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Asymmetric synthesis of tertiary vinyl carbinols by highly stereoselective methylation of α-methyl-β-ketosulfoxides with aluminum reagents

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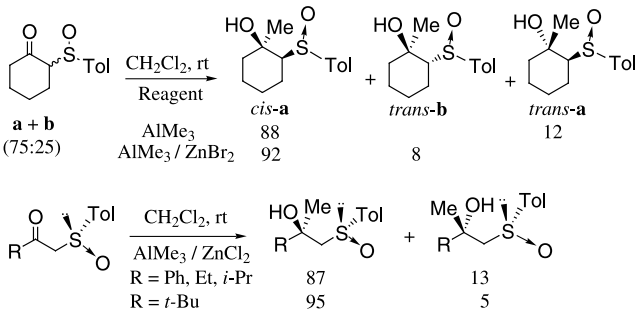
Abstract—Methylation of chiral acyclic α-methyl-β-ketosulfoxides with Me_3Al and Me_2AlCl is reported. Induced configuration at hydroxylic carbon is mainly controlled by the configuration of the sulfinyl group, with de's higher than 90% in most of the cases regardless the configuration at C-α. The stereochemical pathway seems to be different with both reagents, thus affording a higher stereoselectivity with Me_2AlCl. Pyrolytic desulfinylation and hydrogenolysis of the C–S bond allowed the transformation of the resulting hydroxysulfoxides into interesting optically pure tertiary methyl carbinols.

1. Introduction

Aluminum reagents have been widely used in organic synthesis[1] mainly due to their Lewis acidic features, strongly dependent on the aluminum substituents. Their well-known reactivity as alkylating agents[2] has been used in asymmetric synthesis in the presence of chiral catalysis[3] or on substrates containing different chiral inductors.[4,5] In this context, the sulfinyl group has been used to control the stereoselectivity of the alkylations,[6,7] our group pioneering this field with the study of the reactions of Me_3Al with chiral cyclic[8] and α-unsubstituted acyclic[9] β-ketosulfoxides (Scheme 1). Although acyclic substrates afforded hydroxysulfoxides in good yields (90%) and high levels of asymmetric induction (de's >74%), their synthetic interest was limited because methyl carbinols (trialkylaluminum reagents different to Me_3Al were not efficient) resulting from the desulfinylation processes would not be chiral (Scheme 1).

In order to solve this problem in the case of acyclic compounds, it was necessary the use of α-substituted β-ketosulfoxides as the starting compounds. They would yield hydroxysulfoxides containing two chiral carbons which could be transformed into chiral tertiary carbinols by hydrogenolysis of the C–S bond or used to prepare other chiral compounds taking advantage of the reactivity of the sulfinyl group.



Scheme 1.

Herein we report the results obtained in the asymmetric methylation of acyclic α-methyl-β-ketosulfoxides with Me_3Al and Me_2AlCl, the rationalization of these results and some synthetic applicabilities of the resulting hydroxysulfoxides based on the reactivity of the sulfinyl group.

2. Results and discussion

The reactions of α-substituted β-ketosulfoxides with DIBAL[10] had shown to be highly stereoselective only when they were conducted in the presence of ZnX_2, presumably due to the formation of a chelated species activating the substrate. By contrast, a complete control of the stereoselectivity was observed in reactions of

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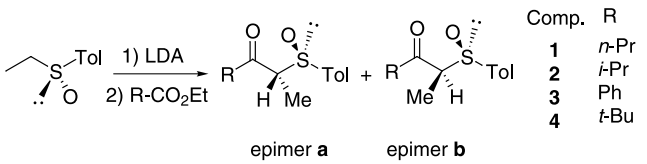
β-ketosulfoxides with Et_2AlCN[11] regardless the presence of ZnX_2 as the catalyst. Regarding the methylation reactions of α-sulfinyl cycloalkanones with Me_3Al and Me_3Al/ZnX_2[8] (they are α-substituted β-ketosulfoxides) the stereoselectivity increased in the presence of ZnX_2, but the reactivity was scarcely modified. On the contrary, only these reactions of R-CO–CH_2–SOTol with $Me_3Al/ZnBr_2$ took place satisfactorily.[9] With these antecedents, we initiated the study of the methylation reactions with Me_3Al. We chose α-methyl β-ketosulfoxides **1**–**4** (Scheme 2), containing aryl and alkyl groups, as the substrates, in order to evaluate the influence of the nature and size of R on the stereoselectivity.



Scheme 2.

The synthesis of the starting sulfoxides **1**–**4** (R-CO–CHMe–SOTol) was accomplished following a previously described procedure by reaction of (*R*)-(+)-ethyl *p*-tolyl sulfoxide with the corresponding esters RCO_2Et in the presence of LDA[11b] (Scheme 2). These reactions yielded ~40:60 mixtures of the two possible epimers (**a** and **b**) at C-α. Only *t*-butyl derivatives **4a** and **4b** could be separated by flash chromatography and therefore isolated as pure diastereoisomers. Hence, mixtures of **a:b** epimers of compounds **1**–**3** were used as the starting materials in methylation reactions.

The reactions of compounds **1**–**4** with Me_3Al (4 equiv.) in CH_2Cl_2 under similar conditions (rt, 30 min) to those previously reported[8,9] afforded the results collected in Table 1. Starting from **1** and **3**, mixtures of the four possible stereoisomers of the corresponding adducts (**A** and **A′** derive from **a** epimers whereas **B** and **B′** derive from the **b** ones, see Scheme 3) were obtained. By contrast, the evolution of **2a** and **2b** was completely stereoselective and only two stereoisomers (**A** and **B**) were obtained from the starting mixture. Reactivity of the *t*-butyl derivatives was lower and **4b** needed 5 h (instead of 30 min required by **1**–**3**) at room temperature to evolve, with moderate yield, into **8B** in a completely stereoselective way. Compound **4a** was even less reactive and required 25 h to be transformed into a 70:30 mixture of diastereoisomers **8A** and **8A′**. A higher reactivity was also detected for **b** isomers of compounds **1** and **2**. The results obtained in the reactions of compounds **1** with Me_3Al/ZnX_2, as well as those conducted in toluene as the solvent, were much less satisfactory (low conversions and scarce stereoselectivity).

