Studies of Diastereoselectivity in Diels−Alder Reactions of (S)*S*-4a,5,8,8a-Tetrahydro-5,8-methane-2-(*p*-tolylsulfinyl)-1,4-naphthoquinones with Cyclopentadiene

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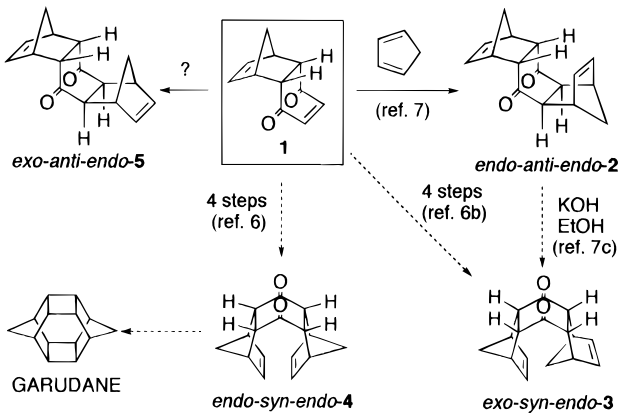
The title compounds **6** and **7** have proved to be adequate rigid models to evaluate the ability of the sulfinyl group to control the diastereoselectivity of the [4 + 2] cycloadditions of cyclopentadiene on the ene-dione moiety. The results of thermal and Lewis acid-catalyzed reactions allowed us to establish that both reactivity and *endo/exo* selectivity were modulated by the presence of the sulfinyl group, the *endo-anti-endo* or the *exo-anti-endo* bisadducts being obtained as major products depending on experimental conditions. The role of the association between the SOTol group and several Lewis acids (BF_3·OEt_2, Eu(fod)$_3$, $ZnBr_2$), which shifted the conformational equilibrium around the C−S bond, was used to explain the stereochemical course of the cycloadditions mainly controlled by steric factors. The synthesis of the *exo-anti-endo* bisadduct **5** was described for the first time.

Introduction

The stereoselectivities associated with [4 + 2] cycloadditions of strained bridged polycyclic molecules have been the subject of several studies.[1] From a synthetic point of view the interest of the resulting molecules rests on the access to polycyclic natural products[2] that can be made from these adducts, as well as new materials[3] showing host−guest complexation properties.[4] Frequently, repetitive Diels−Alder reactions[2−5] have been the method of choice to the synthesis of some of these precursors as in the case of *p*-benzoquinone-cyclopentadiene bisadduct **4** (Scheme 1), an intermediate in the synthesis of garudane.[6] As can be seen in Scheme 1, compound **4** could arise from a second cycloaddition of cyclopentadiene on *endo*-monoadduct **1**. In this reaction four bisadducts with different stereochemistry could result: *endo-anti-endo*-**2**, *exo-syn-endo*-**3**, *endo-syn-endo*-**4**, and *exo-anti-endo*-**5**. Nevertheless, the *endo-anti-endo* bisadduct **2** was the only one formed directly in the cycloaddition of cyclopentadiene[7] because the π-facial selectivity was controlled by the norbornene moiety of **1** and the *endo/exo* selectivity directed by the *endo*-orientating character of the carbonyl groups of the ene-dione system. This result precluded the obtention of the other possible diastereoisomers by direct Diels−Alder reaction on **1**. Two of them, **3** and **4**, could be prepared by alternative methods. So, the *exo-syn-endo*-bisadduct **3** was obtained[7c] by isomerization in basic medium of the *endo-anti-endo* bisadduct **2**, and more recently,[6b] bisadducts **3** and **4** were prepared in two four-step reaction sequences from monoadduct **1**. To our knowledge up to date, the *exo-anti-endo* diastereoisomer **5** has not been synthesized.

Scheme 1



Considering the well demonstrated ability of a sulfinyl group situated on a dienophilic double bond to control the diastereoselectivity of Diels−Alder reactions,[8] we reasoned that the incorporation of a sulfoxide on the ene-

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dione moiety of compound **1** could modify the behavior of the new dienophile in the second cycloaddition of cyclopentadiene. This would make bisadducts with different stereochemistry from that of the *endo-anti-endo* usually obtained from monoadduct **1** accesible. In previous studies devoted to sulfinylbenzo-[9] and naphthoquinones[10] as dienophiles, we showed that π-facial diastereoselectivity could be controlled by choosing the proper Lewis acid catalyst. Further studies on sulfinyl maleates[11] also revealed a strong influence of the catalyst on the *endo/exo* selectivity, mainly in the case of cyclic dienes, making possible the major formation of *exo*-adducts in some cases.[11b] The study of cycloadditions on sulfinylene-diones **6** and **7**, which shared the norbornene moiety of **1** and the chiral sulfoxide, could bring light on the role of the latter in controlling both the *endo/exo* selectivity and the π-facial diastereoselectivity of sulfinyl dienophiles.

