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STUDIES OF STEREOCHEMICAL CONTROL USING α-LITHIOSULFINYL CARBANIONS

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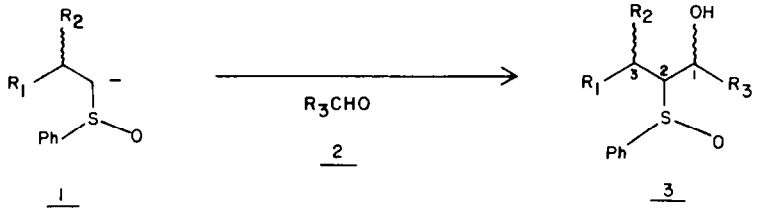
Abstract—The stereoselectivity in reactions of a series of α-lithiosulfinyl carbanions with aldehydes has been unambiguously established. Steric effects and intramolecular chelation of the associated cation are important factors contributing to the observed outcome.

Interest in the development of synthetic methodology for preparation of complex acyclic systems focused our attention on the utility of α-sulfinyl carbanions.[1] The condensation of a reactive carbanion **1**, stabilized by a neighboring asymmetric sulfoxide, with aldehydes **2** could provide a highly convergent route to acyclic molecules bearing an impressive arrangement of stereochemical features. The process requires the



1 2 3

communication of relative asymmetry of the sulfoxide to a new hydroxy functionality. Earlier studies using anions generated from methyl phenylsulfoxide reported very poor stereoselections in reactions with aldehydes and ketones.[2] However, our purposes required an additional asymmetric center ($R_1 \neq R_2$) such that the carbanion **1** would be buttressed on either side by a dissymmetric environment.

Details of the stereochemistry at two new asymmetric centers labeled as C-1 and C-2 in the β-hydroxysulfoxide adducts **3** ($R_2 = H$) were largely unpredictable.[3] Moreover, the importance of an additional asymmetric feature (R_2) at the β-position to sulfur was clearly difficult to assess. This feature was a fundamental element of our overall strategy, which would also explore construction of 1,3-asymmetry by deletion of the sulfoxide substituent from such condensation products via reductive desulfurization. Our contribution has unambiguously established results for the stereochemical consequences in condensations of a series of α-lithiosulfinyl carbanions with aldehyde substrates. We have documented the dramatic effects of internal chelation, and have proposed a working model for these processes.

Condensations

Our initial results were encouraging and, at the same time, perplexing.[4] The racemic sulfoxides **4a,b** were prepared as a diastereomeric mixture by sodium *m*-periodate oxidation of the corresponding sulfide.‡ After chromatographic purification, each isomer was rapidly deprotonated with lithium diisopropylamide (2 equiv) in tetrahydrofuran at −78°.§ Quenching the α-sulfinyl carbanion with benzaldehyde followed by immediate addition of aqueous ammonium chloride at −78° led to a mixture of adducts in 85–90% yields, which were then separated and characterized. As shown in Scheme 1, sulfoxide **4a** afforded diols **5** and **6** in a 72:28 ratio, whereas the (*R*)-sulfoxide diastereomer **4b** gave all four possible adducts **7–10** in a rather unselective 45:28:15:12 composition, respectively.

Although proton magnetic resonance spectra of each isomer displayed remarkably distinctive chemical shifts and coupling constants for the methine