On the basis of the exceptionally high chelating power of Me_2AlCl with β-heterosubstituted carbonyl compounds,[12] that strongly increases their reactivity, we decided to evaluate the ability of this reagent as a methylating agent. It has been used as a catalyst to promote important reactions such as Diels–Alder cycloadditions,[12a,13] ene reactions,[14] conjugated additions,[5] additions to the carbonyl group,[12b,15] amide formation,[16] and formation of aluminium enolates,[17] but only in a few cases it simultaneously acted as a nucleophile on the activated substrate.[2a,c,18]

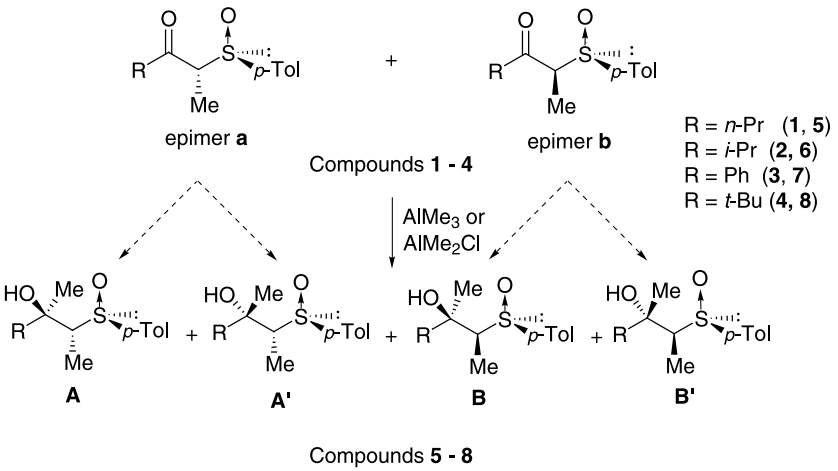
The reactions of ketosulfoxides **1**–**4** with $AlMe_2Cl$ were performed at room temperature in toluene or CH_2Cl_2 as the solvent. In Table 2 are indicated the diastereomeric ratios of the obtained carbinols **A**, **A′**, **B**, **B′** (Scheme 3), that were determined by HPLC from the reaction crudes obtained under different conditions. We first studied the behavior of the mixture **1a**+**1b** (R=*n*-Pr), that was used to evaluate the influence of different factors on the stereoselectivity and yield of the reactions. The order of the addition of the reagents (substrate must be added onto the $AlMe_2Cl$) was important to attain higher conversions (compare entries 4 and 5) and the number of equivalents of $AlMe_2Cl$ was also determinant. Reactions must be performed in the presence of a high excess of the reagent (3 or 4 equiv.), because with lower reagent proportion (2.2 equiv.) the reaction rate sharply decreased and a significant amount of starting ketosulfoxide was recovered (compare entries 8 and 9 with 6 and 7, respectively).

Concerning the stereoselectivity, the results show that the evolution of the epimer **1b** was highly stereoselective under all the studied conditions (de ~ 87–90%) whereas **1a** evolved with only moderated stereoselectivity (de ~ 30–50%). This situation was scarcely modified by any change in the solvent and the temperature. These factors have some influence on the reaction rate, which was slightly lower in CH_2Cl_2 than in toluene (compare entries 1 and 4 with 2 and 6, respectively) and decreased as the temperature became lower. Moreover the epimerization extent was much more significant in toluene and also when the temperature decreased (see Table 2). As the configuration at hydroxylated carbon is *R* for **A** and **B** and *S* for **A′** and **B′** (see Scheme 3), the best conditions from a stereoselective point of view are those optimized with 3 equiv. at 0 °C (at lower

Table 1. Methylation of compounds **1**–**4** with $AlMe_3$

Substrate (**a**:**b** ratio)	Reagent[a]	Product ratio **A**:**A′** : **B**:**B′**	Yield (%)	Recovered substrate % (**a**:**b**)
1 (39:61)	$AlMe_3$	13:10 : 67:10[b]	72	13 (44:56)
2 (36:64)	$AlMe_3$	29:0 : 71:0[c]	58	20 (81:19)
3 (44:56)	$AlMe_3$	33:10 : 38:19[c]	89	—
4a	$AlMe_3$[d]	70:30 : 0:0[c]	40	—
4b	$AlMe_3$[e]	0:0 : 100:0[c]	43	—

[a] Reactions conditions: rt, 30 min and 4 equiv. of Me_3Al in CH_2Cl_2.
[b] Determined by HPLC (column: Zorbax RX-C8; eluent: MeOH: CH_3CN:H_2O 37:13:50; 1.4 mL/min).
[c] Determined by ^1H NMR.
[d] Reaction time: 25 h.
[e] Reaction time: 5 h.



Scheme 3.

Table 2. Reaction of compounds **1**–**4** with Me_2AlCl

Entry	Substrate (**a:b** ratio)	*T* (equiv)	Products[a,b] **A**:**A′** : **B**:**B′**	Yield (%)	Recovered substrate % (**a**:**b**)
1	**1a**,**b** (39:61)	rt (4)[c]	25:13 : 57:5	76	
2	**1a**,**b** (38:62)	rt (4)	11:5 : 80:4	83	—
3	**1a**,**b** (38:62)	0 °C (4)	6:2 : 86:6	68	22(20:80)
4	**1a**,**b** (40:60)	rt (3)[c]	18:9 : 69:4	90	
5	**1a**,**b** (39:61)[d]	rt (3)	26:10 : 61:3	68	—
6	**1a**,**b** (38:62)	rt (3)	11:5 : 80:4	88	—
7	**1a**,**b** (38:62)	0 °C (3)	6:3 : 86:5	67	23(26:74)
8	**1a**,**b** (38:62)	rt (2.2)	10:4 : 82:4	60	28(34:66)
9	**1a**,**b** (38:62)	0 °C (2.2)	23:9 : 57:11[e]	48	46(52:48)
10	**2a**,**b** (36:64)	rt (3)	35:0 : 65:0	98	—
11	**3a**,**b** (44:56)	rt (3)	21 : 2 : 77:0	73	14(100:0)
12	**3a**,**b** (44:56)	rt (3)[f]	23:3 : 74:0	77[g]	—
13	**3a**,**b** (44:56)	0 °C (3)[h]	12:0 : 88:0	53	42(100:0)
14	**4a**	rt (3)[i]	—	—	100
15	**4b**	rt (3)	—	—	100

[a] Reaction conditions: 30 min in toluene.
[b] Diastereomeric ratio measured by HPLC (columm: Zorbax RX-C8; eluent: MeOH–CH_3CN–H_2O 37:13:50; 1.4 mL/min).
[c] Solvent: CH_2Cl_2.
[d] The reagent was added over the substrate.
[e] Reaction time: 43 h.
[f] Reaction time: 3 h.
[g] After separation of **7A′**.
[h] Reaction time: 10 h.
[i] Reaction time: 60 h.

