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Journal of Organometallic Chemistry 643–644 (2002) 130–135

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Reactivity of the lithium anion of the (*S*,*S*)-bis-*p*-tolylsulfinyl methane. A versatile synthesis of enantiopure alkylidene 1,1-bis-*p*-tolylsulfoxides

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Received 19 June 2001; accepted 31 August 2001

Abstract

We describe herein a new synthesis of enantiopure alkylidene 1,1-bis-*p*-tolyl-sulfoxides (**5**), based on a two-steps sequence. The first one involves the alkylation of the lithium anion of the (*S*,*S*)-bis-*p*-tolylsulfinylmethane (**1**) with aldehydes. The second one consists in a mild dehydration of the sulfinyl alcohols **3** and **4** with the morpho CDI reagent. Some features (reactivity, diastereoselectivity) of the alkylation reaction are discussed.

Keywords: Sulfoxides; Diastereoselectivity; Asymmetric synthesis; Carbanions; Condensation

1. Introduction

Enantiopure alkylidene 1,1-bis-*p*-tolyl-sulfoxides (**5**) are attractive molecules because they possess an electron-withdrawing moiety exhibiting a local C_2-symmetry, which should garantee high reactivities and diastereoselectivities in cycloadditions or conjugate additions [1]. This has been recently exploited by Aggarwal who illustrated the concept of chiral ketene equivalent with alkylidene cyclic disulfoxides such as *trans*-1,3-dithiane [2] or dithiolane [3] 1,3-dioxides obtained through asymmetric oxidation. However, acyclic analogs, such as 1,1-bis-aryl substrates, which could present some interesting complementary reactivity have witnessed less interest. Although the simplest term of **5** with R = H is a known compound, reported by Koizumi in 1986 [4], curiously and to the best of our knowledge, substituted derivatives of **5** with R = alkyl or aryl are fairly unknown compounds. Only two special cases have been reported. Solladié, while focusing on the condensation of the lithium anion of (*S*,*S*)-bis-*p*-tolylsulfinylmethane (**1**) with diverse carbonyl derivatives that gave bis-sulfinylalcohols, showed that with α,β-unsaturated aldehydes, the corresponding bis-sulfinyldienes were directly obtained in good yields [5]. Another report by Carretero [6] mentions the synthesis of the (*S*,*S*)-1,1-bis-ethoxycarbonyl-2,2-bis-*p*-tolylsulfinyl ethene, in a two-steps sequence involving first a quantitative condensation with oxomalonate, followed by a dehydration with DEAD.

2. Results and discussion

In that context, we wanted to develop a general synthesis of the alkylidene disulfoxides **5**, and also at the occasion reexamine the diastereoselectivity of the formation of the diastereomeric bis-sulfinyl alcohols **3** and **4** with simple alkylaldehydes (Scheme 1). Dissuaded by a Knoevenagel approch [7], we focussed on a method involving a preformation of the anion of **1** [8]. This was accomplished with 1.1 equivalents of *n*-BuLi at −40 °C. After 1 h at that temperature, 1.5 equivalents of the carbonyl derivative **2** were added at −78 °C. Although the alkylation appeared relatively immediate, we raised the temperature of the reaction medium to −25 °C to garantee an almost complete

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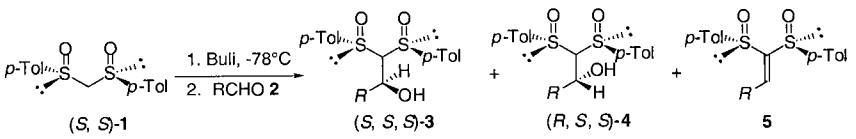
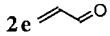
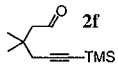
PII: S0022-328X(01)01210-4

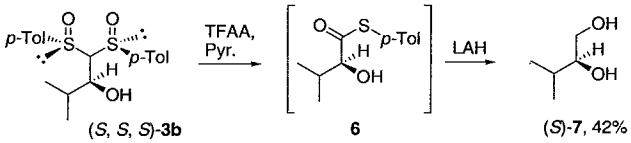


Scheme 1.