In this paper we report the results obtained from the Diels−Alder reactions of **6** and **7** with cyclopentadiene (Scheme 2) under thermal conditions and in the presence of Lewis acids.

Results and Discussion

Compounds **6** and **7** were prepared as previously described[9a,c] from *(S)*-2-(*p*-tolylsulfinyl)-1,4-benzoquinone[12,13] and cyclopentadiene. The reaction of compound **6** with cyclopentadiene took place under very mild conditions, −20 °C in CH_2Cl_2 (Scheme 2, Table 1, entry 1) to afford a 85:15 mixture of two bisadducts **8** and **9**, showing the *endo* and *exo* stereochemistry, respectively, in the newly generated norbornenyl system. This result was not unexpected taking into account the existence of the norbornene moiety in the starting dienophile which makes only the upper face of the ene-dione accesible to the attack of the diene.[7]

Compound **7** produced at 0 °C a 90:10 mixture of diastereoisomers **10** and **11** (Scheme 2, Table 1, entry 11) which again resulted from the *endo* and *exo* approach of cyclopentadiene to the upper face of **7**. These mild conditions for cycloadditions of both dienophiles **6** and **7** contrasted with other results published on Diels−Alder reactions of substituted norbornene-diones which only reacted with cyclopentadiene at high pressures[14] and suggested that the sulfoxide group increased the reactivity of the dienophile. This effect was not evident in Diels−Alder reactions of other sulfinyl dienophiles.[15] All derivatives **8-11** obtained in these reactions could be isolated diastereoisomerically pure by flash chromatography (see Experimental Section).

Scheme 2

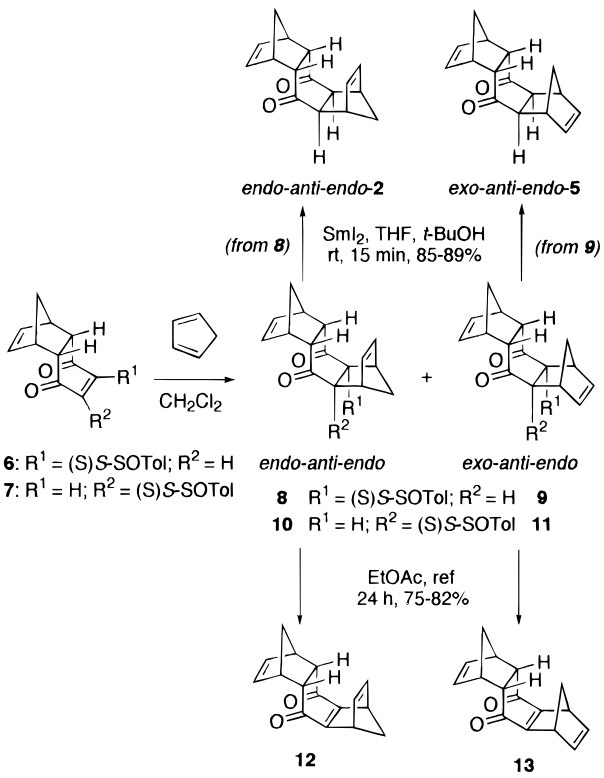

Table 1. Diels−Alder reactions of 6 and 7 with cyclopentadiene

entry	dienophile	T (°C)	cat. (equiv)	time (h)	yield (%)	**8**:**9**	**10**:**11**
1	6	-20	−	48	92	85:15	
2	6	20	−	2	93	85:15	
3	6	20[a]	$BF_3{\cdot}OEt_2$ (2)	24	76	100:0	
4	6	20	$ZnBr_2$ (2)	0.08	90	60:40	
5	6	-20	$ZnBr_2$ (2)	1	87	45:55	
6	6	-40	$ZnBr_2$ (2)	2	89	80:20	
7	6	20[a]	$Eu(fod)_3$ (1)	3	84	75:25	
8	6	20[a]	$Eu(fod)_3$ (2)	2	81	80:20	
9	6	20[a]	$Eu(fod)_3$ (3)	2	77	85:15	
10	6	20[a]	$Eu(fod)_3$ (5)	2	75	85:15	
11	7	0[a]	−	48	89		90:10
12	7	20	−	8	91		90:10
13	7	20	$BF_3{\cdot}OEt_2$ (2)	48	−		−
14	7	-20	$ZnBr_2$ (2)	0.5	84		40:60
15	7	20[a]	$Eu(fod)_3$ (2)	5	84		50:50
16	7	20[a]	$Eu(fod)_3$ (3)	3	80		50:50

[a] No reaction at −20 °C.