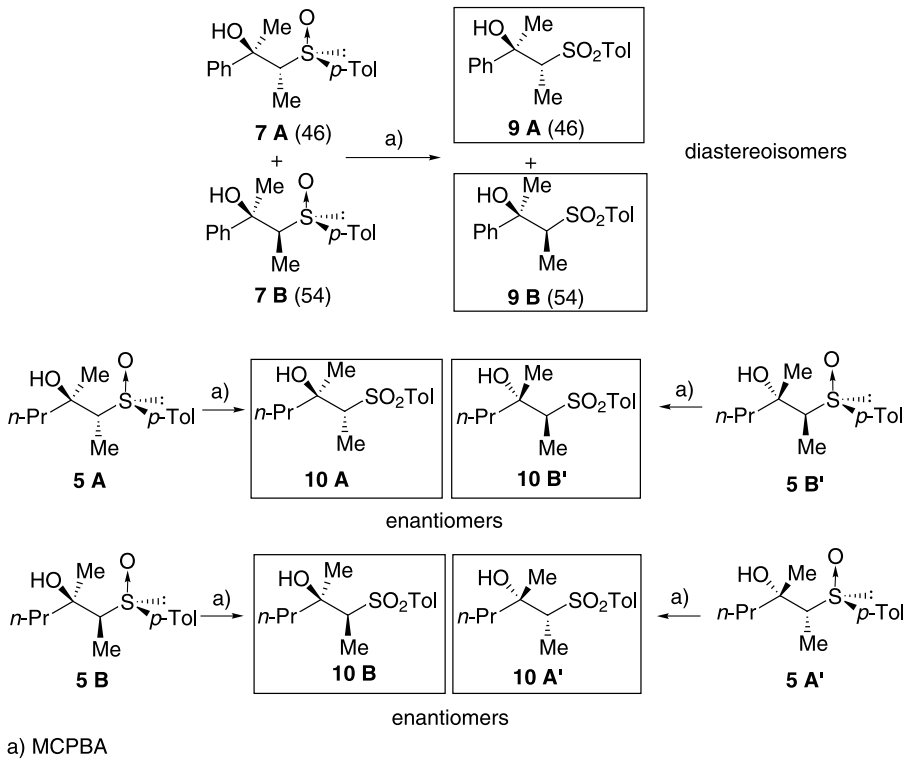
temperatures the reactions are quite slow) or room temperature in toluene (those of the entries 6 and 7), which yielded the higher **A**+**B**/**A′**+**B′** ratios.

Under these conditions the results obtained for compounds **2a**+**2b** and **3a**+**3b** were even better. In the first case, both epimers were quantitatively transformed into the alcohols after 30 min at room temperature with a complete control of the stereoselectivity (entry 10). Under the same conditions **3a**+**3b** gave a mixture of three alcohols (the evolution of **3b** was completely stereoselective) and a 14% of the epimer **a** was recovered, which indicates a slightly lower reactivity (entry 11). A complete conversion was observed after 3 h and a 77% of the mixture **7A**+**7B** could be isolated upon separation of **7A′** by chromatography (entry 12). Better stereoselectivity was obtained when the reaction was performed at 0 °C (entry 13), but the reaction is quite slow, and a 42% of the epimer **A** was recovered. By contrast, none of the *t*-butyl derivatives **4a** or **4b**, could be methylated under similar reaction conditions although the reaction times were increased (entries 14 and 15).

2.1. Configurational assignment

The assignment of the absolute configurations of the obtained α-methyl-β-hydroxysulfoxides was based on the following facts:

(a) The configuration (R_S $R_{C\text{-}\alpha}$) had been previously assigned to ketosulfoxides **a** and the (R_S $S_{C\text{-}\alpha}$) configuration to the epimers **b**.[11b] The complete stereoselectivity observed in reactions of **2a**, **2b**, and **3b** suggests that epimers **A** and **B** derive of the starting ketosulfoxides **a** and **b**, respectively. Therefore, **a** and **b** must exhibit the same configuration at sulfur and C-α than **A** and **B**, respectively.
(b) The oxidation of a 46:54 mixture of phenyl derivatives **7A** and **7B** afforded a mixture of diastereomeric



Scheme 4.

sulfones **9A** and **9B** (Scheme 4) in the same ratio than that of the starting sulfoxides. It indicates that these sulfones only differ in the configuration of one of their two chiral carbons. As a consequence, the configuration of the hydroxylated carbons must be identical for epimers **A** and epimers **B** (they exhibit different configuration at C-α).

(c) The hydroxylic proton of compound **6A** exhibits a long range coupling constant (^4J=1.6 Hz) with the methinic proton of the *i*-Pr group. As this is only possible for hydroxylic protons involved in intramolecular hydrogen bonding exhibiting a W coplanar arrangement with respect to the coupled protons,[19] the configuration of **6A** at the hydroxylic carbon must be *R* (Fig. 1).

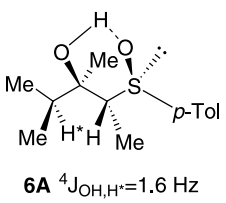


Figure 1. Stereochemistry of the presumably most stable conformation for compound **6A**.

According to these facts, we can assign the [R_S $R_{C\text{-}\alpha}$ R_{C-OH}] configuration to epimers **A** and the [R_S $S_{C\text{-}\alpha}$ R_{C-OH}] configuration to the epimers **B**. The X-ray diffraction analysis of **6A** (Fig. 2) and of a racemic sample of **7B**[20] support this assignment. The conformation exhibited by **6A** in solid state is identical to that shown in Figure 1, deduced from the NMR data.

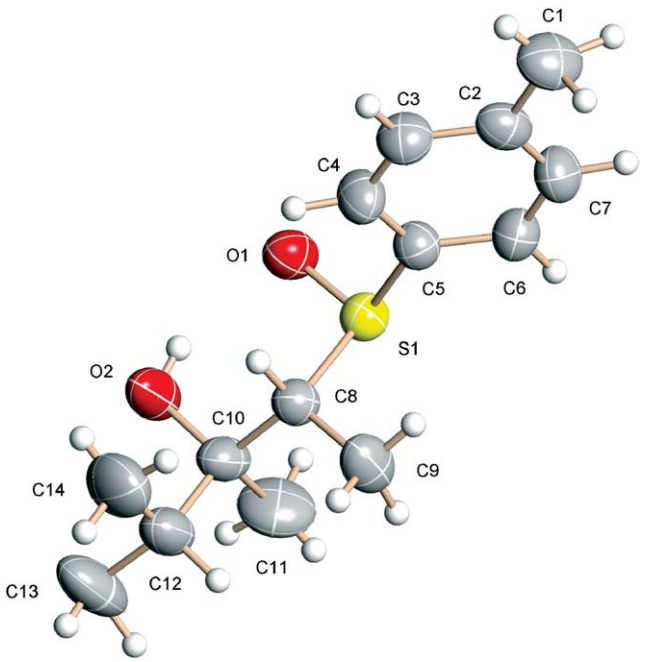


Figure 2. X-ray structure for compound **6A**.

