5-ene-2-carbonitrile [(+)-15]. To a solution of **14** (1 equiv) in CH_2Cl_2 (4 mL) under argon at 0 °C was added NEt_3 (2 equiv). Then $(Tf)_2O$ (1.5 equiv)[12] was added dropwise. The mixture was stirred for 1 h at room temperature, quenched with water (4 mL), and extracted with CH_2Cl_2 (3 × 4 mL). The organic layer was dried (Na_2SO_4) and concentrated. It was crystallized from 1:2 AcOEt−hexane (white solid): mp 105−106 °C; $[\alpha]^{20}_D$ +117.4 (*c* 0.99, $CHCl_3$); ^{1}H NMR δ 7.42 and 7.15 (AA′BB′ system, 4H), 6.46 (dd, 1H, *J* = 1.6 and 5.9 Hz), 6.40 (dd, 1H, *J* = 1.6 and 5.3 Hz), 5.32 (s, 1H), 4.99 (s, 1H), 3.26 (d, 1H, *J* = 7.5 Hz), 2.95 (d, 1H, *J* = 7.5 Hz), 2.35 (s, 3H); ^{13}C NMR δ 138.2, 137.2, 135.2, 132.6 (2C), 130.4, 130.1 (2C), 118.4, 83.6, 82.5, 48.5, 36.4, 21.1; HRMS (FAB) 244.0796 $[M + H]^+$ ($C_{14}H_{16}NO_2S$ requires 244.0800).

(1*R*,2*R*,3*R*,4*S*)-3-[(*p*-Tolyl)sulfenyl]-7-oxabicyclo[2.2.1]-hept-5-ene-2-carbonitrile [(−)-15]. To a solution of (1*R*,2*R*,3*R*,4*S*)-3-[(*R*)-(*p*-tolyl)sulfinyl]-7-oxabicyclo[2.2.1]hept-5-ene-2-carbonitrile (*exo*-**16**)[6] (1 mmol) in MeCN (4 mL) under argon was added PCl_3 (2 equiv). The reaction was stirred for 1 h at room temperature, quenched with water (4 mL), and extracted with CH_2Cl_2 (3 × 4 mL). The organic layer was dried (Na_2SO_4) and concentrated. It was crystallized from 1:2 AcOEt−hexane (white solid): $[\alpha]^{20}_D$ −114.3 (*c* 0.99, $CHCl_3$).

Acknowledgment. Financial support from the Dirección de Investigación Científica y Técnica CAICYT (Projects BQU2000-0246, BQU2000-0248, and PB98-0102) is gratefully acknowledged. C.A. thanks the Spanish Ministerio de Educación y Cultura for a fellowship. R.G. thanks the Junta de Extremadura-Fondo Social Europeo for a predoctoral fellowship. L.G.G. thanks Consejo Nacional de Ciencia y Tecnología (CONACYT-México) for a fellowship.

Supporting Information Available: IR and MS data and copies of ^{1}H NMR spectra of sulfilimines **3A**, **6A**, **7A**, **7B**, and **9A**, of sulfenylcarboxamides **10A**, **11A**, **14**, **17A**, and **17B**, and of sulfenylcarbonitrile **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO016174W