Once separated, the reductive elimination of the sulfinyl group on the *endo-anti-endo* sulfinyl bisadduct **8** by using SmI_2 and *t*-BuOH in THF[16] yielded a 85% of the *endo-anti-endo* bisadduct **2**[7] (Scheme 2). In the same conditions, the *exo-anti-endo* sulfinyl bisadduct **9** afforded the unknown *exo-anti-endo* cyclopentadiene-quinone bisadduct **5** (Scheme 2) in a 89% yield.

Configurational assignment of adducts **8**−**11** was based on a simple chemical correlation with the known compounds **12**[6b,17] and **13**[6b,17] (Scheme 2). The *endo-anti-endo* configuration of **8** and **10** was confirmed by their evolution into **12** upon heating in EtOAc solution. The same pyrolytic elimination on sulfoxides **9** and **11** afforded **13**, allowing us to assign the *exo-anti-endo* configuration to these sulfinyl derivatives.

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Table 2. ^{1}H-NMR Data for Compounds 8−11

	δ (ppm), multiplicity, J (in Hz)			
proton	**8**	**9**	**10**	**11**
H_1	3.34, m	3.38−3.21, m	3.39, m	3.2−3.4, m
H_2	6.58, dd, 2.9, 5.6	6.48, dd, 3.2, 5.5	6.49, dd, 2.8, 5.6	6.56, t, 1.8
H_3	6.43, dd, 3.3, 5.6	6.30, dd, 3.0, 5.5	6.17, dd, 3.2, 5.6	6.56, t, 1.8
H_4	3.66, m	3.62, m	3.39, m	3.67, m
H_5	3.14−3.08, m	3.21−3.38, m	3.10, m	3.4−3.2, m
H_6	4.71, dd, 2.8, 5.6	4.48, dd, 2.8, 5.7	5.72, dd, 3.0, 6.0	4.59, dd, 3.0, 5.6
H_7	5.20, dd, 2.8, 5.6	5.42, dd, 2.5,5.7	5.99, dd, 3.0, 6.0	5.54, dd, 2.7, 5.6
H_8	3.14−3.08, m	3.20, m	3.44, m	3.4−3.2, m
H_{8a}	2.76, m	3.21−3.38, m	2.85, m	3.4−3.2, m
H_{9a}	3.63, d, 3.6 ($J_{9a,1}$)	2.94, d, 1.6 ($J_{9a,11b}$)	3.54, d, 3.8 ($J_{9a,1}$)	2.48, d, 1.5 ($J_{9a,11b}$)
H_{10a}	2.76, m	3.21−3.38, m	2.85, m	3.4−3.2, m
H_{11a}	2.46, dt, 8.9, 1.7	2.10, m	1.82, dt, 9.1, 1.5	2.00, m
H_{11b}	1.43, dt, 8.9, 1.5	1.47, dq, 9.8, 1.6	1.4−1.2, m	1.64, dq, 10.0, 1.5
H_{12a}	1.06, dt, 8.7, 1.5	1.18, 1.27, 2m	1.4−1.2, m	1.18, 2dt, 8.9, 1.6
H_{12b}	1.19, dt, 8.7, 1.9	1.18, 1.27, 2m	1.4−1.2, m	1.26, 2dt, 8.9, 1.6
CH_3	2.35, s	2.34, s	2.42, s	2.37, s
AA′BB′tolyl system	7.40, 7.20	7.31, 7.17	7.69, 7.32	7.41, 7.24

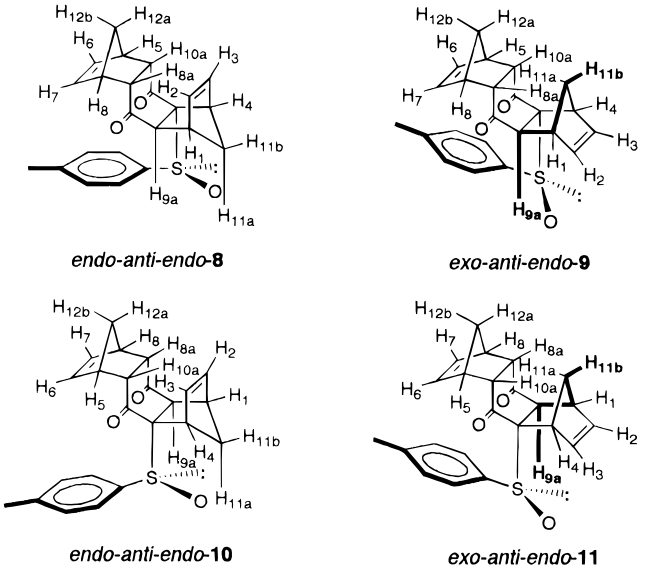

Figure 1.

