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TETRAHEDRON: *ASYMMETRY*

Enantiopure sulfinylthiopyrans and related compounds from alkylsulfinylbuta-1,3-dienes

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Abstract

Uncatalyzed and $LiClO_4$ catalyzed cycloadditions of (R_S)-1-{1-[(1*S*)-isoborneol-10-sulfinyl]vinyl}cyclohexene **1** and (R_S,*E*)-3-[(1*S*)-isoborneol-10-sulfinyl]-1-methoxybuta-1,3-diene **2** with di(*p*-tolyl)- and di(*p*-anisyl)-thioketones **3** and **4** occur with complete regioselectivity. The lack of facial diastereoselectivity, observed in the cycloadditions of **1** with **3** or **4**, appears to be a consequence of the sterical features of both diene and dienophile which, in the transition states, make the topological differentiation induced by the presence of the alkylsulfinyl group as chiral auxiliary uninfluential. No significant improvement in diastereoselectivity is observed in the $LiClO_4$ catalyzed reactions, but the obtained enantiopure cycloadducts are easily separated by column chromatography and isolated in high yields.

1. Introduction

Hetero-Diels–Alder (HDA) reactions give easy access to heterocycles which constitute the structural skeleton of a large number of widespread natural compounds.[1] Although the most common HDA cycloadditions have been directed towards the synthesis of pyran derivatives as carbohydrate precursors, conveniently substituted thiopyrans, obtained by using the HDA approach, have received special attention as intermediates in the synthesis of biologically active agents.[2–4]

The most common thiodienophiles such as thioketones or thioaldehydes have been cycloadded to a variety of suitable dienes, and the kinetics[5,6] and stereochemistry of such reactions have been investigated. The observed regioselectivity appears generally connected to the nature of substituents

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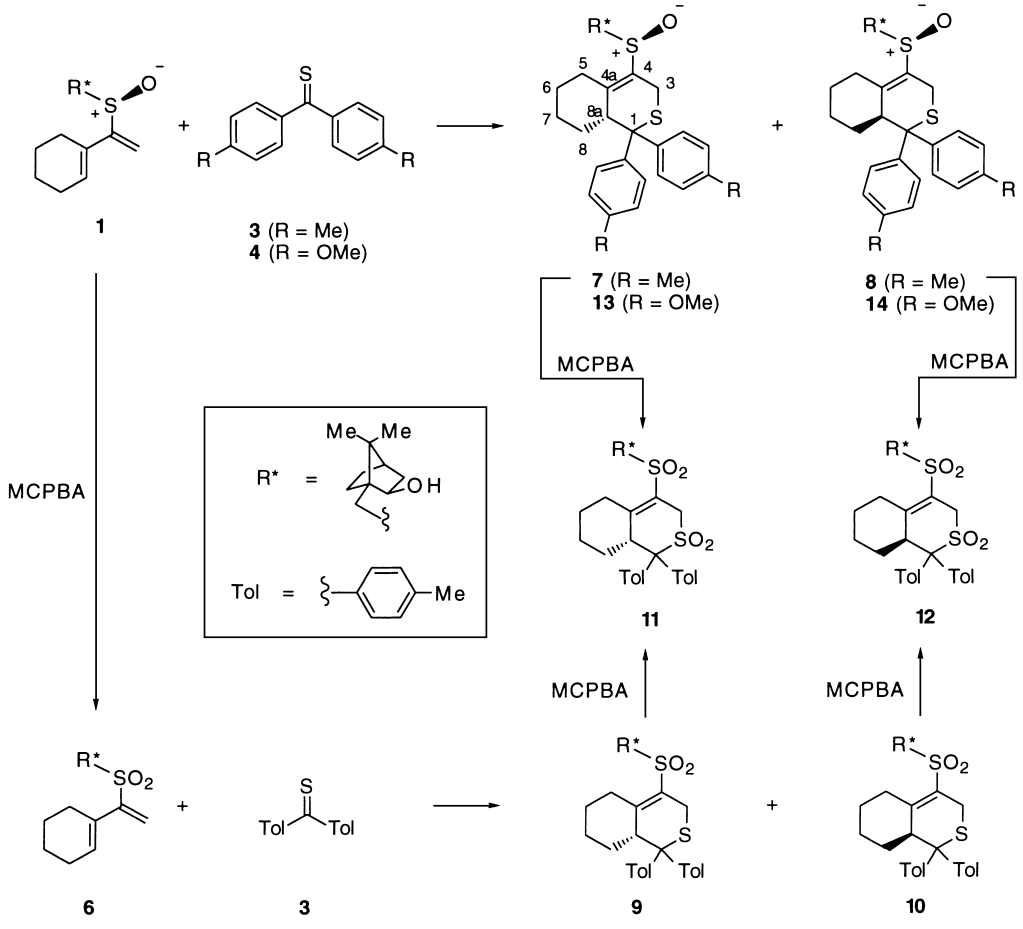
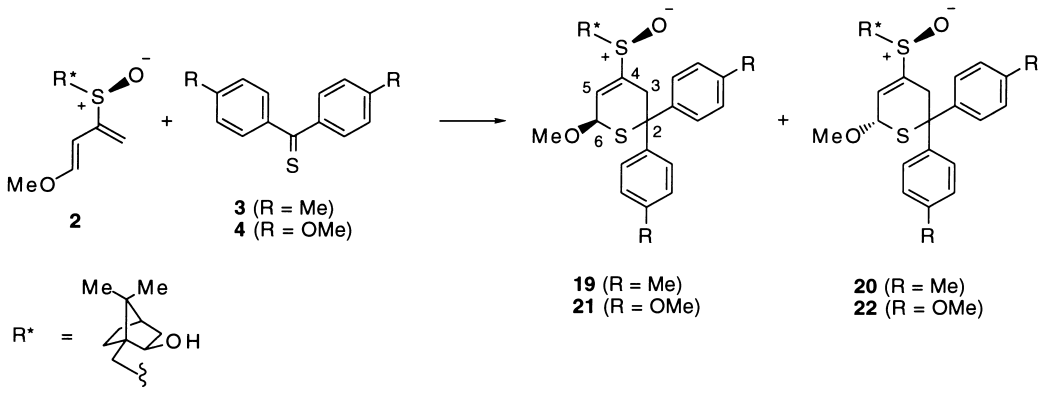
on C=S bond,[7,8] and the *endo/exo* selectivity is moderate unless very bulky thiodienophiles are used.[9] Studies on the facial diastereoselectivity have been performed for thioaldehydes bearing terpene moieties as chiral auxiliaries, and the obtained results were not encouraging.[10] Bonini et al. have extensively investigated HDA reactions of enantiopure thioacylsilanes showing a silicon[11] or carbon[12] stereogenic centre: appreciable diastereoselectivity, 50 and 80%, respectively, was observed. This article is concerned with HDA cycloadditions, not yet described in the literature, of thiodienophiles with enantiomerically pure dienes.