The configuration of the **B′** isomers was unequivocally established in the case of hydroxysulfoxides **5A** and **5B′**. Once isolated from their mixtures, they were independently oxidized with MCPBA at room temperature, affording the corresponding hydroxysulfones **10A** and **10B′** (Scheme 4), which are enantiomers (they have identical spectroscopical properties). The same conclusions could be deduced for compounds **5A′** and **5B**. By assuming that the major compounds of the reaction mixtures, **5B** and **5A**, exhibit the

Table 3. Significant NMR parameters for configurational assignment of compounds **5**–**7**

Product	**5A**	**6A**	**7A**	**8A**	**5A′**	**7A′**	**8A′**	**5B**	**6B**	**7B**	**8B**	**5B′**
δ_{OH}[a]	5.53	5.41	6.11	5.42	5.23	6.50	5.21	2.69	3.16	3.96	—	2.68
$\delta_{\alpha\text{-Me}}$[a]	10.30	9.90	10.90	12.50	10.40	—	12.30	4.00	3.50	4.80	5.21	4.60

[a] Values of δ expressed in ppm.

same configuration than those obtained as sole products in reactions from **2a**+**2b** and **3a**+**3b**, we can assign the configurations [R_S $R_{C\text{-}\alpha}$ S_{C-OH}] and [R_S $S_{C\text{-}\alpha}$ S_{C-OH}] to the minor compounds **5A′** and **5B′**, respectively (and consequently to all **A′** and **B′** isomers).

In Table 3 are indicated the significant NMR parameters which are clearly different for epimers **A** (**A′**) and **B** (**B′**).

The δ values for the hydroxylic protons are clearly different [>5 ppm for isomers **A** (**A′**) but <4 ppm for the **B** (**B′**) ones]. That suggests that **A** epimers exhibit intramolecular hydrogen bonds[21] whereas this is not the case for the **B** epimers. On the other hand, the ^{13}C-δ value ca. 10 ppm observed for the *C*H$_3$–CH carbon in compounds **B** (**B′**) is quite different to the ca. 4 ppm observed for epimers **A** (**A′**). This strong difference, which is indicative of a substantial modification in the shielding patterns of both compounds, could also be a consequence of the formation of hydrogen bonds. In Figure 3 are indicated the presumably most stable conformations of the different isomers able to explain the observed differences in the NMR parameters. Epimers **B** and **B′** must be stabilized by the $n^2 \rightarrow d^0$ interaction between the lone electron pair at oxygen and the empty d orbital at sulfur, which has shown to be even more important than the hydrogen bond in many β-hydroxysulfoxides.[22] By contrast, **A** and **A′** isomers exhibit their predominant rotamers stabilized by intramolecular hydrogen bonding, because the conformation containing the $n^2 \rightarrow d^0$ interaction would be highly unstable due to the (Tol/Me) or (Tol/R) 1,3-parallel interaction. Taking into account the significant deshielding effect produced by the lone electron pair at sulfur on the carbon atoms adopting an antiperiplanar arrangement,[23] the ^{13}C-δ values shown in Table 3 are consistent with the stereochemistry of the conformations shown in Figure 3 for **A** and **B** epimers.

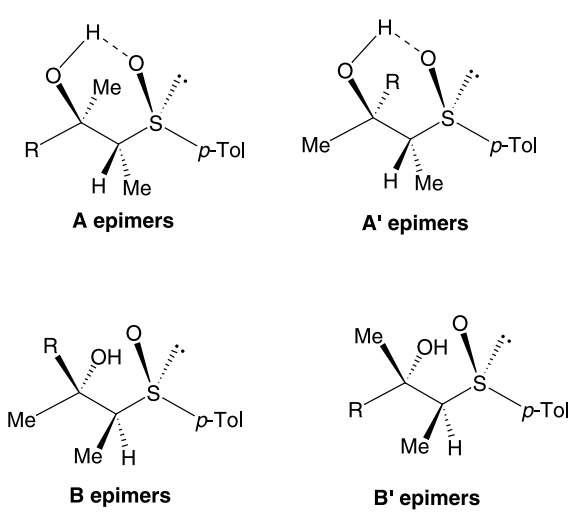


Figure 3. Favored conformations for the different isomers.

3. Mechanistic proposal

The main differences observed in the reactions with Me_3Al and Me_2AlCl are related to reactivity and stereoselectivity. The Me_3Al is able to react with *t*-butyl derivatives (**4b** required 5 h and **4a** more than 1 day), whereas Me_2AlCl did not react. The stereoselectivity was not identical but the epimer obtained as the major one with both reagents was the same (compare Tables 1 with 2).

According to the evolution proposed by Evans in reactions with Me_2AlCl,[12] our β-ketosulfoxides (epimers **a** and **b**) must be transformed into complexes $\mathbf{I_a}$ and $\mathbf{I_b}$ by chelation of the aluminum to both oxygen atoms of the substrate with elimination of the chloride anion, which is captured by a second Me_2AlCl molecule. A third molecule of the reagent must be therefore necessary to introduce the methyl group into the carbonyl moiety. It would explain that 3 equiv. of Me_2AlCl were required to achieve a high conversion (Fig. 4). On the basis of the higher stability of the half-chair structure of the chelate species and taking into account the tendency of the *p*-tolyl group (with higher size than the methyl one) to adopt the pseudoequatorial arrangement, we can propose $\mathbf{I_a}$ and $\mathbf{I_b}$ (Fig. 4) as the presumably most stable conformations resulting from the chelation of the epimers **a** and **b**. The approach of the reagent from the upper face (chair-like TS) would be favored with respect to the attack to the bottom face (twist-like TS) from a steric point of view. Moreover, the stabilizing interaction of the metal with the lone electron pair at sulfur makes even more favorable the approach to the upper face. According to this analysis, $k_1 > k_2$ and $k_3 > k_4$, this would explain why hydroxysulfoxides **A** and **B** were obtained as major isomers from epimers **a** and **b**, respectively. Additionally, $k_3 > k_1$ and $k_2 > k_4$, due to the steric hindrance of the methyl group at C-α in both epimers. It would explain the higher stereoselectivity observed in the evolution of the **b** epimers. Finally, the complete stereoselectivity observed in reaction from **2a** (R and R′=Me in $\mathbf{I_a}$) is not unexpected on the basis of the steric hindrance of the approach of the reagent to the bottom face exerted by R′ (see Fig. 4).