Moreover, the absolute configuration of compound **8** was shown to be [1*S*,4*R*,4a*R*,5*R*,8*S*,8a*R*,9a*S*,10a*S*,(S)*S*] by X-ray diffraction (see supporting information).[18]

Once the absolute configuration of **8** was known, a detailed comparative analysis of the ^{1}H-NMR parameters of compounds **8**−**11** enabled the unambiguous structural assignments of **9**, **10**, and **11** (See Figure 1 and Table 2).

As can be seen, a similar spectroscopic behavior is observed for **8** and **10**, as a consequence of the similar *endo-anti-endo* structure of both bisadducts. The spectroscopic data of **9** and **11** are also very similar. A distinguishing feature is the relative shielding of the H_{9a} proton in **9** (δ 2.94) and **11** (δ 2.48) compared to that of **8** (δ 3.63) and **10** (δ 3.54). This shielding is a characteristic of the *endo* protons of the norbornenyl systems and is a valuable tool to assign (in our case to confirm) the *exo-anti-endo* configuration of **9** and **11**. Moreover, the long range coupling constant observed between H_{9a} and H_{11b} (J = 1.6 and 1.5 Hz, respectively) in **9** and **11** is only possible if the *exo* moiety is present. The coupling constant between H_{9a} and H_1 observed in **8** and **10** (J = 3.6 and 3.8 Hz, respectively) not present in **9** and **11**, is also consistent with the proposed structures where the dihedral angle between H_{9a} and H_1 is *ca.* 30° in the former cases and *ca.* 90° in the latter.

Other important spectroscopic characteristics of both kind of adducts are the chemical shift differences observed in the *exo* adducts **9** and **11** for the olefinic H_6 and H_7 protons ($\Delta\delta$ = 0.94 and 0.95 ppm, respectively), which are larger than those showed for the *endo* derivatives **8** and **10** ($\Delta\delta$ = 0.49 and 0.27 ppm, respectively). This fact must be a consequence of the anisotropic effect of the aromatic ring of the *p*-tolyl group shielding mainly H_6 in the *exo* adducts (interactions between the sulfinylic oxygen and H_{11a} in **8** and **10** arrange the aromatic ring almost equidistant from H_6 and H_7, see Figure 1). The most significant parameter to assign the absolute configuration of **9** and **11** is the chemical shift difference of the H_{9a} protons, which appears *ca.* 0.5 ppm more deshielded in compound **9** as a consequence of the strong deshielding effect of the sulfinylic oxygen.[19] This effect is also apparent from the δ values observed for H_{11a} in compounds **8** (2.46 ppm) and **10** (1.82 ppm).

From the results collected in Table 1 several facts stand out. In thermal conditions diastereoisomer **6** was more reactive than **7.** The latter compound did not react at −20 °C and required longer reaction times than **6** to achieve total conversion at room temperature (compare entries 1 with 11 and 2 with 12 in Table 1).

The addition of $BF_3{\cdot}OEt_2$ to the reaction medium produced unexpected changes in the behavior of both dienophiles **6** and **7**. Surprisingly, the reactivity of compound **6** decreased with respect to the thermal process, but the *endo* selectivity increased giving rise exclusively to compound **8** (compare entries 2 and 3). No reaction was observed from **7** and cyclopentadiene in the same conditions (entry 13) or even at higher temperatures.

The most efficient catalyst for the cycloaddition was shown to be $ZnBr_2$ which produced the highest increase of the reaction rate for both **6** and **7**. In these conditions, the relative reactivity of both dienophiles was inverted making the reaction of **7** slightly faster than that of **6** at −20 °C (entries 5 and 14). With respect to the *endo*/*exo* selectivity, the addition of $ZnBr_2$ increased the ratio of the *exo* adducts **9** and **11** which became the major

(18) The authors have deposited atomic coordinates for **8** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

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products at −20 °C (entries 5 and 14). When the temperature decreased to −40 °C, the *endo/exo* ratio resulting from **6** was similar to that observed in the absence of the Lewis acid (compare entries 6 and 1), but the catalytic effect persisted. We could suggest a difficulty in the formation of the chelated species between the dienophile and $ZnBr_2$ at low temperatures[9c] to account for this result.

Finally, the effect of $Eu(fod)_3$ on both reactivity and selectivity of compound **6** was scarce (compare entries 2 and 7) even with increasing amounts of the catalyst (entries 8−10). On the contrary, compound **7** reacted more quickly than in thermal conditions yielding a higher proportion of the *exo* adduct (compare entry 12 with 15 and 16).