In continuing our research on the behaviour of enantiopure 2-alkylsulfinylbuta-1,3-dienes with heterodienophiles with the intention of evaluating their synthetic potentiality,[13] we turned our attention to the HDA reactions of dienes **1** (Scheme 1) and **2** (Scheme 2) with dienophiles **3** and **4**: these HDA partners were chosen because they are easily accessible and quite stable compounds,[14] unable to undergo enethiolization. Dienes **1**[15] and **2**[16,17] had afforded very good stereochemical results in cycloadditions with common carbodienophiles, generally showing a sensible increase in facial diastereoselectivity when the reactions were catalyzed by suitable Lewis acids such as lithium perchlorate. Facial preference was always controlled by the sulfur configuration.



Scheme 1.

In this paper we mainly describe the behaviour of sulfinyldienes **1** and **2** with sterically demanding thiones **3** and **4** in both thermal and catalyzed HDA cycloadditions.



Scheme 2.

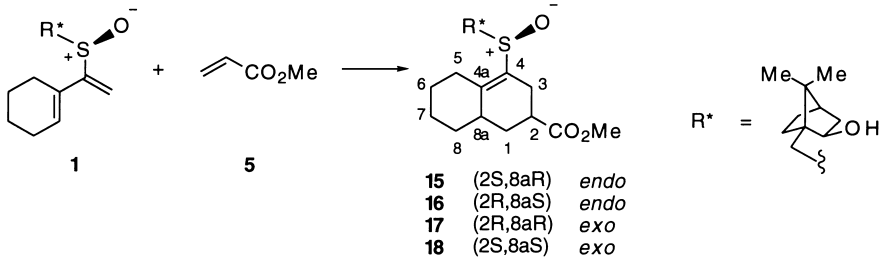
Table 1
[4+2] Cycloadditions of dienes **1**, **2** and **6** to thioketones **3**, **4** and methyl acrylate **5** in CH_2Cl_2

Entry	Diene	Dieno-phile	Temp., °C	Time, h	Catalyst	Total yield, %	Adducts	(ratio)
1	**1**	**3**	40	72	none	100	**7** : **8**	(50 : 50)
2	**1**	**3**	40	24	$LiClO_4$	82	**7** : **8**	(50 : 50)
3	**1**	**4**	25	384	none	100	**13** : **14**	(50 : 50)
4	**1**	**4**	40	90	none	100	**13** : **14**	(50 : 50)
5	**1**	**5**	40	360	none	50	**15** : **16** : **17** : **18**	(54 : 27 : 12 : 7)
6	**1**	**5**	40	290	$LiClO_4$	55	**15** : **16** : **17** : **18**	(59 : 31 : 6 : 4)
7	**2**	**3**	25	6	none	90	**19** : **20**	(70 : 30)
8	**2**	**3**	25	4	$LiClO_4$	90	**19** : **20**	(70 : 30)
9	**2**	**4**	25	36	none	70	**21** : **22**	(70 : 30)
10	**2**	**4**	25	24	$LiClO_4$	80	**21** : **22**	(70 : 30)
11	**6**	**3**	40	5	none	56	**9** : **10**	(50 : 50)

2. Results and discussion

HDA reactions of dienes **1** and **2** with thioketones **3** and **4** were performed under argon atmosphere in dry dichloromethane at reflux for diene **1** and at room temperature for the more reactive diene **2**. The results of these cycloadditions are reported in Table 1 together with the outcomes concerning Diels–Alder (DA) cycloadditions of diene **1** with methyl acrylate **5** (Scheme 3) and sulfonyldiene **6** with thioketone **3** (Scheme 1). Longer reaction times are required for cycloadditions performed with diene **1**, and/or in the absence of lithium perchlorate.[13,16,17] Yields are generally high, with some exceptions which involve the cycloaddition of highly reactive sulfonyldiene **6**, easily involved in side reactions at reflux (entry 11 in Table 1) and the cycloadditions of diene **1** with methyl acrylate **5** (entries 5 and 6 in Table 1) which required very long reaction times at reflux, involving extensive diene decomposition.

The first HDA reaction performed on diene **1** and di(*p*-tolyl)thioketone **3** (Scheme 1) gave cycloadducts **7** and **8** in equal amounts (entry 1 in Table 1). The assignment of their structures was not obvious until we performed a series of experiments which clearly demonstrated the complete regioselectivity and null facial diastereoselectivity of the reaction. Sulfonyldiene **6**, easily obtained by oxidation of the corresponding sulfinyldiene **1**, was cycloadded to thioketone **3**, again giving equal amounts of the two cycloadducts **9** and **10** (entry 11 in Table 1), which are undoubtedly facial diastereoisomers, as



Scheme 3.