Table 1
Formation of the alcohols **3** and **4**

entry	Aldehyde **2**, R	**3** + **4**, yield, %	**3** : **4**[a], %
1	**2a**, *n*-Bu	82	82 : 18
2	**2b**, *i*-Pr	82	81 : 19
3	**2c**, *t*-Bu	89	100 : 0
4	**2d**, Ph	70	95 : 5
5	**2e** 	56[b]	-
6	**2f** 	77	81 : 19

[a]The ratio was determined on the NMR spectrum of the crude product.
[b]Only diene **5e** was obtained.

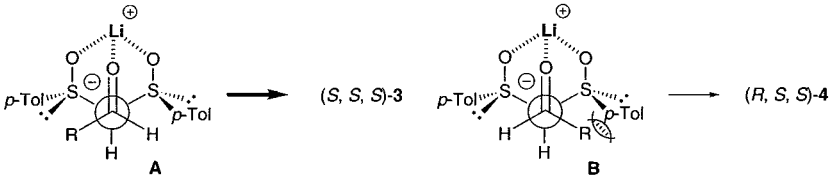


Scheme 2.

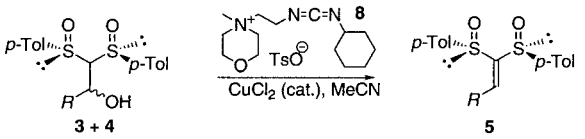
conversion. We have noticed that above that temperature, dehydration occurs [9]. In that basic reaction medium, isomerization to the allylsulfoxide (except for R = Ph or *t*-Bu) followed by a [2,3]-Evans–Mislow rearrangement gives (*E*)-γ-hydroxyvinylsulfoxides [7]. After quenching at −25 °C and usual treatment, good yields of alcohols **3** and **4** (70–89%) were obtained. In the case of benzaldehyde (entry 4), hexamethylphosphorous triamide HMPT (1.5 equivalents) had to be added in the reaction to observe a decent conversion. It should also be noted that after the chromatography process, in addition to the alcohols **3** and **4**, dehydration adducts **5** were observed in a slight extent (ca. 5%) for aldehydes **2a**–**d** and **2f**, and that for acrolein **2e** (entry 5), only bis-sulfinyldiene **5e** was obtained.

To our surprise, this alkylation reaction proved to be fairly diastereoselective even for simple alkyl aldehydes, and even completely diastereoselective with pivalaldehyde (entry 3). This is interesting in view of the results of Aggarwal [10,11] with cyclic disulfoxides, and of Solladié [5] with **1** who generally obtained high selectivities only for aromatic aldehydes. More precisely, for hexanal and *iso*-butyraldehyde **2b** and at −78 °C, Solladié reported diastereomeric excesses of 20 and 10%, respectively. In contrast, while raising the temperature to −25 °C and with aldehydes **2a** and **2b**, we observed selectivities of 64 and 62% (Table 1, entries 1 and 2). We suspected the reaction to be reversible in our conditions and to result in a thermodynamic ratio of products. However, this was refuted by two findings. When we stopped the reaction with **2a** at −78 °C after 15 min, we observed on the crude NMR spectrum the following ratio: **1**–**3a**–**4a**, 31:56:13, demonstrating that the diastereoselectivity was essentially identical at lower temperature. Moreover, when minor diastereomer **4a** was treated at −78 °C with one equivalent of *n*-BuLi and upon raising the temperature to −25 °C and quenching at that temperature, we recovered unaltered **4a**, accompanied by minor amounts of **5a** (< 5%). Thus, no equilibration seems to intervene, and further work will be necessary to address these discrepancies. It should be noted also that the same type of diastereoselectivity was observed when sodium hydride was used instead of butyllithium: **3a**–**4a**, 89:11 (total yield 68%).

In all these reactions, as for Solladié, the main diastereomer corresponds to the (*S*,*S*,*S*)-**3**. This was established by correlation with Solladié's data or by chemical derivatization as for major diastereomer **3b** (Scheme 2). A Pummerer reaction [12], followed by a LAH reduction of the intermediate thioester **6** provided the known (*S*)-(+)-3-methyl-1,2-butanediol (**7**) ($[\alpha]_D^{20}$ + 9.0 (c 3.0, $CHCl_3$), lit. [13] $[\alpha]_D^{20}$ + 11.7 (neat)). This sequence also augurs well for the synthesis of enantiopur α-hydroxy acids if a non-racemizing saponification of thioesters like **6** is found out.



Scheme 3.



Scheme 4.