The formation of *exo* adducts in the Diels−Alder reactions of sulfinylene-diones **6** and **7** (Scheme 2 and Table 1) must be a consequence of the presence of the sulfoxide group in the ene-dione moiety which partially compensates the *endo*-directing power of the carbonyl groups of these dienophiles. A similar situation was observed in cycloadditions with 2-sulfinylmaleates,[11] whereas only *endo* adducts were formed in the reactions of sulfinylquinones with cyclopentadiene.[9,10] Thus, the lack of the quinonic planar structure in **6** and **7** must be responsible of the lower *endo* orientating character of their carbonyl groups. On the other hand, the observed π-facial selectivity in reactions of cyclopentadiene with dienophiles **6** and **7** under different conditions must be a consequence of their norbornene-dione rigid structure, with the convex face only accessible to dienes.[7,20] This fact allowed us to clarify the role of the different Lewis acids used in these cycloadditions.

The relative reactivity, as well as the selectivity observed for these dienophiles, must be related with the spatial arrangement of the substituents around the sulfur atom. According to the well documented steric approach control[21] which governs the Diels−Alder reactions of sulfinyl dienophiles, the attack of the diene must take place from the face bearing the lone electron pair at sulfur. Therefore, considering all the conformers around the C−S bond, rotamers **6A** and **7B**, both displaying the lone electron pair toward the convex face (Figure 2), must be the only one able to evolve into the corresponding adducts under thermal conditions. As can be seen, **6A** has the sulfinylic oxygen in *s-cis* arrangement with respect to the dienophilic double bond, whereas this disposition is adopted by the *p*-tolyl group in **7B**. The interactions of the *s-cis* substituent with the diene in both *endo* and *exo* approaches, more severe in the case of **7B**, would explain the higher reactivity shown by compound **6** (Table 1). This result confirms the higher reactivity of the conformations with the sulfinylic oxygen in *s-cis* arrangement already proposed to explain other results on sulfinyl dienophiles.[10a] On the other hand, the larger *endo/exo* selectivity exhibited by compound **7** could also be explained by assuming that the increased size of the substituent in *s-cis* arrangement (the *p*-tolyl group in **7B** is larger than oxygen in **6A**) favors the *endo* approach of cyclopentadiene with respect to the *exo* one. Nevertheless

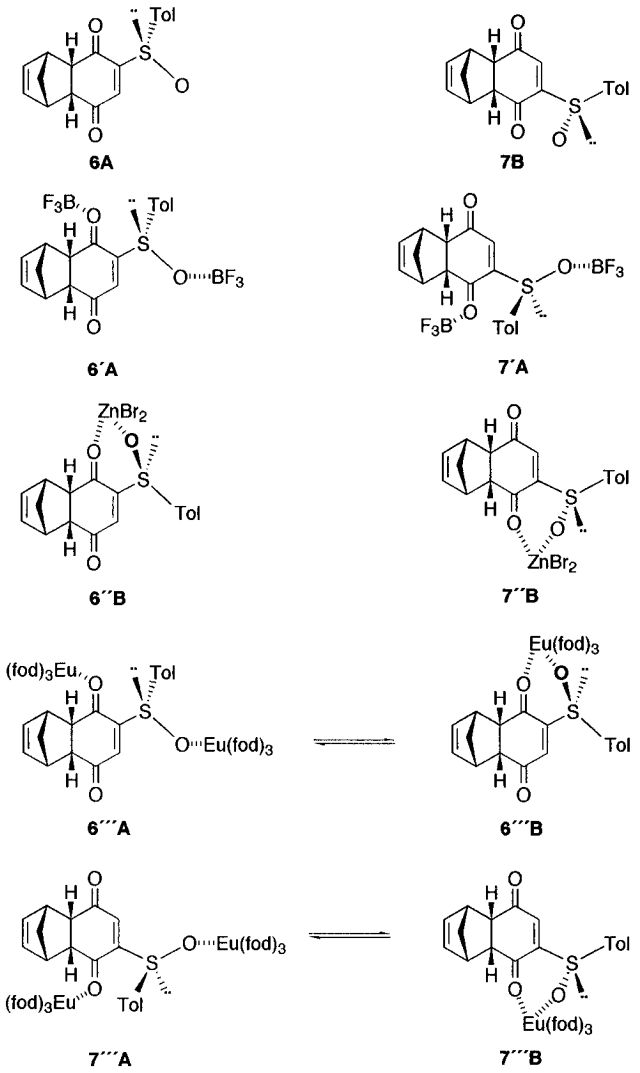

Figure 2.

the reactivity−selectivity principle can also be invoked to explain the higher selectivity of the less reactive dienophile **7B**.