The stereochemical course of the reactions with Me_3Al must be similar. The factors controlling the preferences for the attack of the reagent to pentacoordinated aluminum species formed from Me_3Al[24] (Fig. 5) are the same indicated for the tetracoordinated species generated from Me_2AlCl (Fig. 4). The only difference is the presumable lower stability of the pentacoordinated species, which would explain the less stereoselective evolution observed in reactions with Me_3Al

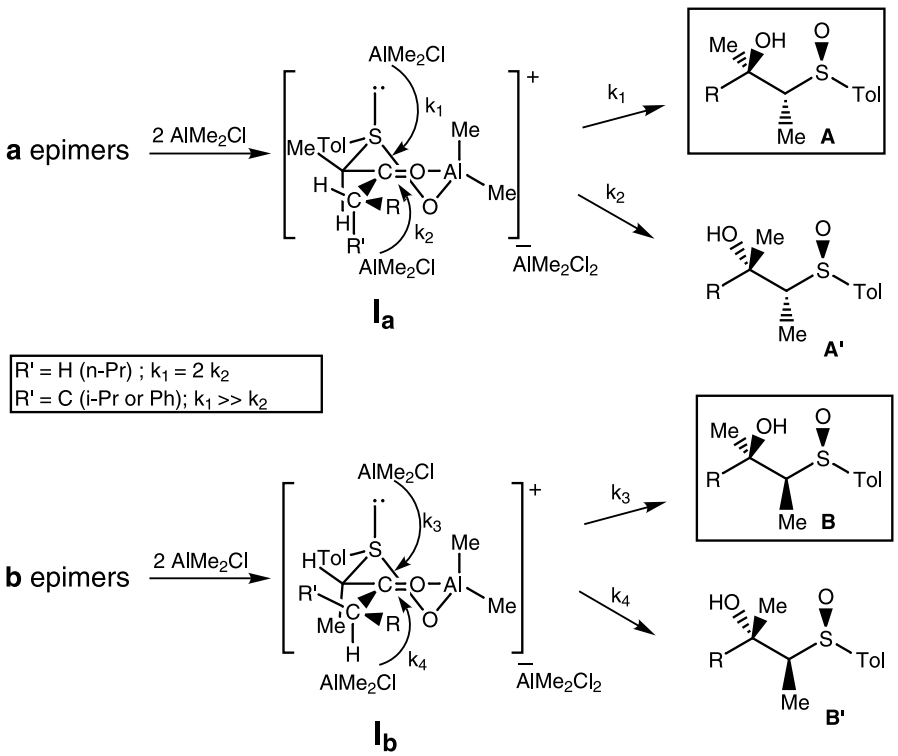


Figure 4. Stereochemical pathway of the reaction with Me_2AlCl.

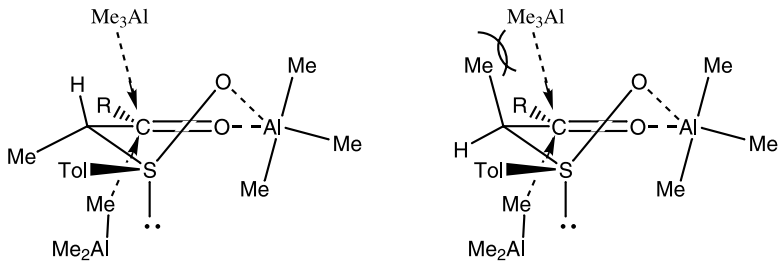
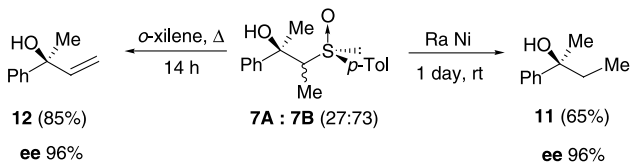


Figure 5. Stereochemical pathway of the reaction with Me_3Al.

(other nor chelated species could also evolve) as well as their higher reactivity.

4. Synthetic applications

The obtained hydroxysulfoxides can be used as starting molecules to prepare different enantiomerically pure compounds taking advantage of the reactivity of the sulfinyl group. As the configuration at the hydroxylated carbon is the same for epimers **A** and **B** (obtained as the major ones or even unique in these reactions), all the transformations involving the removal of the sulfur function can be performed by using a mixture of these epimers, with no previous separation. We have illustrated these possibilities with two of these reactions, hydrogenolysis of the C–S bond and pyrolytic desulfinylation, starting from the mixture **7A**+**7B** (Scheme 5). This mixture was obtained in 77% yield by chromatographic separation from the reaction mixture obtained from **3a**+**3b** (entry 12 of Table 2). Its



Scheme 5.

reaction with Raney Ni (Scheme 5) for 1 day at room temperature (shorter reaction times revealed the presence of the thioether derived from **7**) afforded compound **11** in 65% yield with high optical purity[25] (ee 96%). Otherwise, when the mixture **7A**+**7B** was heated with refluxing xylene in the presence of $NaHCO_3$, compound **12**[26] (ee 96% by chiral HPLC) was obtained in 85% yield (Scheme 5). These results illustrate the usefulness of our method for the preparation of enantiomerically pure tertiary vinyl carbinols,[27] which are not easily synthesized by other procedures.[26b,28]

5. Conclusion

The highly stereoselective methylation of acyclic α-methyl β-ketosulfoxides can be performed with Me_2AlCl. Resulting hydroxysulfoxides can be used in the synthesis of tertiary methyl vinyl and methyl ethyl carbinols in very high optical purities.

6. Experimental

6.1. General

Dry solvents and liquid reagents were distilled under argon just prior to use: THF and toluene were distilled from sodium and benzophenone ketyl; DIA was dried over sodium hydroxide and distilled over calcium hydride; CH_2Cl_2 was dried over P_2O_5 and stored over molecular sieves. All reaction vessels were flame-dried and flushed with argon. TLC was performed on silica gel F_{254} plates with silica gel G (Merck), spots being developed with phosphomolybdic acid in ethanol. Silica gel Merck 60 (230–400 mesh) was used for flash chromatography. Optical rotations were measured with a 241 Perkin–Elmer polarimeter at room temperature (20–23 °C) in the solvent and concentration indicated in each case (concentration in g/100 mL). Melting points were determined in a Gallenkamp MFB-595 apparatus in open capillary tubes and are uncorrected. ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75.5 MHz $CDCl_3$) spectra were performed with a Bruker AC-300 spectrometer. Chemical shifts are given in ppm (δ), relative to $SiMe_4$ as the internal reference; signal multiplicities are quoted as s, singlet; d, doublet; dd, double doublet; dq, double quartet; t, triplet; q, quartet; and m, multiplet. *J* Values are given in hertz. Mass spectra were recorded by the direct insertion technique by electronic impact (EI) at 70 eV or FAB using a VG AutoSpec spectrometer. Elemental analyses were obtained with a Perkin–Elmer 2400 CHNS/O series II. X-ray diffractions were collected with a Siemens P4RA difractometer. Starting ketosulfoxides **1**–**4** were synthesized and purified according to the previously described procedure.[11b] Dimethyl aluminum chloride (1.0 M solution in hexanes) and trimethylaluminum (1.0 M solution in heptane) was purchased from Aldrich. Yields and diastereisomeric ratios of alcohols were established by integration (^{1}H NMR) of well-separated signals of the diastereisomers in the crude reaction mixtures and/or by HPLC. Yields and diastereoisomeric ratios of hydroxysulfoxides **5**–**8** are listed in Tables 1 and 2.