Table 2
Dehydration of alcohols **3** and **4**

Entry	Alcohols **3**+**4**, R	Product **5**, yield (%) [a]
1	**3a**+**4a**, *n*-Bu	**5a**, quant.
2	**3b**+**4b**, *i*-Pr	**5b** (90)
3	**3c**, *t*-Bu	**5c** (82)
4	**3d**+**4d**, Ph	**5d** (85)
5	**3f**+**4f**	**5f** (65)

[a] All reactions are run with 1.2–2 equivalents of **8** and $CuCl_2$ catalyst at 60 °C in MeCN for 2–3 h under N_2.

One could propose the following model of diastereoselection, as depicted on Scheme 3. The most favorable approach involves chelated transition state **A** on which non-bonded interactions between the *p*-tolyl groups of **1** and the R group of aldehyde **2** are minimized compared to **B** [14]. Further refinements will be required to determine how the use of a sodium base and the use of HMPT fit with this proposal.

Finally, a variety of reaction conditions were tested for a mild dehydration of alcohols **3** and **4**. The cerium-based reagent for the dehydration of aldol adducts [15], as well as the Burgess reagent [16,17] did not give satisfactory results. We found the morpho CDI reagent **8**, previously used by Aggarwal [18], quite versatile and convenient for that transformation, as illustrated by the good yields of adducts **5** (Scheme 4; Table 2).

3. Conclusion

We have devised an efficient two-steps procedure for the preparation of the previously unknown enantiopure alkylidene 1,1-bis-*p*-tolyl-sulfoxides (**5**). This study allowed us to reexamine the diastereoselectivity of the condensation reaction of **1** on aldehydes, and notably to improve the results. The produced alcohols **3** and **4** are interesting precursors of enantiopure α-hydroxy acids. No doubt also that alkylidene substrates will find important applications in asymmetric synthesis.

4. Experimental

All reactions were run under an Ar or N_2 atmosphere in anhydrous solvents and dried flask. Thin layer chromatography (TLC) was performed on Merck Silica Gel 60 F 254 and revealed with either an ultraviolet lamp ($\lambda = 254$ nm) or a *p*-anisaldehyde solution. Flash column chromatography has been performed with Silica gel Merck Geduran SI (40–63 nm). Solvents were systematically distilled prior to be used. The aldehydes were dried over $CaSO_4$ and distilled. IR spectra were recorded on a Perkin–Elmer 1420 spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded at room temperature (r.t.), either at 200 and 50 MHz on a AC200 Bruker spectrometer, or at 400 and 100 MHz, respectively on an ARX400 Bruker spectrometer. Shifts are given in ppm and referenced from the solvent residual signal (7.26 ppm for $CDCl_3$) for proton NMR. For carbon NMR, shifts are referenced from the solvent central peak (77.0 ppm for $CDCl_3$). Coupling constants (J) are given in Hertz (Hz). The letters m, s, d, t, q, hept mean, respectively multiplet, singulet, doblet, triplet, quadruplet, heptuplet. Elemental analysis were performed by the Service Régional de Microanalyse de l'Université Pierre et Marie Curie. Melting points were obtained on a Reichert apparatus and are uncorrected. Chiral GC was run using a column CP-Chirasil-DEX CB (25 m), FID and N_2 as carrier gas.

4.1. General procedure for the synthesis of bis-sulfinyl alcohols *3* and *4*

To a solution of 1.75 g (6 mmol, one equivalent) of (*S*,*S*)-bis-*p*-tolylsulfinylmethane (**1**) [8] (previously dried at 70 °C under vacuum) in THF (25 ml) were added, at −40 °C, *n*-BuLi in hexanes (7.2 mmol, 1.2 equivalents) and the solution was stirred at −40 °C for 1 h. Then, the reaction mixture was cooled to −78 °C and the freshly distilled aldehyde was added neat (1.5–2.0 equivalents). The reaction was stirred at this temperature for half an hour, at −40 °C for 1 h and finally at −25 °C for an additional hour. Then, it was quenched with an (aq.) saturated NH_4Cl solution. The THF was evaporated and then extracted twice with CH_2Cl_2 and the combined organic layers were washed with brine and dried over $MgSO_4$. The residue was purified by flash chromatography to give by order of elution the two diastereomeric alcohols **4** (sometimes contaminated by minor amounts ca. 5% of **5**) then **3**.