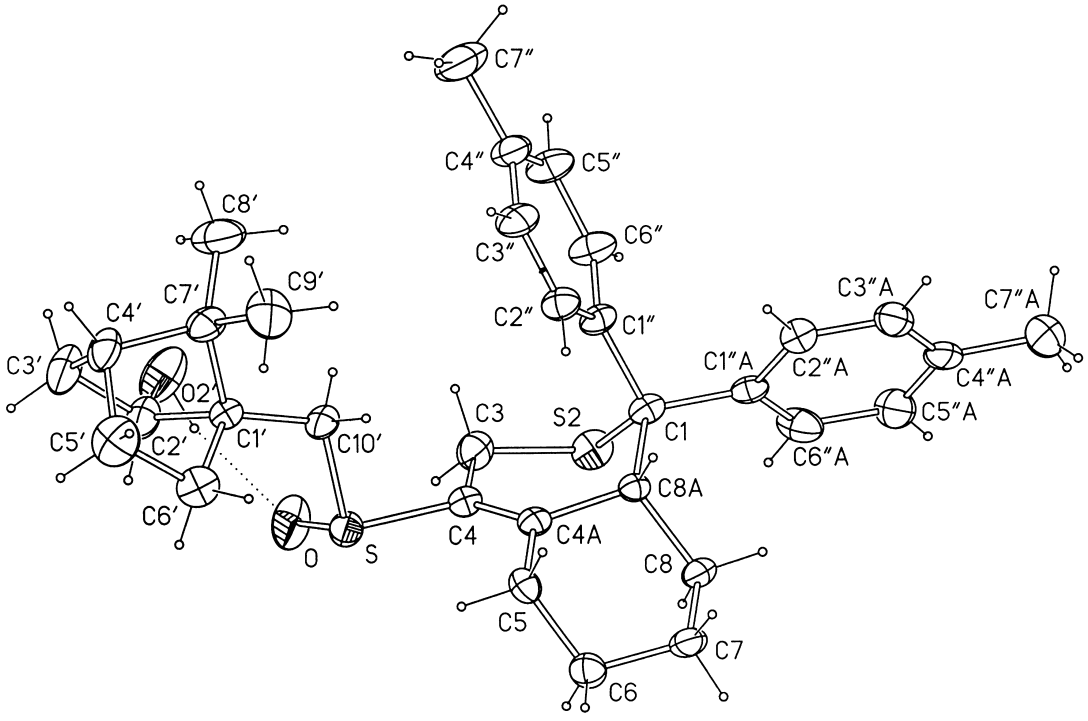


Figure 1. X-Ray structure of adduct **7**

demonstrated previously.[16,18] Sulfonylbenzothiins **9** and **10** were separated by column chromatography and individually oxidized to the bis-sulfones **11** and **12** (Scheme 1) which were also obtained as oxidation products of sulfinylbenzothiins **7** and **8**, respectively. These last results confirmed the stereochemical relationship between the diastereomeric cycloadducts **7** and **8**. X-Ray crystallographic analysis, subsequently performed on sulfinylbenzothiin **7**, allowed the assignment of the (*R*) configuration to the new stereogenic centre at C-8a (Fig. 1) and confirmed the regiochemistry of cycloadducts **7** and **8**, previously proposed on the basis of electronic characteristics of diene and dienophile[19] substituents. Structures of cycloadducts **13** and **14** were correlated with those of **7** and **8** by comparison of suitable ^{1}H NMR chemical shifts (H_2-3, 10′, H_A-5, H-8a, which are more affected by C-8a configuration (see Experimental)).

The lack of facial diastereoselectivity in HDA cycloaddition of diene **1** to thiobenzophenones **3** or **4** can be ascribed to the combined steric characteristics of the cyclohexene moiety of the diene and aryl substituents of the dienophile in the transition states of the cycloadditions. These high steric requirements, which are due in the dienophile to the approximately perpendicular disposition of the aryl groups with

respect to the C=S plane,[5] make the topological differentiation between the diene faces, induced by the alkylsulfinyl auxiliary, uninfluential and poor stereochemical results are observed.†

In order to corroborate the above interpretation, we reacted thioketones **3** and **4** with the less sterically demanding diene **2**, and the facial diastereoselectivity value (**19**/**20** and **21**/**22**, 70:30, entries 7 and 9 in Table 1) was as expected for thermal cycloadditions of (R_S,*E*)-3-[(1*S*)-isoborneol-10-sulfinyl]-3-methoxybuta-1,3-diene **2**. The attribution of the (*R*) configuration to the new stereogenic centre of the major adducts **19** and **21** is based on the (*R*) configuration of the sulfur atom, which renders the *Re* face of the diene **2** more easily approachable by the dienophile, as widely demonstrated before.[13,16,17]

Entries 5 and 6 in Table 1 are not strictly in line with the main subject of this paper, but the previously discussed results concerning complete regioselectivity of HDA reactions of diene **1** with thiobenzophenones allowed us to assign the structure to the four adducts which are products of the cycloaddition between diene **1** and methyl acrylate **5**, thus completing our study on the reactivity of enantiopure 2-alkylsulfinylbuta-1,3-dienes towards acrylate.[16,20] The reaction depicted in Scheme 3 occurs with complete regioselectivity, and the observed *endo/exo* and facial diastereoselectivities are in accordance with previous results.[16] Complete regioselectivity appears to be the more rational result of the reaction between **1** and **5** if one considers that both complete facial and *endo* diastereoselectivities were not observed even when **1** was reacted with the cyclic and *endo*-orientating *N*-phenylmaleimide as dienophile.[15]

The tabulated results (entries 2, 6, 8 and 10 in Table 1) show that the presence of the Lewis acid is unimportant for the stereochemical outcome of the cycloadditions under study. Lithium perchlorate always shortened the reaction times but did not affect the facial diastereoselectivity. This result is general for both dienes **1** and **2** involved in HDA reactions with thioketones **3** and **4**, and suggests a coordination of the catalyst to only one partner of the cycloaddition. The failed increase of facial diastereoselectivity in the catalyzed cycloaddition of diene **1** with methyl acrylate **5** was unexpected on the basis of the results obtained previously in the cycloaddition of diene **2** with the same dienophile **5** and in the presence of the same catalyst.[16] However, the previously observed coordination via lithium cation of both diene and dienophile[16] requires a suitable diene conformation in the transition state where the sulfinyl oxygen is directed towards the dienophile; this situation could be too sterically demanding and thus unfavoured when **1** and **5** are involved in a DA reaction.

In conclusion, the HDA cycloaddition of enantiopure alkylsulfinyldienes to thioketones constitutes a possible route towards thiopyran derivatives having the desired absolute configuration, once the chiral auxiliary is removed. Even if the observed facial diastereoselection was unsatisfactory (Scheme 2, entries 7–10 in Table 1) or completely absent (Scheme 1, entries 1–4), the easy separation and high yields of cycloadducts can render this procedure attractive from a synthetic point of view.