A detailed analysis of the reactive species existing in the presence of $BF_3{\cdot}OEt_2$ could account for the diminished reactivity observed in these conditions for cycloadditions on both sulfinylene-diones **6** and **7**. Thus, the acidic $BF_3{\cdot}OEt_2$ must be associated with the oxygens, determining the complete shift of the conformational equilibrium around the C−S bond toward the rotamers **6′**A and **7′**A (Figure 2) with the sulfinylic oxygen in *s-cis* arrangement to minimize steric and electronic interactions between oxygens. This association, which increases the effective size of the sulfinylic oxygen and therefore the interactions with the approaching diene in the transition states, should be responsible of the unexpected decrease of the reactivity of compound **6**. This increased size could also be related with the complete *endo* selectivity observed in this reaction, but the increase of the *endo* orientating character of the carbonyl groups as a consequence of the Lewis acid association cannot be ignored. As we can see in Figure 2, conformation **7′**A has the bulky *p*-tolyl group oriented toward the upper convex face, precluding the diene approach and justifying the lack of reactivity of this dienophile. This result reinforces the steric approach control model suggested to explain the diastereoselectivity of sulfinyl dienophiles[21] and rules out

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(21) (a) Koizumi, T.; Hakamada, I.; Yoshii, E. *Tetrahedron Lett.* **1984**, *25*, 87. (b) Koizumi, T.; Arai, Y.; Takayama, T. *Tetrahedron Lett.* **1987**, *28*, 3689. (c) Arai, Y.; Matsui, M.; Koizumi, T.; Shiro, M. *J. Org. Chem.* **1991**, *56*, 1983.

other models based on electronic interactions, which suggested that the approach of the diene became favored from the face supporting the *p*-tolyl group.[22]

The behavior of both dienophiles in the presence of $ZnBr_2$ suggested the formation of the chelated species **6″**B and **7″**B (Figure 2).[23] The higher reactivity of the latter could be a consequence of the disposition of the lone electron pair at sulfur toward the only accessible upper face of the dienophile. On the other hand, this double association with the Zn atom must distort the planarity of the ene-dione system, decreasing the *endo* orienting character of the carbonyl groups, which results in an increase of the *exo* adduct proportion. This increase is similar for both dienophiles.

Finally, the different influence of $Eu(fod)_3$ on the selectivity of **6** (**8**:**9** ratio similar to that obtained in the absence of catalyst) and **7** (50:50 mixture of **10** and **11** almost identical to that obtained in the presence of $ZnBr_2$) suggested that in the first case a mixture of the species **6‴**A and **6‴**B could be the reactive substrates for the cyclopentadiene attack. Starting from **7** only the species **7‴**B could evolve into the bisadduct (in **7‴**A the arrangement of the *p*-tolyl group would preclude the attack of the diene), and thus the observed selectivity is similar to that observed in the reaction in the presence of $ZnBr_2$.

Conclusions

Our study showed that the presence of the sulfinyl group on the ene-dione moiety of **1** can be used to modify the reactivity and to alter the expected *endo*-selectivity of their Diels−Alder reactions making it possible to obtain, under very mild conditions, the *endo-anti-endo*-bisadducts **8** and **10** as well as the *exo-anti-endo*-bisadducts **9** and **11**. These results reinforce the model based on the steric approach control proposed to explain the diastereoselective cycloadditions of sulfinyl dienophiles and clarify the role of the different Lewis acids used in these reactions. Moreover, the presence of the sulfoxide in compounds **8-11** makes them enantiomerically pure synthetic equivalents of *p*-benzoquinone−cyclopentadiene bisadducts.

To our knowledge, the results presented here constitute the first examples where the *exo* addition of cyclopentadiene becomes favored in these kind of dienophiles. In addition, the desulfurization of sulfinyl bisadduct **9** allowed us to achieve the first synthesis of the unknown *endo-anti-exo* cyclopentadiene−quinone bisadduct **5**.

Experimental Section

Melting points were obtained in open capillary tubes and are uncorrected. IR spectra are given in cm^{-1}. ^1H- and ^{13}C-NMR spectra were recorded at 200.1 and 50.3 MHz in $CDCl_3$. Diastereomeric adducts ratios were established by integration of well-separated signals of both diastereomers in the crude reaction mixtures and are listed in Table 1. ^1H-NMR data of compounds **8-11** are collected in Table 2. All reactions were monitored by TLC which was performed on precoated sheets of silica gel 60, and flash column chromatography was carried out with silica gel 60 (230−400 mesh) of Macherey-Nagel. Eluting solvents are indicated in the text. The apparatus for inert atmosphere experiments were dried by flaming it in a stream of dry argon. Cyclopentadiene was freshly distilled. CH_2Cl_2 was dried over P_2O_5. $ZnBr_2$ was flamed-dried in the reaction flask, under a stream of dry argon, before use. For routine workup, hydrolysis was carried out with water, extractions with CH_2Cl_2, and solvent drying with Na_2SO_4.