4.1.1. (*S*$_S$,*S*$_S$,2*S*)-1,1-Di-*p*-tolylsulfinyl-hexan-2-ol (*3a*)

Yield: 67%. White solid, m.p. 114 °C. $[\alpha]_D^{20} + 141.2°$ (*c* 1.5, $CHCl_3$). Anal. Calc. for $C_{20}H_{26}O_3S_2$: C, 63.46; H, 6.92. Found: C, 63.23; H, 7.13%. IR (cm^{-1}) ν_{max}: 3447, 2962, 1084, 1055. ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 7.62$ (d, $J = 8.2$ Hz, 2H), 7.40 (d, $J = 8.2$ Hz, 2H), 7.22 (d, $J = 8.2$ Hz, 2H), 7.02 (d, $J = 8.2$ Hz, 2H), 4.49 (dd, $J = 8.3$; 5.3 Hz, 1H), 3.32 (s, 1H), 2.47 (s, 3H), 2.36 (s, 3H), 1.85–1.76 (m, 1H), 1.37–1.29 (m, 1H), 1.22–1.03 (m, 4H), 0.77 (t, $J = 6.7$ Hz, 3H). ^{13}C-NMR ($CDCl_3$, 50 MHz): $\delta = 142.2$, 141.7, 139.8, 138.3, 130.3 (4C), 124.5 (2C), 123.7 (2C), 91.8, 67.0, 34.6, 27.3, 22.1, 21.5, 21.3, 13.8.

*4.1.2. (S_S,S_S,2R)-1,1-Di-p-tolylsulfinyl-hexan-2-ol (**4a**)*

Contaminated with ca. 5% of **5a**. Yield: 15%. Colorless oil. IR (cm^{-1}) ν_{max}: 3447, 2962, 1084, 1055. ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 7.50$ (d, $J = 8.2$ Hz, 2H), 7.36 (d, $J = 8.2$ Hz, 2H), 7.08 (d, $J = 8.2$ Hz, 2H), 6.71 (d, $J = 8.2$ Hz, 2H), 4.58 (m, 1H), 3.62 (d, $J = 8.6$ Hz, 1H), 2.46 (s, 3H), 2.30 (s, 3H), 1.80–1.20 (m, 6H), 0.88 (t, $J = 7.0$ Hz, 3H). ^{13}C-NMR ($CDCl_3$, 50 MHz): $\delta =$ 142.4, 141.5, 141.0, 136.6, 130.2 (2C), 129.9 (2C), 124.8 (2C), 124.0 (2C), 89.6, 69.8, 34.1, 27.1, 22.4, 21.4, 21.2, 13.9.

*4.1.3. (S_S,S_S,2S)-1,1-Di-p-tolylsulfinyl-3-methyl-butan-2-ol (**3b**)*

Yield: 66%. White solid, m.p. 116 °C. $[\alpha]_D^{20} + 158.0°$ (*c* 1.2, $CHCl_3$). Anal. Calc. for $C_{19}H_{24}O_3S_2$: C, 62.60; H, 6.64. Found: C, 62.20; H, 6.83%. IR (cm^{-1}) ν_{max}: 3420, 2961, 1084, 1050. ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 7.65$ (d, $J = 8.4$ Hz, 2H), 7.41 (d, $J = 7.9$ Hz, 2H), 7.21 (d, $J = 7.9$ Hz, 2H), 6.97 (d, $J = 8.4$ Hz, 2H), 4.07 (dd, $J = 8.9$; 1.0 Hz, 1H), 3.48 (d, $J = 1.0$ Hz, 1H), 2.47 (s, 3H), 2.34 (s, 3H), 1.92 (m, 1H), 0.91 (d, $J = 6.4$ Hz, 3H), 0.50 (d, $J = 6.4$ Hz, 3H). ^{13}C-NMR ($CDCl_3$, 50 MHz): $\delta = 142.2$, 141.5, 139.7, 138.1, 130.3 (2C), 130.2 (2C), 124.5 (2C), 123.5 (2C), 90.3, 71.5, 31.7, 21.5, 21.3, 18.5, 18.4.