3. Experimental

3.1. General methods and materials

Starting products **1**–**4** were prepared following literature methodologies.[14,16,21] Solvents were purified according to standard procedures. All reactions were monitored by TLC on commercially available precoated plates (Aldrich silica gel 60 F 254) and the products were visualized with vanillin [vanillin (1 g) dissolved in MeOH (60 ml) and conc. H_2SO_4 (0.6 ml)]. Silica gel used for column chromatography

† In fact, a moderate increase of facial diastereoselection was observed when diene **1** was reacted with thiofluorenone.

was Aldrich 60. Mps were measured on a microscopic apparatus and are uncorrected. Optical rotations were measured in $CHCl_3$ solutions at 25°C and are given in 10^{-1} deg cm^2 g^{-1}; concentrations *c* are expressed in g/100 ml. Mass spectra were measured by fast atom bombardment (FAB, *m*-nitrobenzyl alcohol as matrix) with a Finnigan MAT 90 instrument. X-Ray diffraction analysis was performed on a Siemens automated four-circle single-crystal diffractometer R3μ/V. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer at 300 and 75 MHz, respectively, in $CDCl_3$ solutions with $SiMe_4$ as internal standard; *J* values are given in hertz; the attributions are supported by attached proton test (APT) and decoupling experiments. Proton and carbon indexes, marked with (′), pertain to the isoborneol moiety. The symbol (″) identifies nuclei pertaining to aryl residues in compounds **7**–**14**, **19**–**22**, and vinyl nuclei in sulfonyldiene **6**. Diastereomeric adduct ratios were established by integration of well-separated proton signals of the diastereomers in the crude adduct mixtures and are listed in Table 1.

3.2. General procedure for Diels–Alder reactions in thermal conditions

A solution of the diene (0.35 mmol) in 3 ml of anhydrous CH_2Cl_2 was added to the neat dienophile [an equimolar amount of thioketone dienophile was used, while an excess of methyl acrylate **5** was reacted with diene **1** (6:1 molar ratio)]. The reaction mixture was stirred under argon until the diene totally disappeared, as verified by TLC monitoring (light petroleum:ethyl acetate, 80:20). The solvent was removed under vacuum and the crude mixture was column chromatographed. Reaction temperatures, times and yields are shown in Table 1.

3.3. General procedure for Diels–Alder reactions in the presence of $LiClO_4$

$LiClO_4$ (0.28 mmol) was added to a solution of the diene (0.35 mmol) and thioketone dienophile (0.35 mmol) in anhydrous CH_2Cl_2 (3 ml) under argon (when methyl acrylate **5** was the dienophile, the relative amounts of reagents were diene:dienophile:catalyst, 1:6:0.8). The reaction mixture was stirred until the diene had totally disappeared, as verified by TLC monitoring. Isolation and purification of cycloadducts were performed as described previously.

3.4. General procedure for MCPBA oxidations

Commercial MCPBA (90% after careful drying over P_2O_5) was slowly added to a solution of substrate in anhydrous CH_2Cl_2 (10 ml/50 mg of substrate) at 0°C. The reaction mixture was allowed to spontaneously reach the room temperature, and was maintained under stirring until the starting product had totally disappeared, as verified by TLC monitoring (light petroleum:EtOAc, 75:25, as eluant for observing the disappearance of diene **1**, and CH_2Cl_2:EtOAc, 95:5, for the remaining substrates). Anhydrous KF was added (25 mg/20 mg MCPBA) and the mixture stirred overnight. After filtration, the evaporation of the solvent under reduced pressure gave the oxidation product, not needing any purification. The yields were almost quantitative. Different MCPBA/substrate molar ratios were used: 1.5:1 for oxidation of sulfoxide **1** to sulfone **6**, 3:1 for converting sulfonylthioethers **9** and **10** into bis-sulfones **11** and **12**, and 4.5:1 for obtaining the same bis-sulfones **11** and **12** from sulfinylthioethers **7** and **8**, respectively.

*3.5. Cycloadducts from sulfinyldiene **1** and di-(*p*-tolyl)thioketone **3**, reported in order of increasing retention times (eluant CH_2Cl_2:EtOAc, 98:2)*

*3.5.1. (8a*S,R$_S$*)-1,1-Di(*p*-tolyl)-3,5,6,7,8,8a-hexahydro-4-[(1*S*)-isoborneol-10-sulfinyl]-1*H*-2-benzothiin **8***

Mp 145°C; $[\alpha]_D^{25}$ +371.7 (*c* 0.965) (found: C, 73.80; H, 7.83; $C_{33}H_{42}O_2S_2$ requires: C, 74.12; H, 7.92%); δ_H: 7.2–7.0 (m, ArH), 4.05 (dd, $J_{2',3'}$=8.2 and 4.2, H-2′), 3.46 and 2.17 (AB system, $J_{10'A,10'B}$=13.2, H$_2$-10′), 3.34 (AB d, $J_{3A,3B}$=17.5, H$_A$-3), 2.96 (split d, $J_{5A,5B}$=13.0, H$_A$-5), 2.80 (split dd, $J_{8,8a}$=9.6 and 1.7, H-8a), 2.60 (split AB d, H$_B$-3), 2.30 and 2.27 (two s, ArMe), 2.1–1.0 (m, H$_2$-3′, 5′, 6, 6′, 7, 8, H-4′, H$_B$-5), 1.09 (s, H$_3$-8′), 0.79 (s, H$_3$-9′); δ_C: 148.44 (C-4), 142.11 and 142.00 (C-1″), 136.26 (C-4″), 130.63 (C-4a), 128.85 and 128.45 (C-2″, 6″), 127.96 and 127.27 (C-3″, 5″), 76.82 (C-2′), 57.23 (C-10′), 54.43 (C-1), 51.47 (C-1′), 49.45 (C-8a), 48.14 (C-7′), 45.01 (C-4′), 38.35 (C-3′), 32.33, 32.28, 31.09, 29.68, 27.10 and 26.42 (C-5, 5′, 6, 6′, 7, 8), 21.60 (C-3), 20.94, 20.90, 20.37 and 19.88 (Me); *m/z* (%): 535 (M+1, 18), 91 (86), 89 (82), 77 (100).