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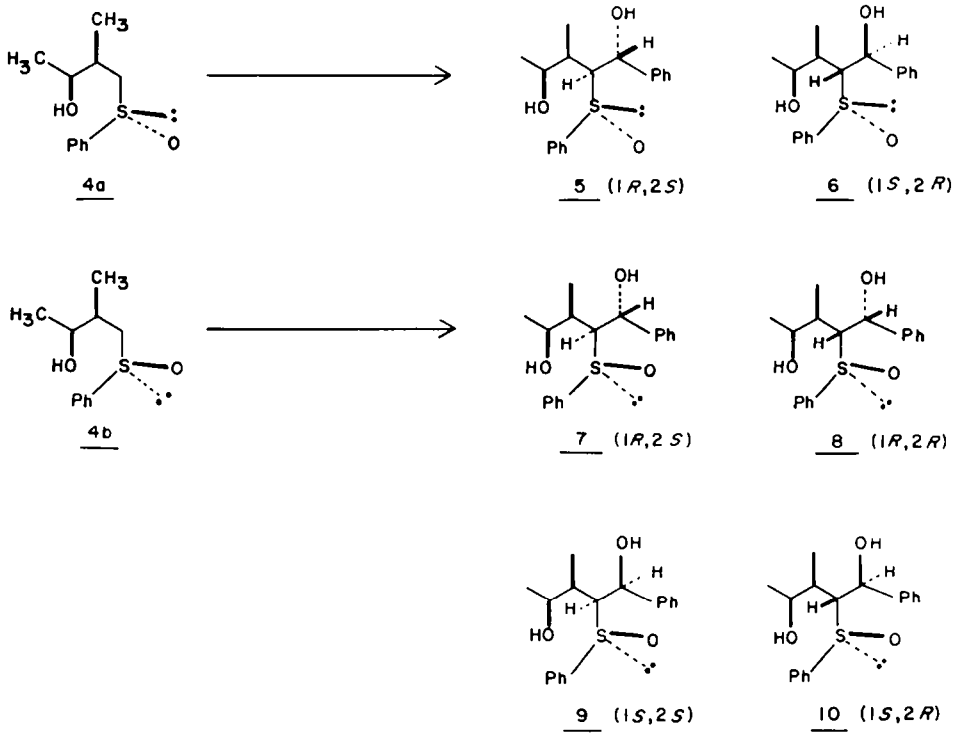
‡ The sulfide was obtained by nucleophilic ring opening of *trans*-2,3-epoxybutane at −60° with α-lithiomethyl phenylsulfide (generated from thioanisole, t-BuLi, HMPA, THF at −78°) in 74% yield: b.p. 111–114° at 0.4 mm Hg. Oxidation with sodium *meta*-periodate in aqueous MeOH–THF (70:15:15 by volume) at 22° for 16–24 h gave the sulfoxides in yields of 85–95%. Most compounds in this paper are *racemic*. However, a single *enantiomer* has been depicted for purposes of clarity. Compounds **22–25** were prepared in the chiral series, and specific rotations are quoted in the experimental section.

§ The use of alkyllithium reagents for deprotonations of sulfoxides generally leads to numerous side reactions in our cases. Common alkyllithium reagents failed to afford any products of hydroxyalkylation in the cases of **4a,b** and **14a,b**.



Scheme 1.

hydrogens at C-1, C-2 and C-3, assignments of stereochemistry were not initially feasible. Subsequent X-ray crystallographic analyses revealed the stereochemical features of **8** and **9** as illustrated†‡ and reductive transformations established the interrelationships which led to the assignment of all diastereomers. Thus, desulfurizations with Raney nickel at 22° in absolute ethanol proceeded in high yields (90–96%) and demonstrated that **5**, **7** and **8** each afforded the same diol **11**, while isomer **12** was produced by reduction of **6**, **9** and **10**. Furthermore, the major condensation products **5** and **7** resulting from the diastereomeric sulfoxides **4a,b** gave the same sulfide **13** upon reduction with borane in tetrahydrofuran (25°, 24 h, 95%). Likewise, reduction of **6** and **10** gave identical sulfides, whereas each of the phenylsulfides from **8** and **9** were unique.§

Similarly, condensations of the individual racemic sulfoxides **14a,b**,‖ possessing inverted configuration of the β-methyl substituent at C-3 afforded the products illustrated in Scheme 2. In this case, the (*R*)-sulfoxide **14a** cleanly provided an impressively selective 91:9 ratio of **15** and **16** in 85% isolated yield, whereas (*S*)-sulfoxide **14b** gave four adducts, **17–20** in 94% yield of 67:17:13:3 composition, respectively. The structure of the major product **15** was unambiguously determined by single crystal diffraction of its diacetate (Ac_2O, pyridine, 22°)¶ and the reductive chemical correlations as previously described for isomers **5–10** led to the indicated assignments.