*4.1.4. (S_S,S_S,2R)-1,1-Di-p-tolylsulfinyl-3-methyl-butan-2-ol (**4b**)*

Contaminated with ca. 5% of **5b**. Yield: 16%. Colorless oil. IR (cm^{-1}) ν_{max}: 3420, 2961, 1084, 1051. ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 7.47$ (d, $J = 8.1$ Hz, 2H), 7.33 (d, $J = 8.1$ Hz, 2H), 7.05 (d, $J = 8.1$ Hz, 2H), 6.71 (d, $J = 8.1$ Hz, 2H), 4.38 (ddd, $J = 10.2$; 8.7; 5.1 Hz, 1H), 3.71 (d, $J = 8.7$ Hz, 1H), 2.43 (s, 3H), 2.27 (s, 3H), 1.15 (dd, $J = 10.2$; 6.6 Hz, 1H), 0.98 (d, $J = 6.6$ Hz, 3H), 0.90 (d, $J = 6.6$ Hz, 3H). ^{13}C-NMR ($CDCl_3$, 50 MHz): $\delta = 142.4$, 141.4, 141.0, 136.5, 130.1 (2C), 129.8 (2C), 124.7 (2C), 124.0 (2C), 87.7, 73.0, 30.0, 21.3, 21.1, 19.6, 15.3.

*4.1.5. (S_S,S_S,2S)-3,3-Dimethyl-1,1-di-p-tolylsulfinyl-butan-2-ol (**3c**)*

Yield: 89%. White solid, m.p. 121–122 °C. $[\alpha]_D^{20} +$ 89.5 (c 1.1, $CHCl_3$). Anal. Calc. for $C_{20}H_{26}O_3S_2$: C, 63.46; H, 6.92. Found: C, 63.18; H, 7.28%. IR (cm^{-1}) ν_{max}: 3430, 2961, 1085, 1051. ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 7.90$ (d, $J = 8.4$ Hz, 2H), 7.43 (d, $J = 7.9$ Hz, 2H), 7.18 (d, $J = 7.9$ Hz, 2H), 6.85 (d, $J = 8.4$ Hz, 2H), 4.11 (d, $J = 3.7$ Hz, 1H), 3.03 (d, $J = 3.7$ Hz, 1H), 2.48 (s, 3H), 2.32 (s, 3H), 0.77 (s, 9H). ^{13}C-NMR ($CDCl_3$, 50 MHz): $\delta = 142.0$, 141.3, 139.9, 138.6, 130.3 (2C), 130.2 (2C), 124.6 (2C), 123.4 (2C), 90.1, 71.5, 34.9, 26.3, 21.5, 21.3 (3C).

*4.1.6. (S_S,S_S,2S)-1,1-Di-p-tolylsulfinyl-2-phenyl-ethan-2-ol (**3d**)*

Yield: 67%. White solid, m.p. 151 °C. $[\alpha]_D^{20} - 56.5$ (c 1.0, $CHCl_3$). Anal. Calc. for $C_{22}H_{22}O_3S_2$: C, 63.43; H, 5.81. Found: C, 63.76; H, 5.59%. IR (cm^{-1}) ν_{max}: 3452, 2928, 1084, 1053. ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta =$ 7.32–7.10 (m, 13H), 5.71 (bs, 1H), 3.54 (d, $J = 1.0$ Hz, 1H), 2.41 (s, 3H), 2.39 (s, 3H). ^{13}C-NMR ($CDCl_3$, 50 MHz): $\delta = 141.9$, 141.8, 139.8, 139.4, 137.8, 130.4 (2C), 130.1 (2C), 128.6 (2C), 127.9, 125.7 (2C), 123.9 (2C), 123.8 (2C), 93.9, 68.4, 21.4 (2C).

*4.1.7. (S_S,S_S,2S)-1,1-Di-p-tolylsulfinyl-4,4-dimethyl-7-trimethylsilyl-hept-6-yn-2-ol (**3f**)*

Yield: 62%. White solid, m.p. 109 °C. $[\alpha]_D^{20} + 69.7$ (c 1.2, $CHCl_3$). Anal. Calc. for $C_{26}H_{36}O_3S_2Si$: C, 63.89; H, 7.42. Found: C, 63.70; H, 7.62%. IR (cm^{-1}) ν_{max}: 3446, 2960, 2928, 2246, 2171, 1249, 1083, 1048. ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 8.37$ (d, $J = 8.4$ Hz, 2H), 7.38 (d, $J = 8.4$ Hz, 2H), 7.22 (d, $J = 8.4$ Hz, 2H), 7.03 (d, $J = 8.4$ Hz, 2H), 4.70 (bd, $J = 7.4$ Hz, 1H), 3.29 (d, $J = 1.0$ Hz, 1H), 2.46 (s, 3H), 2.34 (s, 3H), 2.02 (s, 2H), 1.90 (dd, $J = 14.3$; 8.4 Hz, 1H), 1.29 (dd, $J = 14.3$; 3.5 Hz, 1H), 0.93 (s, 3H), 0.84 (s, 3H), 0.07 (s, 9H). ^{13}C-NMR ($CDCl_3$, 50 MHz): $\delta = 142.2$, 141.8, 139.6, 138.3, 130.3 (4C), 124.5 (2C), 123.7 (2C), 105.0, 93.2, 86.6, 64.7, 45.8, 33.7, 33.2, 27.1, 26.8, 21.5, 21.3, 0.1 (3C).