*3.5.2. (8a*R,R$_S$*)-1,1-Di(*p*-tolyl)-3,5,6,7,8,8a-hexahydro-4-[(1*S*)-isoborneol-10-sulfinyl]-1*H*-2-benzothiin **7***

Mp 224°C; $[\alpha]_D^{25}$ −315.6 (*c* 0.890) (found: C, 73.69; H, 8.27; $C_{33}H_{42}O_2S_2$ requires: C, 74.12; H, 7.92%); δ_H: 7.2–7.0 (m, ArH), 4.00 (dd, $J_{2',3'}$=7.9 and 4.0, H-2′), 3.66 (AB d, $J_{3A,3B}$=17.4, H$_A$-3), 3.15 (split d, $J_{5A,5B}$=12.7, H$_A$-5), 2.97 and 1.84 (AB system, $J_{10'A,10'B}$=13.3, H$_2$-10′), 2.88 (split dd, $J_{3B,8a}$=2.4, $J_{8,8a}$=10.9 and 2.3, H-8a), 2.44 (AB ddd, $J_{3B,5B}$=2.4, H$_B$-3), 2.30 and 2.29 (two s, ArMe), 2.1–1.0 (m, H$_2$-3′, 5′, 6, 6′, 7, 8, H-4′, H$_B$-5), 0.93 (s, H$_3$-8′), 0.81 (s, H$_3$-9′); δ_C: 148.64 (C-4), 142.34 and 141.61 (C-1″), 136.29 and 136.21 (C-4″), 131.56 (C-4a), 128.85 and 128.38 (C-2″, 6″), 128.16 and 127.25 (C-3″, 5″), 76.71 (C-2′), 57.19 (C-10′), 53.06 (C-1), 51.19 (C-1′), 49.47 (C-8a), 48.14 (C-7′), 44.93 (C-4′), 38.31 (C-3′), 33.01, 31.79, 30.74, 29.07, 27.07 and 26.44 (C-5, 5′, 6, 6′, 7, 8), 20.94, 20.85, 20.45 and 19.66 (Me), 19.75 (C-3); *m/z* (%): 535 (M+1, 4), 105 (46), 95 (47), 91 (53), 81 (78), 69 (80), 67 (46), 57 (58), 55 (100), 43 (69), 41 (69).

*3.6. Cycloadducts from sulfinyldiene **1** and di-(*p*-anisyl)thioketone **4**, reported in order of increasing retention times (eluant light petroleum:Et_2O, 80:20)*

*3.6.1. (8a*R,R$_S$*)-1,1-Di(*p*-anisyl)-3,5,6,7,8,8a-hexahydro-4-[(1*S*)-isoborneol-10-sulfinyl]-1*H*-2-benzothiin **13***

Mp 227–229°C; $[\alpha]_D^{25}$ −135.2 (*c* 0.304) (found: C, 69.99; H, 7.89; $C_{33}H_{42}O_4S_2$ requires: C, 69.93; H, 7.47%); δ_H: 7.2–6.7 (m, ArH), 4.00 (m, H-2′), 3.78 and 3.77 (two s, OMe), 3.68 (AB d, $J_{3A,3B}$=17.0, H$_A$-3), 3.14 (split d, $J_{5A,5B}$=12.6, H$_A$-5), 3.02 and 1.86 (AB system, $J_{10'A,10'B}$=13.3, H$_2$-10′), 2.83 (split d, $J_{8,8a}$=10.8, H-8a), 2.46 (split AB d, H$_B$-3), 2.1–1.2 (m, H$_2$-3′, 5′, 6, 6′, 7, 8, H-4′, H$_B$-5), 0.95 (s, H$_3$-8′), 0.81 (s, H$_3$-9′); δ_C: 158.02 and 157.89 (C-4″), 148.75 (C-4), 137.30 and 136.84 (C-1″), 131.45 (C-4a), 129.50 and 128.39 (C-2″, 6″), 113.42 and 112.69 (C-3″, 5″), 76.75 (C-2′), 56.69 (C-10′), 55.22 and 55.18 (OMe), 53.16 (C-1), 51.28 (C-1′), 49.83 (C-8a), 48.19 (C-7′), 45.06 (C-4′), 38.44 (C-3′), 33.13, 32.02, 30.88, 29.17, 27.17 and 26.55 (C-5, 5′, 6, 6′, 7, 8), 20.63 (C-3), 19.88 (C-8′, 9′); *m/z* (%): 567 (M+1, 28), 259 (30), 258 (35), 155 (39), 149 (30), 138 (51), 137 (100), 107 (53), 91 (31), 89 (40), 77 (46).

*3.6.2. (8a*S,R$_S$*)-1,1-Di(*p*-anisyl)-3,5,6,7,8,8a-hexahydro-4-[(1*S*)-isoborneol-10-sulfinyl]-1*H*-2-benzothiin* ***14***

Mp 109°C; $[\alpha]_D^{25}$ +265.8 (*c* 1.140) (found: C, 69.53; H, 7.22; $C_{33}H_{42}O_4S_2$ requires: C, 69.93; H, 7.47%); δ_H: 7.2–6.7 (m, ArH), 4.05 (m, H-2′), 3.78 and 3.76 (two s, OMe), 3.47 and 2.17 (AB system, $J_{10'A,10'B}$=13.2, H$_2$-10′), 3.35 (AB d, $J_{3A,3B}$=17.2, H$_A$-3), 2.96 (split d, $J_{5A,5B}$=12.6, H$_A$-5), 2.75 (split d, $J_{8,8a}$=10.2, H-8a), 2.61 (split AB d, H$_B$-3), 2.1–1.2 (m, H$_2$-3′, 5′, 6, 6′, 7, 8, H-4′, H$_B$-5), 1.12 (s, H$_3$-8′), 0.83 (s, H$_3$-9′); δ_C: 158.08 and 157.97 (C-4″), 148.55 (C-4), 137.18 and 137.14 (C-1″), 130.60 (C-4a), 129.22 and 128.49 (C-2″, 6″), 113.43 and 113.03 (C-3″, 5″), 76.81 (C-2′), 56.69 (C-10′), 55.16 and 55.13 (OMe), 54.38 (C-1), 51.46 (C-1′), 49.75 (C-8a), 48.14 (C-7′), 45.00 (C-4′), 38.34 (C-3′), 32.33, 31.07, 29.66, 29.22, 27.09 and 26.41 (C-5, 5′, 6, 6′, 7, 8), 21.66 (C-3), 20.36 and 19.86 (C-8′, 9′); *m/z* (%): 567 (M+1, 27), 259 (36), 258 (45), 155 (27), 149 (36), 138 (36), 137 (100), 135 (30), 107 (42), 91 (28), 89 (33), 81 (44), 77 (37).