It must be noted that major products **15** and **17**, as well as **5** and **7** from Scheme 1 share the same relative stereochemistry along the carbon backbone, in spite of the inversion of sulfoxide configuration. However, a selective condensation was maintained only when both the β-methyl (C-3) and sulfoxide configurations were inverted in unison as seen in **4a**

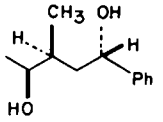
† The structural assignments of sulfoxide **8** were determined from its corresponding diacetate by single crystal analysis (−162°). All atoms were located, including hydrogens, and refined by full-matrix techniques to final residuals of $R(F) = 0.037$ and $R_w(F) = 0.042$. Complete crystallographic data are available from Indiana University Chemistry Library. Request Molecular Structure Center Report 82066.

‡ Stereochemistry of sulfoxide **9** was, in fact, established by our reductive transformations, but was subsequently confirmed by X-ray crystallography of its corresponding THF cyclization product (**14**, see the following paper).

§ Experimental information for the borane reductions and data for *all* phenylsulfides are contained in the following paper.

‖ Sulfoxides **14a,b** were obtained by nucleophilic opening of *cis*-2,3-epoxybutane in 95% yield with subsequent oxidation and chromatography as in Ref. 4.

¶ Structure **15** was determined as its diacetate by single crystal analysis (−172°). Crystal data are: space group $P2/a$; $a = 7.139(4)$, $b = 34.280(4)$, $c = 8.366(4)$ Å, $\beta = 97.29(3)^c$, $Z = 4$. The structure was solved by direct methods using 2867 intensities of amplitudes ≥ 2.33 (I) as obtained from 0–20 scan techniques using MoK$_\alpha$ radiation. Experimental detail and data reduction were previously described.[5] Atoms were located (including hydrogens) and refined by full-matrix techniques to final residuals of $R(F) = 0.046$ and $R_w(F) = 0.005$. Complete crystallographic data are available from Indiana University Chemistry Library. Request Molecular Structure Center Report 8041.



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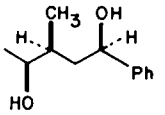

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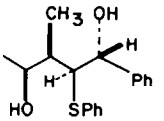


13

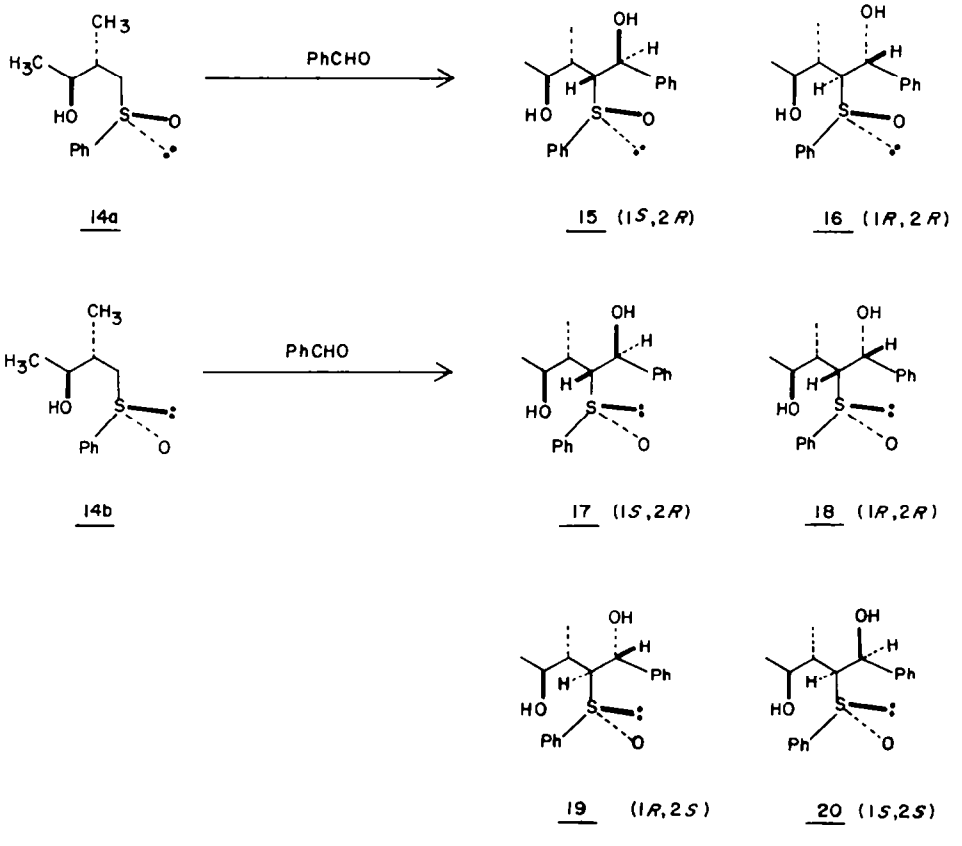
and **14a**. Moreover, the major adducts each displayed the 1,3-hydroxy-methyl substituents in an *anti* relationship (as illustrated in the extended zig-zag conformation). This has been observed as a general tendency in condensations of our sulfinyl carbanions **1**, providing for 1,3-asymmetry as previously confirmed by our synthesis of the naturally occurring juvabiol diastereoisomers.[6] In fact, Stork *et al.* have reported a highly convergent route to erythronolide A, which has demonstrated this strategy for 1,3-stereocontrol in a most complex situation.[7]