*4.1.8. (S_S,S_S,2R)-1,1-Di-p-tolylsulfinyl-4,4-dimethyl-7-trimethylsilyl-hept-6-yn-2-ol (**4f**)*

Contaminated with ca. 5% of **5f**. Yield: 15%. Pale yellow oil. IR (cm^{-1}) ν_{max}: 3446, 2961, 2927, 2245, 2171, 1249, 1084, 1045. ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 7.52$ (d, $J = 8.0$ Hz, 2H), 7.39 (d, $J = 8.0$ Hz, 2H), 7.10 (d, $J = 8.0$ Hz, 2H), 6.73 (d, $J = 8.0$ Hz, 2H), 4.77 (bt, $J = 8.9$ Hz, 1H), 3.56 (d, $J = 8.9$ Hz, 1H), 2.47 (s, 3H), 2.32 (s, 3H), 2.23 (s, 2H), 2.10 (dd, $J = 14.3$; 1.0 Hz, 1H), 1.73 (dd, $J = 14.3$; 9.6 Hz, 1H), 1.09 (s, 6H), 0.13 (s, 9H). ^{13}C-NMR ($CDCl_3$, 50 MHz): $\delta = 142.4$, 141.5, 140.9, 137.0, 130.2 (2C), 130.0 (2C), 124.8 (2C), 124.0 (2C), 105.3, 90.6 (2C), 68.1, 45.1, 33.9 (2C), 27.2, 27.0, 21.5, 21.3, 0.1 (3C).

*4.1.9. (S_S,S_S)-1,1-Di-p-tolylsulfinyl-buta-1,3-diene (**5e**)*

Yield: 56%. Pale yellow solid, m.p. 93–95 °C. $[\alpha]_D^{25} + 162.0°$ (*c* 1.1, $CHCl_3$). Anal. Calc. for $C_{18}H_{18}O_2S_2$: C, 65.42; H, 5.49. Found: C, 65.32; H, 5.57%. IR (cm^{-1}) ν_{max}: 3050, 2920, 1595, 1490, 1080, 1045. ^{1}H-NMR ($CDCl_3$, 400 MHz): $\delta = 7.47$ (d, $J =$ 11.2 Hz, 1H), 7.23–7.16 (m, 3H), 7.02–6.93 (m, 6H), 5.85 (d, $J = 16.1$ Hz, 1H), 5.77 (d, $J = 9.4$ Hz, 1H), 2.31 (s, 3H), 2.28 (s, 3H). ^{13}C-NMR ($CDCl_3$, 50 MHz): $\delta = 148.3$, 142.6, 140.9, 139.1, 138.2, 137.9, 129.5 (4C), 126.5 (2C), 123.9 (2C), 129.1, 129.0, 21.5, 21.3.

4.2. General procedure for the dehydration of bis-sulfinyl alcohols **3** and **4**

To a solution of the mixture of alcohols **3** and **4** (2.0 mmol, one equivalent) in CH_3CN (20 ml) were added 1.5–2.0 equivalents of 1-cyclohexyl-3-(2-morpholinoethyl)-carbodiimide metho-*p*-toluenesulfonate (**8**) and a catalytic amount of $CuCl_2$ (0.1 equivalent). The reaction was controlled by TLC and was generally over after 2–3 h at 70 °C. After cooling, the reaction mixture was diluted in CH_2Cl_2 and filtered over a short pad of celite and silica and concentrated in vacuo.