General Procedure for Diels−Alder Reactions in Thermal Conditions. To a solution of **6**[9a,c] or **7**[9a,c] (100 mg, 0.3 mmol) in 5 mL of dry CH_2Cl_2 at the temperature indicated in each case (see Table 1 for conditions) was added cyclopentadiene (200 mg, 3 mmol) under argon. After completion of the reaction (see Table 1 for reaction times), the solvent was evaporated at reduced pressure and the residue was chromatographed on silica gel (eluent CH_2Cl_2:acetone = 40:1).

General Procedure for Diels−Alder Reactions in the Presence of Lewis Acids. A solution of **6**[9a,c] or **7**[9a,c] (100 mg, 0.3 mmol) in 5 mL of dry CH_2Cl_2 was added to the appropiate Lewis acid (see Table 1 for conditions) under argon, and the mixture was stirred for 1 h at rt. After the solution was cooled at the desired temperature (see Table 1 for conditions) cyclopentadiene (40 mg, 0.6 mmol) was added. After completion of the reaction (see Table 1 for reaction times) and workup, the residue was chromatographed on silica gel (eluent CH_2Cl_2:acetone = 40:1).

***endo-anti-endo*-[1*S*,4*R*,4a*R*,5*R*,8*S*,8a*R*,9a*S*,10a*S*,(S)*S*]-1,4,4a,5,8,8a,9a,10a-Octahydro-1,4:5,8-dimethano-4a-(*p*-tolylsulfinyl)anthracene-9,10-dione (8).** Compound **8** was obtained from **6** under the experimental conditions and in the ratios showed in Table 1 as a white solid: mp 145−146 °C dec (hexane); $[\alpha]^{20}_D = -17$ (*c* 1, $CHCl_3$); IR (KBr) 1670, 1250, 1195, 1080, 1045, 810; ^{13}C-NMR δ 21.3, 44.7, 45.6, 47.5, 48.2, 49.1, 49.5, 51.7, 55.8, 57.5, 80.5, 128.0 (2C), 129.3 (2C), 134.6, 136.2, 136.7, 138.2, 139.0, 142.6, 209.3, 209.5. Anal. Calcd for $C_{23}H_{22}SO_3$: C, 73.02; H, 5.82. Found: C, 73.05; H, 6.20.

***exo-anti-endo*-[1*R*,4*S*,4a*R*,5*R*,8*S*,8a*R*,9a*S*,10a*S*,(S)*S*]-1,4,-4a,5,8,8a,9a,10a-Octahydro-1,4:5,8-dimethano-4a-(*p*-tolylsulfinyl)anthracene-9,10-dione (9).** Compound **9** was obtained from **6** under the experimental conditions and in the ratios showed in Table 1 as a white solid: mp 96−7 °C dec; $[\alpha]^{20}_D = -15$ (*c* 1.5, $CHCl_3$); IR (KBr) 1690, 1245, 1180, 1085, 1050; ^{13}C-NMR δ 21.2, 45.0, 46.0, 46.1, 47.6, 48.4, 51.3, 51.5, 54.4, 57.2, 80.4, 128.0 (2C), 129.0 (2C), 132.7, 133.6, 137.0, 139.0, 139.1, 142.2, 208.5, 209.5. Anal. Calcd for $C_{23}H_{22}SO_3$: C, 73.02; H, 5.82. Found: C, 72.80; H, 6.03.

***endo-anti-endo*-[1*R*,4*S*,4a*S*,5*S*,8*R*,8a*S*,9a*R*,10a*R*,(S)*S*]-1,4,4a,5,8,8a,9a,10a-Octahydro-1,4:5,8-dimethano-4a-(*p*-tolylsulfinyl)anthracene-9,10-dione (10).** Compound **10** was obtained from **7** under the experimental conditions and in the ratios showed in Table 1 as an oil: $[\alpha]^{20}_D = +51$ (*c* 0.8, $CHCl_3$); IR (NaCl) 1685, 1235, 1210, 1040, 810; ^{13}C-NMR δ 21.3, 46.8, 46.9, 47.7, 48.2, 50.4, 51.9, 53.3, 53.8, 54.8, 78.0, 126.5 (2C), 129.5 (2C), 135.8, 136.1, 136.5, 137.1, 140.3, 141.8, 209.0, 209.8. Anal. Calcd for $C_{23}H_{22}SO_3$: C, 73.02; H, 5.82. Found: C, 73.11; H, 6.11.

***exo-anti-endo*-[1*S*,4*R*,4a*S*,5*S*,8*R*,8a*S*,9a*R*,10a*R*,(S)*S*]-1,4,-4a,5,8,8a,9a,10a-Octahydro-1,4:5,8-dimethano-4a-(*p*-tolylsulfinyl)anthracene-9,10-dione (11).** Compound **11** was obtained from **7** under the experimental conditions and in the ratios showed in Table 1 as an oil: $[\alpha]^{20}_D = -25$ (*c* 0.5, $CHCl_3$); IR (NaCl) 1685, 1230, 1185, 1095, 1030; ^{13}C-NMR δ 21.2, 44.7, 45.6, 46.6, 47.5, 51.4, 51.5, 53.7, 53.8, 55.9, 78.5, 126.2 (2C), 129.4 (2C), 134.5, 135.7, 136.2, 137.3, 139.5, 141.6, 205.4, 208.7. Anal. Calcd for $C_{23}H_{22}SO_3$: C, 73.02; H, 5.82. Found: C, 73.16; H, 5.69.