Exploring the reactivity of **4a** and **14a**, we have demonstrated similar yields and the same general stereoselectivity with aliphatic aldehydes as seen with benzaldehyde. Longer reaction times for deprotonation of the starting sulfoxide and for condensation did not alter product ratios, and subsequent addition of a second aldehyde substrate failed to provide evidence of reversibility in the carbanion addition process.

Recognizing that the secondary hydroxyl group of our sulfoxides had been appropriately positioned for an internally directed deprotonation and/or coordination of the α-lithiosulfinyl species,† we explored condensations of sulfoxides **21** lacking the γ-heteroatom substitution. These continued to generate selectivity as illustrated in Scheme 3. Thus, reactions of the (*R*)-sulfoxides **21a** (R = phenyl, *p*-tolyl, t-butyl) afforded 80% isolated yields of all four possible diastereoisomers in which **22** and **23** were major components, and **24** and **25** were minor products in ratios ranging from 9:9:2:1 to 6:6:3:1 for the adducts **22–25**, respectively.

Similar results and product ratios in the series of (*S*)-sulfoxides **21b** led to the identification of **26** and **27** as major components along with **28** and **29** as minor adducts. All of these products were purified by preparative thin-layer chromatography, and in cases of difficult separations, the purifications were achieved by HPLC. The stereochemical elucidations

† Other systems in which chelation plays an important role are reported as carbanions/enolates derived from α-sulfinyl hydrazones, oximes, and esters.[8]