6.2. General procedure for $AlMe_3$ addition. Method A

A solution of β-ketosulfoxide (0.283 mmol) in anhydrous toluene (1.3 mL) was dropwise added into a solution of trimethylaluminum (1.132 mmol) in anhydrous toluene (1.3 mL) under argon, and the mixture was stirred for 30 min at room temperature. Then the mixture was cooled to 0 °C and methanol (0.55 mL) was slowly added. When the mixture reached room temperature, it was treated with 9 mL of aqueous saturated solution of sodium potassium tartrate–ethyl acetate (1:1) and stirred for 30 min. The aqueous layer was extracted with ethyl acetate (3×6 mL) and the organic layer was dried ($MgSO_4$) and evaporated. The residue was purified by chromatography (the eluent was indicated in each case).

6.3. General procedure for Me_2AlCl addition. Method B

A solution of β-ketosulfoxide (0.30 mmol) in anhydrous toluene (1.5 mL) was dropwise added into a solution of dimethyl aluminum chloride in anhydrous toluene (1.0 M, 0.90 mL, 0.90 mmol) under argon, and the mixture was stirred for 30 min at room temperature. Then the mixture was cooled to 0 °C and methanol (0.60 mL) was slowly added. When the mixture reached room temperature, it was treated with 10 mL of aqueous saturated solution of sodium potassium tartrate–ethyl acetate (1:1) and then stirred for 30 min. The aqueous layer was extracted with ethyl acetate (3×10 mL) and the organic layer was dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography on silica gel (the eluent was indicated in each case).

6.3.1. 3-Methyl-2-*p*-tolylsulfinylhexan-3-ol (5). The treatment of a 38:62 mixture of **1a**+**1b** following the method B afforded a diastereoisomeric mixture of hydroxysulfoxides **5A**, **5A′**, **5B**, and **5B′** as a colorless oil. The mixture was purified by chromatography (hexane–ethyl acetate 4:1) and yielded pure (**5A** and **5B**) and enriched (**5A′** and **5B′**) hydroxysulfoxides.

6.3.2. Compound [(2*R*,3*R*,(S)*R*)]5A. It was obtained as a colorless oil. Yield: 2%; $[\alpha]_D$=+181 (*c* 5.6, chloroform). ^{1}H NMR: δ 7.65 and 7.33 (AA′BB′ system, 4H, C_6H_4), 5.53 (bs, 1H, OH), 2.97 (q, 1H, *J*=7.3 Hz, CHS), 2.42 (s, 3H, CH_3Ar), 1.54 (s, 3H, CH_3COH), 1.53–1.19 (m, 4H, CH_2CH_2), 0.88 (t, 3H, *J*=7.1 Hz, CH_3CH_2), 0.83 (d, 3H, *J*=7.3 Hz, CH_3CH). ^{13}C NMR: δ 142.8, 139.4, 129.9, 126.1, 75.6, 66.5, 44.2, 23.2, 21.5, 15.6, 14.4, 10.3. MS: (*m*/*z*)(%): 254 (M+,<1), 239 (84), 221 (11), 149 (36), 140 (100), 139 (32), 115 (20), 92 (31), 91 (21), 83 (22), 71 (36), 57 (29), 55 (31). HRMS: calcd for $C_{14}H_{22}SO_2$ 254.1331; found 254.1340.

6.3.3. Compound [(2*R*,3*S*,(S)*R*)]5A′. It was characterized from a 55:45 mixture of **5A** and **5A′**. ^{1}H NMR: δ 7.65 and 7.33 (AA′BB′ system, 4H, C_6H_4), 5.23 (bs, 1H, OH), 2.97 (q, 1H, *J*=7.1 Hz, CHS), 2.42 (s, 3H, CH_3Ar), 2.02–1.70 (m, 4H, CH_2CH_2), 1.18 (s, 3H, CH_3COH), 1.00 (t, 3H, *J*=7.1 Hz, CH_3CH_2), 0.89 (d, 3H, *J*=7.1 Hz, CH_3CH). ^{13}C NMR: δ 142.8, 139.5, 129.9, 126.1, 76.1, 69.1, 38.7, 26.4, 23.2, 16.5, 14.6, 10.4.

6.3.4. Compound [(2*S*,3*R*,(S)*R*)]5B. It was obtained as a white solid (mp 156–159 °C). Yield: 32%. $[\alpha]_D$=+139 (*c* 2.4, chloroform). ^{1}H NMR: δ 7.40 and 7.32 (AA′BB′ system, 4H, C_6H_4), 2.69 (bs, 1H, OH), 2.51 (q, 1H, *J*=7.2 Hz, CHS), 2.42 (s, 3H, CH_3Ar), 1.77–1.65 (m, 2H, CH_2), 1.55 (s, 3H, CH_3COH), 1.52–1.25 (m, 2H, CH_2), 1.02 (d, 3H, *J*=7.2 Hz, CH_3CH), 0.97 (t, 3H, *J*=7.5 Hz, CH_3CH_2). ^{13}C NMR: δ 140.7, 139.0, 129.7, 124.0, 74.5, 67.7, 42.3, 25.9, 21.3, 16.8, 14.5, 4.0. IR (KBr): 3360, 1022. MS (FAB+): 255 (M+1)(100), 239 (77), 49 (56), 139 (62), 97 (82), 91 (22), 71 (36), 57 (47), 54 (54). HRMS (M+H): calcd for $C_{14}H_{22}SO_2$ 255.141; found 255.1426.

6.3.5. Compound [(2*S*,3*S*,(S)*R*)]5B′. It was characterized from a mixture of **5B** and **5B′**. ^{1}H NMR: δ 7.40 and 7.32 (AA′BB′ system, 4H, C_6H_4), 2.69 (bs, 1H, OH), 2.51 (q, 1H, J=7.2 Hz, CHS), 2.42 (s, 3H, CH_3Ar), 1.77–1.65 (m, 2H, CH_2), 1.55 (s, 3H, CH_3COH), 1.52–1.25 (m, 2H, CH_2), 1.02 (d, 3H, J=7.2 Hz, CH_3CH), 0.97 (t, 3H, J=7.5 Hz, CH_3CH$_2$). ^{13}C NMR: δ 140.6, 139.5, 129.9, 124.2, 74.6, 68.1, 43.8, 24.7, 23.7, 16.8, 14.5, 4.6.

6.3.6. 3,4-Dimethyl-2-*p*-tolylsulfinylpentan-3-ol (6). The treatment of a 36:64 mixture of **2a**+**2b** following the method B afforded a diastereoisomeric mixture of hydroxysulfoxides **6A** and **6B** as a colorless oil. The mixture was purified by chromatography (hexane–ethyl acetate 2:1) to yield pure hydroxysulfoxide **6A** and enriched **6B** hydroxysulfoxides.