*3.7. 1-{1-[(1*S*)-Isoborneol-10-sulfonyl]vinyl}cyclohexene* ***6****, obtained by MCPBA oxidation of diene* ***1***

Oil; δ_H: 6.46 (m, H-2), 6.27 and 5.84 (two s, H$_2$-2″), 4.18 (dd, $J_{2',3'}$=7.8 and 4.5, H-2′), 3.39 and 2.94 (AB system, $J_{10'A,10'B}$=13.5, H$_2$-10′), 2.3–1.1 (m, H$_2$-3, 3′, 4, 5, 5′, 6, 6′, H-4′), 1.06 (s, H$_3$-8′), 0.80 (s, H$_3$-9′); δ_C: 151.44 (C-1″), 131.82 (C-2), 130.16 (C-1), 123.01 (C-2″), 76.28 (C-2′), 52.45 (C-10′), 50.93 (C-1′), 49.17 (C-7′), 44.26 (C-4′), 39.05 (C-3′), 30.42, 28.02, 27.56, 25.92, 22.71 and 21.50 (C-3, 4, 5, 5′, 6, 6′), 20.59 and 19.93 (C-8′, 9′); *m/z* (%): 307 (M+1−H$_2$O, 7), 201 (19), 55 (100).

3.8. Cycloadducts from sulfonyldiene ***6*** *and di(*p*-tolyl)thioketone* ***3****, reported in order of increasing retention times (eluant light petroleum:EtOAc, 98:2)*

*3.8.1. (8a*R*)-1,1-Di(*p*-tolyl)-3,5,6,7,8,8a-hexahydro-4-[(1*S*)-isoborneol-10-sulfonyl]-1*H*-2-benzothiin* ***9***

Mp 215°C (found: C, 71.80; H, 7.75; $C_{33}H_{42}O_3S_2$ requires C, 71.96; H, 7.69%); δ_H: 7.1–7.0 (m, ArH), 4.10 (dd, $J_{2',3'}$=7.7 and 4.4, H-2′), 3.84 (split d, $J_{5A,5B}$=11.8, H$_A$-5), 3.51 (AB d, $J_{3A,3B}$=17.7, H$_A$-3), 3.07 and 2.74 (AB system, $J_{10'A,10'B}$=13.6, H$_2$-10′), 2.97 (split d, $J_{8,8a}$=10.4, H-8a), 2.59 (split AB d, H$_B$-3), 2.30 and 2.29 (two s, ArMe), 2.2–1.1 (m, H$_2$-3′, 5′, 6, 6′, 7, 8, H-4′, H$_B$-5), 1.01 (s, H$_3$-8′), 0.84 (s, H$_3$-9′); δ_C: 158.20 (C-4), 141.95 and 141.37 (C-1″), 136.51 and 136.45 (C-4″), 130.25 (C-4a), 128.95 and 128.48 (C-2″, 6″), 127.96 and 127.12 (C-3″, 5″), 76.26 (C-2′), 56.76 (C-10′), 54.88 (C-1), 50.91 (C-8a), 50.90 (C-1′), 49.14 (C-7′), 44.15 (C-4′), 38.81 (C-3′), 34.33, 33.02, 30.73, 30.15, 27.53 and 26.35 (C-5, 5′, 6, 6′, 7, 8), 26.03 (C-3), 20.94, 20.91, 20.63 and 19.74 (Me).

*3.8.2. (8a*S*)-1,1-Di(*p*-tolyl)-3,5,6,7,8,8a-hexahydro-4-[(1*S*)-isoborneol-10-sulfonyl]-1*H*-2-benzothiin* ***10***

Mp 189°C (found: C, 71.66; H, 7.70; $C_{33}H_{42}O_3S_2$ requires: C, 71.96; H, 7.69%); δ_H: 7.2–7.0 (m, ArH), 4.11 (m, H-2′), 3.82 (split d, $J_{5A,5B}$=12.1, H$_A$-5), 3.51 (AB d, $J_{3A,3B}$=17.7, H$_A$-3), 3.34 and 2.51 (AB system, $J_{10'A,10'B}$=13.7, H$_2$-10′), 3.00 (split d, $J_{8,8a}$=10.2, H-8a), 2.61 (split AB d, H$_B$-3), 2.30 and 2.28 (two s, ArMe), 2.2–1.0 (m, H$_2$-3′, 5′, 6, 6′, 7, 8, H-4′, H$_B$-5), 1.10 (s, H$_3$-8′), 0.76 (s, H$_3$-9′); δ_C: 158.05 (C-4), 141.97 and 141.33 (C-1″), 136.44 and 136.39 (C-4″), 130.41 (C-4a), 128.96 and 128.51 (C-2″, 6″), 128.01 and 127.09 (C-3″, 5″), 76.31 (C-2′), 56.80 (C-10′), 54.63 (C-1), 50.91 (C-1′), 50.82 (C-8a), 49.13 (C-7′), 44.14 (C-4′), 39.03 (C-3′), 34.37, 33.07, 30.60, 30.14, 27.42 and 26.32 (C-5, 5′, 6, 6′, 7, 8), 25.99 (C-3), 20.93, 20.89, 20.38 and 19.99 (Me).