1α,4α,5α,8α,8a*β*,10a*β*-Hexahydro-1,4:5,8-dimethano-9,10-anthraquinone (12). Compound **12** was obtained as a bright yellow solid from 40 mg (0.1 mmol) of **8** (75% yield) or **10** (78% yield) by refluxing in 5 mL of EtOAc for 24 h, evaporation of the solvent, and flash chromatography (eluent EtOAc:hexane = 1:20): mp 153−4 °C (lit.[6b,17] 155 °C); ^1H-NMR δ 1.46 (2H, m), 2.18 (2H, m), 3.26 (2H, d, J = 2.0 Hz), 3.46 (2H, m), 3.98 (2H, m), 5.79 (2H, t, J = 2.0 Hz), 6.78 (2H, t, J = 2.0 Hz).

1α,4α,5*β*,8*β*,8aα,10aα-Hexahydro-1,4:5,8-dimethano-9,10-anthraquinone (13). Compound **13** was obtained as

(22) (a) Kahn, S. D.; Hehre, W. J. *Tetrahedron Lett.* **1986**, *27*, 6041. (b) Kahn, S. D.; Pau, C. F.; Overman, L. E.; Hehre, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 7381. (c) Kahn, S. D.; Hehre, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 7399.

(23) The formation of these species must not be favored at −40 °C which would explain the results obtained at this temperature (entry 6 in Table 1). This effect has been observed in other $ZnBr_2$-catalyzed cycloadditions of sulfinylquinones.[9c,10a]

above from **9** (82% yield) or **11** (80% yield) as a bright yellow solid: mp 150−2 °C (lit.[6b,17] 153−5 °C); ^{1}H-NMR δ 1.48 (2H, m), 2.10 (2H, m), 3.15 (2H, d, J = 2.0 Hz), 3.48 (2H, m), 3.92 (2H, m), 6.00 (2H, t, J = 2.0 Hz), 6.76 (2H, t, J = 2.0 Hz).

***endo-anti-endo*-1,4,4a,5,8,8a,9a,10a-Octahydro-1,4:5,8-dimethanoanthracene-9,10-dione (2).** *t*-BuOH (200 μL, 2 mmol) was added to a solution of compound **8** (76 mg, 0.2 mmol) in dry THF (5 mL) at rt under argon. After being stirred for 10 min, a 0.1 M solution of SmI_2 in THF (10 mL, 1 mmol) was added, and the mixture was stirred for 15 min. The reaction mixture was worked up with cold water and 5% HCl and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (eluent CH_2Cl_2:EtOAc = 98:2) to obtain **2** as a white solid (85% yield): mp 155−6 °C (methanol) (lit.[7b] 155−6 °C); ^{1}H-NMR δ 6.17 (4H, t, J = 2.0 Hz), 3.34 (4H, br s), 2.86 (4H, br s), 1.44 (2H, dt, J = 8.6 and 1.8 Hz), 1.27 (2H, br d, J = 8.6 Hz).

***exo-anti-endo*-1,4,4a,5,8,8a,9a,10a-Octahydro-1,4:5,8-dimethanoanthracene-9,10-dione (5).** Compound **5** was obtained as above from **9** as a white solid (89% yield): mp 160−1 °C (methanol); ^{1}H-NMR δ 6.20 and 6.19 (4H, 2t, J = 2.1 Hz), 3.40 (2H, m), 3.35 (2H, m), 3.23 (2H, br s), 2.12 (2H, d, J = 1.7 Hz), 1.54 (1H, dt, J = 8.6 and 1.8 Hz), 1.39 (1H, dt, J = 8.6 and 1.5 Hz), 1.31 (1H, dquint, J = 9.3 and 1.7 Hz), 1.21 (1H, dt, J = 9.3 and 1.6 Hz); ^{13}C-NMR δ 211.7 (2C), 137.2 (2C), 135.8 (2C), 53.6 (2C), 52.4 (2C), 50.4, 48.7 (2C), 47.6, 46.4 (2C). Anal. Calcd for $C_{16}H_{16}O_2$: C, 80.00; H, 6.67. Found: C, 79.91; H, 6.52.

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Supporting Information Available: An ORTEP drawing and X-ray experimental data of **8** (2 pages). This material is contained in libraries on microfiches, inmediately follows this article in the microfilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information.

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