6.3.7. Compound [(2*R*,3*R*,(S)*R*)]6A. It was obtained as a white solid (mp 77–79 °C). Yield: 35%; $[\alpha]_D$=+179.4 (*c* 9.1, chloroform). ^{1}H NMR: δ 7.68 and 7.35 (AA′BB′ system, 4H, C_6H_4), 5.41 (d, 1H, J=1.6 Hz, OH), 3.04 (q, 1H, J=7.2 Hz, CHS), 2.43 (s, 3H, CH_3Ar), 1.67 (m, 1H, CH(CH$_3$)$_2$), 1.54 (s, 3H, CH_3COH), 1.00 (d, 3H, J=6.9 Hz, CH_3CHCH$_3$), 0.89 (d, 3H, J=6.9 Hz, CH_3CHCH$_3$), 0.83 (d, 3H, J=7.2 Hz, CH_3CH). ^{13}C NMR: δ 142.8, 139.3, 129.9, 126.2, 76.7, 66.2, 35.5, 21.5, 21.4, 16.2, 16.1, 9.9. IR (KBr): 3335, 2993, 1083. MS: (*m*/*z*)(%): 254 (M^+,<1), 221 (15), 151 (20), 140 (100), 139 (49), 115 (22), 97 (13), 92 (49), 91 (29), 71 (57), 55 (31). Anal. calcd for $C_{14}H_{22}SO_2$: C, 66.34; H, 8.69; S, 12.51. Found: C, 66.10; H, 8.72; S, 12.61.

6.3.8. Compound [2*S*,3*R*,(S)*R*)]6B. It was characterized from a mixture of **6A** and **6B**. Yield: 65%. ^{1}H NMR: δ 7.39 and 7.29 (AA′BB′ system, 4H, C_6H_4), 3.16 (bs, 1H, OH), 2.58 (q, 1H, J=6.9 Hz, CHS), 2.39 (s, 3H, CH_3Ar), 2.03 (sep, 1H, J=6.9 Hz, CH(CH$_3$)$_2$), 1.52 (s, 3H, CH_3COH), 1.01 (d, 3H, J=6.9 Hz, CH_3CHCH$_3$), 0.99 (d, 3H, J=6.9 Hz, CH_3CHCH$_3$), 0.81 (d, 3H, J=6.9 Hz, CH_3CH). ^{13}C NMR: δ 140.8, 138.5, 129.8, 124.0, 76.5, 65.0, 34.8, 21.3, 20.8, 17.4, 16.3, 3.5. IR (KBr): 3480, 2950, 1500, 1380, 1010. MS (FAB): 255 (M+1, 100), 155 (13), 154 (38), 139 (55), 135 (50), 115 (21), 97 (71), 91 (31), 72 (91), 71 (49), 69 (33), 57 (36), 54 (49). HRMS (M+H): calcd for $C_{14}H_{22}SO_2$ 255.1419; found 255.1420.

6.3.9. 2-Phenyl-3-*p*-tolylsulfinylbutan-2-ol (7). The treatment of a 44:56 mixture of **3a**+**3b** following the method B afforded a diastereoisomeric mixture of hydroxysulfoxides **7A** and **7B** as a colorless oil. The mixture was purified by flash chromatography (hexane–ethyl acetate 3:1) yielding pure **7B** and enriched **7A**.

6.3.10. Compound [(2*R*,3*R*,(S)*R*)]7A. It was characterized from a 52:48 mixture of **7A** and **7B**. $[\alpha]_D$=+58 (*c* 1.8, chloroform). ^{1}H NMR: δ 7.64 and 7.16 (m, 9H, aromatic protons), 6.11 (bs, 1H, OH), 3.02 (q, 1H, J=7.1 Hz, CHS), 2.35 (s, 3H, CH_3Ar), 1.95 (s, 3H, CH_3COH), 0.55 (d, 3H, J=7.2 Hz, CH_3CH). ^{13}C NMR: δ 145.2, 141.0, 139.2, 129.9, 128.0, 127.4, 125.9, 124.6, 76.3, 68.6, 22.1, 21.4, 10.9. IR (KBr): 3480, 2950, 1500, 1380, 1010. MS: (*m*/*z*)(%): 151 (14), 148 (72), 140 (100), 139 (17), 105 (27), 92 (49), 91 (42), 79 (17), 77 (26), 71 (16).

6.3.11. Compound [(2*R*,3*S*,(S)*R*)]7B. It was obtained as a white solid (mp 101–103 °C). Yield: 31%; $[\alpha]_D$=+144 (*c* 6.8, chloroform). ^{1}H NMR: δ 7.47 and 7.22 (m, 9H, aromatic protons), 3.96 (bs, 1H, OH), 2.76 (q, 1H, J=6.9 Hz, CHS), 2.36 (s, 3H, CH_3Ar), 2.00 (s, 3H, CH_3COH), 0.74 (d, 3H, J=6.9 Hz, CH_3CH). ^{13}C NMR: δ 146.1, 141.1, 137.8, 129.8, 128.2, 126.9, 124.6, 124.1, 76.4, 66.7, 29.9, 21.3, 4.8. MS (*m*/*z*)(%): 151 (10), 148 (62), 140 (100), 139 (17), 105 (21), 92 (43), 91 (39), 79 (15), 77 (23), 71 (13). Anal. calcd for $C_{17}H_{20}SO_2$: C, 70.80; H, 6.99; S, 11.12. Found: C, 70.61; H, 6.79; S, 11.00.

6.3.12. 3,4,4-Trimethyl-2-*p*-tolylsulfinylpentan-3-ol (8). Starting from **4a**, method A afforded a diastereoisomeric mixture of hydroxysulfoxides **8A** and **8A′**. The mixture was purified by chromatography (hexane–ethyl acetate 2:1) to yield pure hydroxysulfoxides **8A** and **8A′** as a white solids. Starting from **4b**, hydroxysulfoxide **8B** was exclusively obtained. The product was purified by chromatography (hexane–ethyl acetate 2:1) to afford pure **8B** as a white solid.

6.3.13. Compound [(2*R*,3*R*,(S)*R*)]8A. It was obtained as a white solid (mp 88–91 °C). Yield: 27%; $[\alpha]_D$=+141.9 (*c* 1.69, chloroform). ^{1}H NMR: δ 7.68 and 7.38 (AA′BB′ system, 4H, C_6H_4), 5.42 (s 1H, OH), 3.21 (q, 1H, J=7.2 Hz, CHS), 2.43 (s, 3H, CH_3Ar), 1.46 (s, 3H, CH_3COH), 1.00 (s, 9H, (CH$_3$)$_3$C), 0.94 (d, 3H, J=7.2 Hz, CH_3CH). ^{13}C NMR: δ 142.6, 139.4, 129.9, 126.7, 78.9, 66.7, 39.9, 25.8, 21.5, 18.7, 12.5.