*3.9. (8a*R*)-1,1-Di(*p*-tolyl)-3,5,6,7,8,8a-hexahydro-4-[(1*S*)-isoborneol-10-sulfonyl]-1*H*-2-benzothiin 2,2-dioxide **11**, obtained by MCPBA oxidation of both **7** and **9***

Mp 281°C; $[\alpha]_D^{25}$ −202.1 (*c* 1.225) (found: C, 67.97; H, 7.18; $C_{33}H_{42}O_5S_2$ requires: C, 68.01; H, 7.26%); δ_H: 7.3–7.1 (m, ArH), 4.12 (dd, $J_{2',3'}$=7.1 and 3.7, H-2′), 3.94 (split d, $J_{5A,5B}$=12.6, H_A-5), 3.77 (AB d, $J_{3A,3B}$=17.6, H_A-3), 3.4–3.3 (m, H_B-3, H-8a), 3.39 and 2.91 (AB system, $J_{10'A,10'B}$=13.7, H_2-10′), 2.34 and 2.32 (two s, ArMe), 2.3–1.0 (m, H_2-3′, 5′, 6, 6′, 7, 8, H-4′, H_B-5), 1.06 (s, H_3-8′), 0.86 (s, H_3-9′); δ_C: 156.72 (C-4), 139.42 (C-1″), 137.55 and 135.56 (C-4″), 129.53 and 129.21 (C-2″, 6″), 129.00 and 128.28 (C-3″, 5″), 126.33 (C-4a), 76.22 (C-2′), 73.54 (C-3), 55.33 (C-8a, 10′), 50.89 (C-1), 49.30 (C-1′), 47.33 (C-7′), 44.13 (C-4′), 39.13 (C-3′), 33.60, 30.68, 29.66, 27.46 and 26.83 (C-5, 5′, 6, 6′, 7, 8), 21.01, 20.99, 20.62 and 19.83 (Me).

*3.10. (8a*S*)-1,1-Di(*p*-tolyl)-3,5,6,7,8,8a-hexahydro-4-[(1*S*)-isoborneol-10-sulfonyl]-1*H*-2-benzothiin 2,2-dioxide **12**, obtained by MCPBA oxidation of both **8** and **10***

Mp 121°C; $[\alpha]_D^{25}$ +156.6 (*c* 0.770) (found: C, 68.30; H, 7.70; $C_{33}H_{42}O_5S_2$ requires: C, 68.01; H, 7.26%); δ_H: 7.2–7.1 (m, ArH), 4.07 (dd, $J_{2',3'}$=7.9 and 3.9, H-2′), 3.94 (split d, $J_{5A,5B}$=13.7, H_A-5), 3.76 (AB d, $J_{3A,3B}$=17.5, H_A-3), 3.55 and 2.76 (AB system, $J_{10'A,10'B}$=13.6, H_2-10′), 3.34 (m, H-8a), 3.30 (split AB d, H_B-3), 2.34 and 2.32 (two s, ArMe), 2.3–1.0 (m, H_2-3′, 5′, 6, 6′, 7, 8, H-4′, H_B-5), 1.10 (s, H_3-8′), 0.82 (s, H_3-9′); δ_C: 156.47 (C-4), 139.37 (C-1″), 137.55 and 135.57 (C-4″), 129.20 (C-2″, 6″), 128.98 (C-3″, 5″), 126.56 (C-4a), 76.07 (C-2′), 73.59 (C-3), 55.48 (C-10′), 55.23 (C-8a), 51.11 (C-1), 49.35 (C-1′), 47.40 (C-7′), 44.18 (C-4′), 39.59 (C-3′), 33.60, 30.74, 29.67, 27.38 and 26.80 (C-5, 5′, 6, 6′, 7, 8), 21.11, 21.01, 20.46 and 20.01 (Me).

*3.11. Cycloadducts from sulfinyldiene **2** and di(*p*-tolyl)thioketone **3**, reported in order of increasing retention times (eluant light petroleum:EtOAc, 95:5)*

*3.11.1. (6*S,R$_S$*)-3,6-Dihydro-2,2-di(*p*-tolyl)-4-[(1*S*)-isoborneol-10-sulfinyl]-6-methoxy-2*H*-thiin **20***

Low-melting solid; δ_H: 7.6–7.1 (m, ArH), 6.81 (ddd, $J_{3A,5}$= $J_{5,6}$=2.2, $J_{3B,5}$=2.3, H-5), 4.67 (ddd, $J_{3A,6}$=2.2, $J_{3B,6}$=2.3, H-6), 4.04 (dd, $J_{2',3'}$=8.2 and 4.0, H-2′), 2.90 (AB ddd, $J_{3A,3B}$=17.2, H_A-3), 3.11 (s, 6-OMe), 2.83 and 1.94 (AB system, $J_{10'A,10'B}$=13.3, H_2-10′), 2.76 (AB ddd, H_B-3), 2.32 (s, ArMe), 1.8–1.0 (m, H_2-3′, 5′, 6′, H-4′), 1.03 (s, H_3-8′), 0.69 (s, H_3-9′).

*3.11.2. (6*R,R$_S$*)-3,6-Dihydro-2,2-di(*p*-tolyl)-4-[(1*S*)-isoborneol-10-sulfinyl]-6-methoxy-2*H*-thiin **19***

Low-melting solid; $[\alpha]_D^{25}$ −77.2 (*c* 0.765); δ_H: 7.6–7.1 (m, ArH), 6.61 (ddd, $J_{5,6}$=1.9, $J_{3A,5}$=1.8, $J_{3B,5}$=2.1, H-5), 4.72 (ddd, $J_{3A,6}$=1.8, $J_{3B,6}$=3.4, H-6), 3.98 (dd, $J_{2',3'}$=7.7 and 3.8, H-2′), 3.29 (AB ddd, $J_{3A,3B}$=17.6, H_A-3), 3.08 (s, 6-OMe), 2.93 and 1.83 (AB system, $J_{10'A,10'B}$=13.2, H_2-10′), 2.90 (AB ddd, H_B-3), 2.32 (s, ArMe), 1.8–1.0 (m, H_2-3′, 5′, 6′, H-4′), 0.94 (s, H_3-8′), 0.76 (s, H_3-9′).