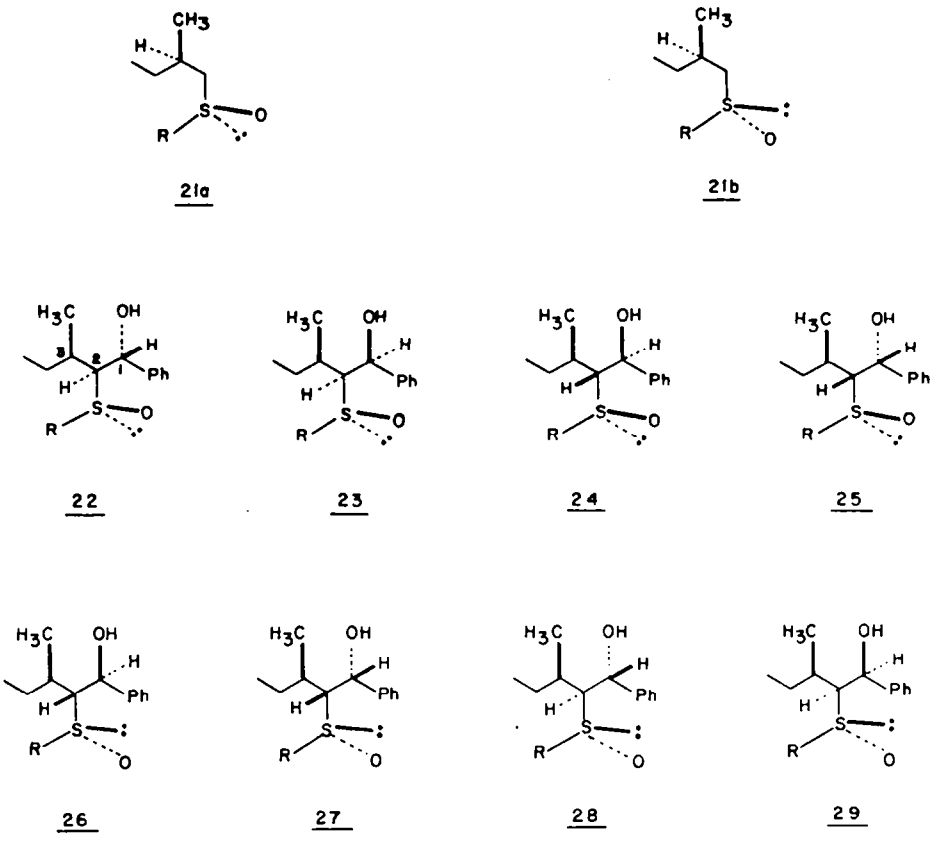


14a 15 (1*S*,2*R*) 16 (1*R*,2*R*)

14b 17 (1*S*,2*R*) 18 (1*R*,2*R*)

19 (1*R*,2*S*) 20 (1*S*,2*S*)

Scheme 2.



Scheme 3.

were interrelated by the reductive methodology previously described,† and ^{1}H-NMR data were correlated to the known structures of Schemes 1 and 2. Generally the pair of *syn*-β-hydroxysulfides displayed larger vicinal proton (C_1–C_2) coupling (J_{AB} = 7–10 Hz) compared to the corresponding pair of *anti*-diastereoisomers (J_{AB} = 4–7 Hz).‡ Furthermore, the alcohols available from Raney nickel reductions in Schemes 1–3 consistently demonstrated a 1,3-*syn*-(*R*,*R*) stereorelationship with the diagnostic observation of a distorted triplet for the benzylic hydrogen H_A, whereas the 1,3-*anti*-(*R*,*S*) arrangement gave rise to a clear doublet of doublets pattern for H_A.§

Finally, introduction of a sulfur substituent with the capacity for internal chelation of the lithiated carbanions derived from **21** reestablished a high degree of stereocontrol.‖ For example, the N-methyl-2-imidazolyl-(*R**)-sulfoxide **30** was condensed with benzaldehyde providing 65–75% isolated yields of a single hydroxysulfoxide **31**, which was readily separable from a more polar mixture of minor diastereomers (15%). Likewise, the corresponding (*S**)-sulfoxide **32** gave the β-hydroxysulfoxide **33** in 65% yield. Both products **31** and **33** were unambiguously defined by X-ray diffraction studies.¶††

Rationale

In light of the complexities of these reactions, it seems appropriate that we offer an explanation which may merit attention as a convention of some predictive value. One would anticipate a difference in the kinetic acidity of the diastereotopic hydrogens at the α-position to the sulfoxide moiety. Observations by Baldwin *et al.*[10] first confirmed that the *pro*-*R* diastereotopic proton of benzyl methyl sulfoxide could

† Experimental information for the borane reductions and data for *all* phenylsulfides are contained in the following paper.

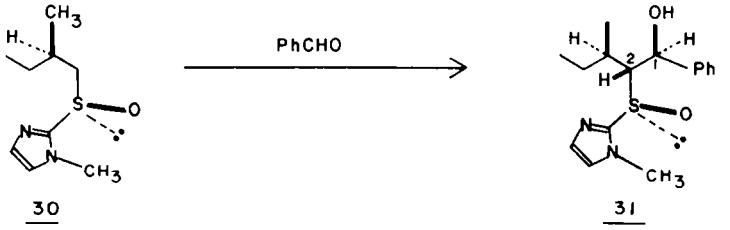
‡ An additional noteworthy feature in the ^{1}H-NMR spectra of our products of borane reductions became useful for recognition of stereochemical isomers. In all cases, the *anti* relationship of non-hydrogen substituents at C-1 and C-2 was indicated by a substantial downfield chemical shift (δ 0.5–0.2 ppm) of the methine hydrogen at C-3 by comparison to the corresponding *syn*-isomers.

§ The stereoassignments of Scheme 3 were unambiguous since the 1,3-*anti*- and 1,3-*syn*-3-methyl-1-phenylpentan-1-ols (via Raney Ni reductions) were each obtained from sulfoxide adducts **31** and **33**, which were clearly defined via X-ray studies.