6.3.14. Compound [(2*R*,3*S*,(S)*R*)]8A′. It was obtained as a white solid (mp 88–91 °C). Yield: 13%; $[\alpha]_D$=+168.2 (*c* 0.65, chloroform). ^{1}H NMR: δ 7.67 and 7.34 (AA′BB′ system, 4H, C_6H_4), 5.21 (s 1H, OH), 3.12 (q, 1H, J=7.5 Hz, CHS), 2.43 (s, 3H, CH_3Ar), 1.33 (s, 3H, CH_3COH), 1.21 (s, 9H, (CH$_3$)$_3$C), 0.97 (d, 3H, J=7.5 Hz, CH_3CH). ^{13}C NMR: δ 142.6, 140.2, 129.9, 126.1, 80.9, 69.8, 40.1, 27.7, 26.2, 21.5, 12.3.

6.3.15. Compound [(2*S*,3*R*,(S)*R*)]8B. It was obtained as a white solid (mp 123–125 °C). Yield: 43%. $[\alpha]_D$=+124.5 (*c*0.6, chloroform). ^{1}H NMR: δ 7.44 and 7.31 (AA′BB′ system, 4H, C_6H_4), 2.88 (q, 1H, J=6.9 Hz, CHS), 2.42 (s, 3H, CH_3Ar), 1.57 (s, 3H, CH_3COH), 1.11 (d, 3H, J=6.9 Hz, CH_3CH), 1.13 (s, 9H, (CH$_3$)$_3$C). ^{13}C NMR: δ 140.6, 140.1, 129.7, 124.1, 76.6, 65.4, 39.4, 26.4, 21.7, 21.3, 5.21. Anal. calcd for $C_{15}H_{24}SO_2$: C, 67.12; H, 9.01; S, 11.95. Found: C, 66.95; H, 8.80; S, 11.81.

6.4. Sulfinyl group oxidation

A $CDCl_3$ solution of the corresponding hydroxysulfoxides was added to an NMR tube containing an excess of previously dried (anhydrous magnesium sulfate) MCPBA solution in the same solvent. The sulfone ratios and NMR signals were obtained from the crude mixtures.

6.4.1. 2-Phenyl-3-*p*-tolylsulfonylbutan-2-ol (9). Hydroxysulfone **9** was prepared as a 46:54 diastereoisomeric mixture of **9A** and **9B** by MCPBA oxidation of a 46:54 mixture of **7A** and **7B**, respectively.

6.4.2. Compound (2*R*,3*R*)9A. ^{1}H NMR: δ 8.10–7.31 (m, 9H, aromatic protons), 3.42 (q, 1H, J=7.1 Hz, CHS), 2.38 (s, 3H, CH_3Ar), 1.88 (s, 3H, CH_3COH), 0.88 (d, 3H, J=7.1 Hz, CH_3CH).

6.4.3. Compound (2*R*,3*S*)9B. ^{1}H NMR: δ 8.10–7.31 (m, 9H, aromatic protons), 3.38 (q, 1H, J=7.2 Hz, CHS), 2.37 (s, 3H, CH_3Ar), 1.82 (s, 3H, CH_3COH), 0.98 (d, 3H, J=7.2 Hz, CH_3CH).

6.4.4. (2*R*,3*R*) and (2*S*,3*S*)-3-Methyl-2-*p*-tolylsulfonyl-hexan-3-ol (10A) and (10B′). The MCPBA oxidation of hydroxysulfoxide **5A** yielded hydroxysulfone **10A**. **10B′** (enantiomer of **10A**) was obtained by oxidation of **5B′**. ^{1}H NMR: δ 8.10–7.31 (AA′BB′ system, 4H, C_6H_4), 3.20 (q, 1H, J=7.1 Hz, CHS), 2.48 (s, 3H, CH_3Ar), 1.55 (s, 3H, CH_3COH), 1.51–1.20 (m, 4H, CH_2CH_2), 1.21 (d, 3H, J=7.1 Hz, CH_3CH), 0.9 (t, 3H, J=7.0 Hz(CH_3CH_2).

6.4.5. (2*R*,3*S*) and (2*S*,3*R*)-3-Methyl-2-*p*-tolylsulfonyl-hexan-3-ol (10A′) and (10B). The MCPBA oxidation of hydroxysulfoxide **5A′** yielded hydroxysulfone **10A′**. **10B** (enantiomer of **10A′**) was obtained by oxidation of **5B**. ^{1}H NMR: δ 8.10–7.30 (AA′BB′ system, 4H, C_6H_4), 3.25 (q, 1H, J=7.2 Hz, CHS), 2.46 (s, 3H, CH_3Ar), 2.0–1.41 (m, 4H, CH_2CH_2), 1.30 (s, 3H, CH_3COH), 1.20 (d, 3H, J=7.2 Hz, CH_3CH), 0.95 (t, 3H, J=7.0 Hz(CH_3CH_2).

6.5. Sulfinyl group reductive elimination

6.5.1. (*S*)-2-Phenyl-2-butanol (11). To a solution of a 27:73 mixture of **7A** and **7B** (0.59 mmol) in EtOH was added a suspension of activated Raney nickel (1.726 g) in EtOH (4 mL). The reaction was stirred for 1 day at room temperature, filtered over Celite®, and the residue was purified by chromatography (hexane–ethyl acetate 99:1) to give a colorless oil. Yield: 65%. $[\alpha]_D$=−16.6 (*c* 3.5, acetone). [Lit. $[\alpha]_D$=−16.7 (*c* 1.50, acetone, 96% ee)].[25a] ^{1}H NMR: δ 7.26–7.19 (m, 5H, C_6H_5), 1.86 (q, 2H, J=7.5 Hz, CH_3CH_2), 1.79 (s, 1H, OH), 1.55 (s, 3H, CH_3COH), 0.80 (t, 3H, J=7.5 Hz, CH_3CH_2).

6.6. Sulfinyl group pyrolysis

6.6.1. (*S*)-2-Phenylbut-3-en-2-ol (12). A 25 mL two-necked round bottomed flask equipped with a stirrer and a reflux condenser and containing sodium bicarbonate (13.1 mmol), was flame-dried under Ar steam. A solution of a 27:73 of **7A** and **7B** (0.328 mmol) in *o*-xylene (6 mL) was added via cannula and was heated at 140 °C for 14 h. The reaction was filtered over Celite® and washed with dichlorometane. Dichlorometane was eliminated under reduced pressure without heating, in order to avoid evaporation of any reaction product. Flash chromatography using successively hexane (to remove the remaining *o*-xilene) and then hexane–ethyl acetate 9:1, yielded pure **12** (85%) as an oil $[\alpha]_D$=−28.3 (*c* 2.1, acetone, 96% ee).[26] The ee was determined by HPLC (Daicel CHIRALPAK AD, Hexane/ *i*-PrOH: 90/10, 0.8 mL/min). ^{1}H NMR: δ 7.51–7.24 (m, 5H, C_6H_5), 6.19 (dd, 1H, J=17.2, 10.8 Hz, $CH{=}CH_2$), 5.22 (dd, 2H, J=17.2, 1.1 Hz, $CH{=}CH_2$), 1.67 (s, 3H, CH_3COH).

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