*3.12. Cycloadducts from sulfinyldiene **2** and di(*p*-anisyl)thioketone **4**, reported in order of increasing retention times (eluant CH_2Cl_2:EtOAc, 98:2)*

*3.12.1. (6*R,R$_S$*)-3,6-Dihydro-2,2-di(*p*-anisyl)-4-[(1*S*)-isoborneol-10-sulfinyl]-6-methoxy-2*H*-thiin **21***

Low-melting solid; $[\alpha]_D^{25}$ −99.4 (*c* 0.815); δ_H: 7.6–6.8 (m, ArH), 6.61 (ddd, $J_{3A,5}$=1.6, $J_{3B,5}$=2.3, $J_{5,6}$=1.8, H-5), 4.72 (ddd, $J_{3A,6}$=1.6, $J_{3B,6}$=3.6, H-6), 4.00 (dd, $J_{2',3'}$=8.0 and 4.1, H-2′), 3.81 and 3.80 (two s, ArOMe), 3.29 (AB ddd, $J_{3A,3B}$=17.6, H_A-3), 3.10 (s, 6-OMe), 2.97 and 1.86 (AB system, $J_{10'A,10'B}$=13.2, H_2-10′), 2.93 (AB ddd, H_B-3), 0.96 (s, H_3-8′), 0.77 (s, H_3-9′).

*3.12.2. (6*S,R$_S$*)-3,6-Dihydro-2,2-di(*p*-anisyl)-4-[(1*S*)-isoborneol-10-sulfinyl]-6-methoxy-2*H*-thiin* ***22***

Low-melting solid; δ_H: 7.6–6.8 (m, ArH), 6.80 (m, H-5), 4.65 (ddd, $J_{3A,6}$=1.6, $J_{3B,6}$=$J_{5,6}$=2.9, H-6), 4.04 (dd, $J_{2',3'}$=8.0 and 4.4, H-2′), 3.79 (s, ArOMe), 3.12 (s, 6-OMe), 2.92 (AB ddd, $J_{3A,3B}$=17.1, $J_{3A,5}$=1.6, H_A-3), 2.84 and 1.98 (AB system, $J_{10'A,10'B}$=13.3, H_2-10′), 2.76 (AB ddd, $J_{3B,5}$=2.1, H_B-3), 1.03 (s, H_3-8′), 0.70 (s, H_3-9′).

3.13. Isolated cycloadducts from sulfinyldiene ***1*** *and methyl acrylate* ***5****, reported in order of increasing retention times (eluant light petroleum:EtOAc, 95:5)*

*3.13.1. (2*S,*8a*R,R$_S$*)-4-[(1*S*)-Isoborneol-10-sulfinyl]-2-methoxycarbonyl-1,2,3,5,6,7,8,8a-octahydronaphthalene* ***15***

Oil; $[\alpha]_D^{25}$ −27.0 (*c* 1.365); δ_H: 4.09 (dd, $J_{2',3'}$=8.1 and 4.0, H-2′), 3.71 (s, OMe), 3.46 and 2.08 (AB system, $J_{10'A,10'B}$=12.9, H_2-10′), 3.1–1.1 (m, H_2-1, 3, 5, 6, 7, 8, H-2, 8a), 1.09 (s, H_3-8′), 0.81 (s, H_3-9′); δ_C: 174.08 (CO), 147.45 (C-4), 132.87 (C-4a), 76.87 (C-2′), 52.18 (C-10′), 51.61 (OMe), 51.35 (C-1′), 48.12 (C-7′), 45.07 (C-4′), 43.71 (C-2), 41.62 (C-8a), 38.36 (C-3′), 31.66, 30.87, 30.38, 28.34, 27.07, 26.14, 20.08 and 17.85 (C-1, 3, 5, 5′, 6, 6′, 7, 8), 20.51 and 19.92 (C-8′, 9′).

*3.13.2. (2*R,*8a*S,R$_S$*)-4-[(1*S*)-Isoborneol-10-sulfinyl]-2-methoxycarbonyl-1,2,3,5,6,7,8,8a-octahydronaphthalene* ***16***

Oil; $[\alpha]_D^{25}$ +93.6 (*c* 0.850); δ_H: 4.09 (dd, $J_{2',3'}$=8.3 and 4.3, H-2′), 3.71 (s, OMe), 3.46 and 2.03 (AB system, $J_{10'A,10'B}$=13.2, H_2-10′), 2.9–1.1 (m, H_2-1, 3, 5, 6, 7, 8, H-2, 8a), 1.12 (s, H_3-8′), 0.82 (s, H_3-9′); δ_C: 174.03 (CO), 145.82 (C-4), 132.67 (C-4a), 76.84 (C-2′), 53.30 (C-10′), 51.57 (OMe), 51.38 (C-1′), 48.08 (C-7′), 45.04 (C-4′), 43.10 (C-2), 41.47 (C-8a), 38.40 (C-3′), 31.15, 31.06, 30.50, 28.39, 27.11, 26.02, 20.82 and 20.05 (C-1, 3, 5, 5′, 6, 6′, 7, 8), 20.41 and 19.90 (C-8′, 9′).

*3.14. X-Ray analysis of (8a*S,R$_S$*)-1,1-di(*p*-tolyl)-3,5,6,7,8,8a-hexahydro-4-[(1*S*)-isoborneol-10-sulfinyl]-1*H*-2-benzothiin* ***7***[‡]

The space group of the monoclinic $C_{33}H_{42}O_2S_2$ crystal (from EtOAc, M=534.79) was $P2_1$ with *a*=11.324(2), *b*=7.3923(9), *c*=18.455(3) Å, β=105.65(1)°. Other crystal parameters were as follows: *V*=1487.6(4) Å^3, *Z*=2, d_{calc}=1.194 g/cm^3. The structure, solved by direct methods (SIR97),[22] was subsequently completed by a combination of least squares technique and Fourier syntheses, and refined by the full-matrix least squares technique (SHELXTL PLUS) based on F.[23] The H atoms were included in the refinement following the 'riding model' with a unique common fixed isotropic displacement parameter. The structure refinement, with all anisotropic non-H atoms, reached *R*(F)=0.0388 including a parameter for extinction correction into the last cycles. The Flack enantiomorphic parameter converged to the final value of 1.5(4), overestimated in comparison with the theoretical value +1 which characterizes the assigned absolute configuration.[24] The final Fourier difference maps revealed no significant residual (<0.2 eÅ^{-3}).

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‡ Tables of bond distances, bond angles, and positional and thermal parameters are available on request from the corresponding author.

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