‖ Recently condensations using *o*-pyridylsulfoxides have been reported with increased stereoselectivity.[9]

¶ Structure **31** was determined by single crystal analysis (−158°). All atoms were located, including hydrogens, and refined by full-matrix techniques to final residuals of $R(F)$ = 0.039 and $R_w(F)$ = 0.043. Complete crystallographic data are available from Indiana University Chemistry Library. Request Molecular Structure Center Report 84067.

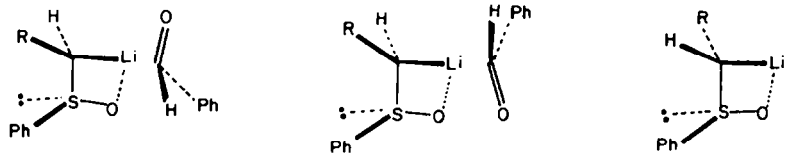
†† Sulfoxide **33** was determined by single crystal analysis (−157°). All atoms were located, including hydrogens, and refined by full-matrix techniques to final residuals of $R(F)$ = 0.40 and $R_w(F)$ = 0.041. Complete crystallographic data are available from Indiana University Chemistry Library. Request Molecular Structure Center Report 83112.



30 31

32 33

be exchanged approximately 15 times faster than the *pro-S* proton in D_2O–1 M NaOD. This result was highly variable as a function of solvent effects.[11] However, subsequent studies with optically active (*R*)-benzyl t-butylsulfoxide have demonstrated low temperature deuteration and hydroxyalkylation (with acetone) with selective replacement of the *pro-R* diastereotopic hydrogen.[12] While our results, as presented in Scheme 3, are in good agreement with these reports, we offer *no* definitive conclusions concerning



34a 34b 35

the kinetic acidities of the starting sulfoxides as well as the configurational stability or hybridization state of the resulting carbanions.† For purposes of our discussion, we will assume an sp^3 carbanion with nucleophilic approach to the carbonyl occurring with retention of configuration at the carbanion site. Thus, the (*R*)-phenylsulfoxide **21a** may yield two diastereomeric α-sulfinyl anions illustrated as the internally coordinated chelates **34a,b** and **35**.‡

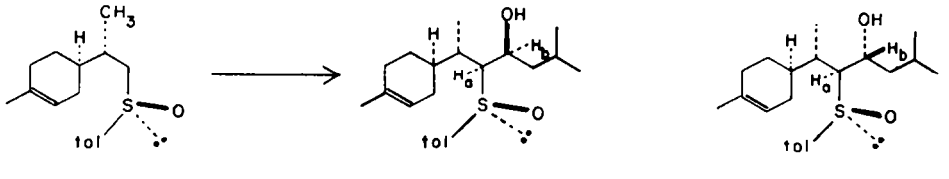
Subsequent bonding to the carbonyl in two orientations, as shown by the staggered *anti* S—C—C—O arrangement **34a** or a *gauche* S—C—C—O arrangement **34b**, will position the phenyl ring of benzaldehyde *syn* with respect to the sulfur lone pair and α-hydrogen of our "metallocycle", thereby minimizing steric interactions leading to the observed major products **22** and **23**.§ The same considerations may be applied to the (*S*)-phenylsulfoxide **21b** demonstrating the product preferences. In both cases, the β-methyl substituent adds a steric bulk to the side chain which is roughly equated to the situation for *R* as isopropyl for **34** and **35** above.‖ Reactions with

† A chelated planar (sp^2) carbanion has been proposed for cyclic α-lithiosulfoxides based on ^{1}H- and ^{13}C-NMR studies.[13]

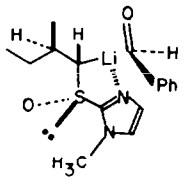
‡ Chelated structures of this variety have been considered by many investigators. Recent calculations suggest that only the chelated structure can be considered under salt-free conditions.[14]

§ The precise role and location of the metal cation is a focal point for concern in all reactions of "sp^3" carbanions. Sulfinyl carbanions undergo alkylations with inversion of carbanion configuration, but deuterations and hydroxyalkylations occur with retention. In our model, the lithium cation may be initially transferred to the sulfoxide oxygen along the reaction coordinate, followed by reassociation with the newly formed alkoxide.