4.2.1. (S_S,S_S)-1,1-Di-p-tolylsulfinyl-hex-1-ene (**5a**)

Yield: quant. White solid, m.p. 63–65 °C. $[\alpha]_D^{25}$ − 3.0° (*c* 1.5, $CHCl_3$). Anal. Calc. for $C_{20}H_{24}O_2S_2$: C, 66.63; H, 6.71. Found: C, 66.59; H, 6.82%. IR (cm^{-1}) ν_{max}: 3050, 2960, 2920, 1590, 1490, 1050. ^{1}H-NMR ($CDCl_3$, 400 MHz): $\delta = 7.05$ (dd, $J = 9.0$; 6.7 Hz, 1H), 7.12 (d, $J = 8.1$ Hz, 2H), 6.92–6.88 (m, 6H), 2.76–2.70 (m, 1H), 2.56–2.51 (m, 1H), 2.24 (s, 3H), 2.23 (s, 3H), 1.56–1.49 (m, 2H), 1.40–1.34 (m, 2H), 0.89 (t, $J = 7.3$ Hz, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz): $\delta = 147.9$, 143.3, 142.1, 140.7, 139.3, 137.5, 129.3 (4C), 126.1 (2C), 123.8 (2C), 30.6, 29.1, 22.1, 21.3, 21.1, 13.7.

4.2.2. (S_S,S_S)-1,1-Di-p-tolylsulfinyl-3-methyl-but-1-ene (**5b**)

Yield: 90%. White solid, m.p. 105–107 °C. $[\alpha]_D^{25}$ + 26.0 (c 1.3, $CHCl_3$). Anal. Calc. for $C_{19}H_{22}O_2S_2$: C, 65.86; H, 6.40. Found: C, 65.82; H, 6.46%. IR (cm^{-1}) ν_{max}: 3040, 2970, 1595, 1085, 1045. ^{1}H-NMR ($CDCl_3$, 400 MHz): $\delta = 7.10$ (d, $J = 8.1$ Hz, 2H), 6.94–6.85 (m, 7H), 3.31–3.25 (m, 1H), 2.23 (s, 3H), 2.22 (s, 3H), 1.14 (d, $J = 6.5$ Hz, 3H), 1.12 (d, $J = 6.5$ Hz, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz): $\delta = 149.6$, 146.2, 142.6, 141.3, 140.0, 137.7, 129.8 (4C), 126.5 (2C), 124.4 (2C), 29.4, 22.5 (2C), 21.7, 21.6.

4.2.3. (S_S,S_S)-3,3-Dimethyl-1,1-di-p-tolylsulfinyl-but-1-ene (**5c**)

Yield: 82%. White solid, m.p. 172–174 °C. $[\alpha]_D^{25}$ − 123.0 (c 1.1, $CHCl_3$). Anal. Calc. for $C_{20}H_{24}O_2S_2$: C, 66.63; H, 6.71. Found: C, 66.46; H, 6.81%. IR (cm^{-1}) ν_{max}: 3040, 2960, 1590, 1040. ^{1}H-NMR ($CDCl_3$, 400 MHz): $\delta = 7.12$ (s, 1H), 6.96 (m, 4H), 6.86 (d, $J = 8.1$ Hz, 2H), 6.80 (d, $J = 8.1$ Hz, 2H), 2.21 (s, 3H), 2.17 (s, 3H), 1.33 (s, 9H). ^{13}C-NMR ($CDCl_3$, 100 MHz): $\delta =$ 152.3, 145.5, 141.7, 140.7, 140.5, 138.5, 129.4 (2C), 129.2 (2C), 125.6 (2C), 124.6 (2C), 36.1, 31.1, 21.3, 21.2 (3C).

4.2.4. (S_S,S_S)-2-Phenyl-1,1-di-p-tolylsulfinyl-ethylene (**5d**)

Yield: 85%. White solid, m.p. 132–134 °C (dec.) $[\alpha]_D^{25}$ − 333.0° (*c* 1.2, $CHCl_3$). Anal. Calc. for $C_{22}H_{20}O_2S_2$: C, 69.44; H, 5.30. Found: C, 69.38; H, 5.36%. IR (cm^{-1}) ν_{max}: 3040, 2920, 1590, 1080, 1040. ^{1}H-NMR ($CDCl_3$, 400 MHz): $\delta = 7.94$ (s, 1H), 7.64 (m, 2H), 7.42 (m, 3H), 7.21 (d, $J = 8.1$ Hz, 2H), 6.93–6.86 (m, 6H), 2.25 (s, 3H), 2.23 (s, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz): $\delta =$ 148.1, 142.3, 140.7, 139.7, 138.5, 137.4, 132.3, 130.9 (2C), 130.6 (2C), 129.5 (2C), 129.4 129.1 (2C), 126.3 (2C), 124.2 (2C), 21.4, 21.2.