‖ In analogous fashion, condensation of the carbanion of (*R*)-sulfoxide **i** with 3-methylbutanal afforded two adducts, **ii** and **iii**, in a 3 : 2 ratio (87% yield), respectively. Characteristic vicinal proton coupling of the corresponding *p*-tolylsulfides led to the assignment of the *syn*-sulfide of **ii** (J_{AB} = 8 Hz), and *anti*-sulfide of **iii** (J_{AB} = 5 Hz). The stereochemistry of the hydroxyl substituent was confirmed by transformation of **ii** to (+)-juvabiol (see Ref. 6).



i ii iii



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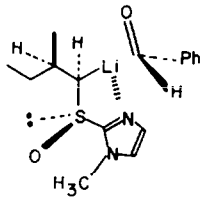

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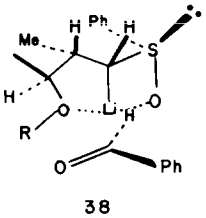
the *trans*-substituted 4-membered metallocycle **35** will be impeded by either 1,2- or 1,3-steric congestion.†

The imidazolylsulfoxides **30** and **32** exhibit a dramatic reversal of stereoselectivity at C-2 when compared to the corresponding phenylsulfoxides. This observation is accommodated by internal coordination of the α-lithiosulfinyl anion with the imidazole nitrogen as illustrated in **36** and **37**. Reactions with benzaldehyde will favorably dispose the phenyl ring toward the less congested face of the 5-membered metallocycle. Furthermore, this highly electronegative sulfoxide moiety may accentuate the need to minimize the developing dipole moment through the staggered *anti* carbonyl orientation.‡

The situation is further complicated by the chelation effects of proximate heteroatoms in the carbon chain as observed in the examples of Schemes 1 and 2. The (*R*)-sulfoxide **14a** is deprotonated affording two diastereomeric anions **38** and **39**. The normal preferred mode of addition would place the approaching phenyl substituent *syn* with respect to the methine hydrogen and sulfur nonbonded electron pair of the four-centered metallocycle as diagrammed in **34a,b**. However, this internally coordinated carbanion is destabilized by the serious steric congestion of the *S*-phenyl group and the β-methyl located on the concave side of the [3.2.0]bicycle **38**, leading to the minor adduct **16**. The major product **15** would arise from the *trans*-substituted 4-membered chelate **39**, thus overcoming a 1,3-phenyl-phenyl interaction.



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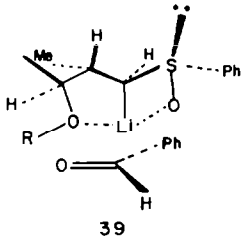

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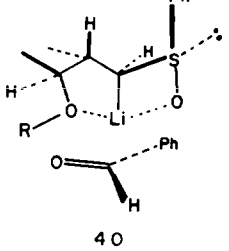

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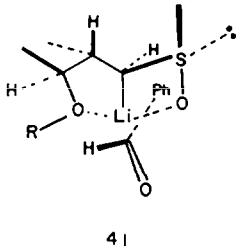

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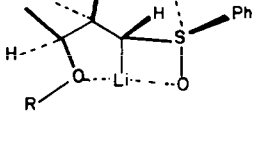

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†Our products do *not* conform to a cyclic, chairlike transition-state rationale with the equatorial arrangement of bulky substituents. Such an analysis would lead to the most minor products of Scheme 3. The stereoselective condensation of (+)-(*S*)-*p*-tolylthiomethyl sulfoxide with benzaldehyde has been reported as rationalized in an aldol-type transition state without proof of C—S bond geometry.[15]

‡Our products would predict a general tendency to favor the staggered *anti* carbonyl arrangement. However, more detailed studies are needed to probe this electronic effect.

§A highly substrate-specific deprotonation (compare **14a** vs **4b**) with configurational stability of the carbanion cannot be ruled out.

‖Use of other cations, known for strong chelation, have been disappointing. All attempts to study the series of magnesium coordinated sulfinyl anions gave very poor yields (10% or less), attributed to low reactivity. Similarly the effects of zinc halides have been reported.[16] See also Ref. 8.