4.2.5. (S_S,S_S)-1,1-Di-p-tolylsulfinyl-4,4-dimethyl-7-trimethylsilyl-hept-6-yn-2-ene (**5f**)

Yield: 65%. White solid, m.p. 134–135 °C. $[\alpha]_D^{25}$ − 17.2° (*c* 1.1, $CHCl_3$). Anal. Calc. for $C_{26}H_{34}O_2S_2Si$: C, 66.33; H, 7.28. Found: C, 63.45; H, 7.35%. IR (cm^{-1}) ν_{max}: 3054, 2961, 2253, 2170, 1249, 1084, 1045. ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 7.21$–7.15 (m, 3H), 7.00–6.92 (m, 6H), 2.84 (dd, $J = 14.8$; 9.4 Hz, 1H), 2.64 (dd, $J = 14.8$; 6.5 Hz, 1H), 2.31 (s, 3H), 2.29 (s, 3H), 2.23 (s, 2H), 1.12 (s, 6H), 0.14 (s, 9H). ^{13}C-NMR ($CDCl_3$, 50 MHz): $\delta = 150.2$, 142.3, 140.9, 140.1, 139.6, 137.6, 129.4 (4C), 126.3 (2C), 124.1 (2C), 104.0, 87.7, 40.1, 35.1, 33.3, 26.7, 26.6, 21.4, 21.3, 0.1 (3C).

4.3. Synthesis of the alcohol (+)-**7**

To a solution of alcohol **3b** (500 mg, 1.37 mmol, one equivalent) in dry CH_2Cl_2 (15 ml) at 0 °C, under a N_2 atmosphere, were successively added 0.97 ml (6.90 mmol, five equivalents) of freshly distilled TFAA and 0.89 ml (10.96 mmol, eight equivalents) of dry pyridine and stirred for 30 min. The reaction mixture was quenched with cold water and diluted with CH_2Cl_2 (15 ml). The layers were separated and the organic layer was washed with brine (15 ml), dried over $MgSO_4$ and evaporated to give 307 mg of an oil.

This oil was immediately dissolved in ether (10 ml) and reduced with 70 mg (1.80 mmol) of $LiAlH_4$. The reaction mixture was stirred for 1 h at r.t., diluted with CH_2Cl_2 (5 ml) and carefully hydrolyzed by an aq. saturated Na_2SO_4 solution until precipitation of the white aluminium salts. The precipitate was removed by filtration over Celite and the crude product was purified by silica gel chromatography.

4.4. (+)-(S)-2-Methyl-3,4-butanediol (+)-**7**

Yield: 42%. Colorless oil. $[\alpha]_D^{20}$ + 9.0° (*c* 3.0, $CHCl_3$), e.e. (GC) 92%. IR (cm^{-1}) ν_{max}: 3360, 2960, 2870. ^{1}H-NMR ($CDCl_3$, 200 MHz): $\delta = 3.77$–3.38 (m, 3H), 2.06 (bs, 2H), 1.70 (m, 1H), 0.97 (d, $J = 6.9$ Hz, 3H), 0.91 (d, $J = 6.9$ Hz, 3H). ^{13}C-NMR ($CDCl_3$, 50 MHz): $\delta =$ 77.1, 64.7, 30.8, 18.7, 18.2.

4.5. Synthesis of the alcohol (±)-**7**

To a solution of 500 mg (4.24 mmol, one equivalent)

of the commercially available (±)-2-hydroxy-3-methylbutyric acid in ether (10 ml) was added 177 mg (4.66 mmol, 1.1 equivalents) of $LiAlH_4$. The reaction mixture was stirred for 1 h at r.t., diluted with CH_2Cl_2 (5 ml) and carefully hydrolyzed by an (aq.) saturated Na_2SO_4 solution until precipitation of the white aluminium salts. The precipitate was removed by filtration over Celite and the crude product was purified by silica gel chromatography yielding (±)-**7** in 75%.

Acknowledgements

We thank the CNRS for a Poste Rouge to Dr F.N. and the Ministère for a grant to B.D. We feel grateful to Dr Françoise Colobert (Strasbourg) for helpful discussions and to Maxime Vitale for running some of these experiments.

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