On the other hand, diastereomeric (*S*)-sulfoxide **14b**, can provide a sterically preferred anion configuration for subsequent addition to benzaldehyde with staggered *anti* and *gauche* arrangements **40** and **41**, leading to **17** and **18**, respectively. Minor adducts arise from the sulfinyl anion **42**, thus demonstrating the same stereoselectivities as found in simple systems **21b** above. Similar arguments can accommodate the results of Scheme 1.

This may suggest an initial kinetic deprotonation affording an unequal pair of diastereomeric anions, such as **34** and **35**, or **38** and **39**, which are capable of interconversion by pyramidal inversion and C—S bond rotation.§ Overall, the reaction scheme of an aldehyde with a highly coordinated α-lithiosulfinyl carbanion appears to be primarily governed by the steric environment of the process.‖

EXPERIMENTAL

M.ps were determined on a Thomas–Hoover capillary apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer 298 spectrophotomer. ^{1}H-NMR spectra were obtained at 220 and 360 MHz, and are given in ppm (δ) downfield relative to Me_4Si as an internal standard. The spectral descriptors s, d, t, q, and m refer to singlet, doublet, triplet, quartet, and multiplet, respectively, and coupling constants (J) are given in Hertz. ^{13}C-NMR were conducted at 90.8 MHz with proton decoupling. Mass spectra were determined with Kratos MS 80RFA and Hewlett–Packard 5992a GC/MS instrumentation operating at 70 eV. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Anhyd solvents were routinely distilled from LAH, CaH_2, and sodium benzophenone ketyl, and purified N_2 or Ar was used in all reactions requiring an inert atmosphere. The progress of reactions was monitored by TLC using precoated glass plates (E. M. Merck silica gel 60 F-254) with visualization by UV light, iodine vapor, and phosphomolybdic acid. Silica gel 60 from E. M. Merck (0.063–0.2 mm), silica gel-H for flash chromatography, and precoated glass plates (60F-254) were employed throughout. Preparative separations were routinely accomplished by using a Waters Prep-500A instrument.

General procedure for condensations of α-lithiosulfinyl carbanions with aldehydes

Lithium diisopropylamide was prepared by dropwise addition of 1 equiv of freshly titrated n-BuLi in hexanes (Aldrich) to dry diisopropylamine (1.1 equiv) at 0° under Ar. After 20 min the white semi-solid was dissolved upon addition of anhyd THF (10 ml of THF per 3 mmol of LDA) with immediate cooling to −78°. A concentrated soln of the sulfoxide substrates (2 ml THF per 0.5 g of sulfoxide) was cooled to −78°, and added via cannulation under Ar to the reaction flask. A slight excess (5–7%) of LDA was used in all cases. Stirring was continued for 1 min, as the hydroxysulfoxides **4a,b** and **14a,b** gave reddish solns, while sulfoxides without the additional OH function gave bright yellow-gold solns. Immediately aldehyde (1.5 mmol/1.0 mmol sulfoxide) was added by syringe, and the reaction was quenched after an additional minute by introduction of sat aq NH_4Cl. Dilution with water, followed by extraction with EtOAc or $CHCl_3$, led to combined organic layers which were dried ($MgSO_4$), and evaporated *in vacuo* to give a crude product mixture. Purifications by silica gel chromatography and characterizations are itemized below.

(±)-(1*R**, 2*S**, 3*S**, 4*S**)-3-*Methyl*-1-*phenyl*-2-[(*S**)-*phenylsulfinyl*]-1,4-*pentanediol* (**5**). R_f 0.47 (EtOAc–hexane 6:4); ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.75 (m, 2), 7.59 (m, 3), 7.20 (m, 3), 7.00 (m, 2), 5.48 (s, 1H), 4.80 (br s, OH), 3.55 (m, 1H), 2.91 (s, 1H), 2.27 (m, 1H), 1.45 (d, 3H, J = 6 Hz), 1.05 (d, 3H, J = 7 Hz); IR ($CHCl_3$) 3450, 3060, 3000, 1455, 1445, 1060, 1020, 695 cm^{-1}; MS, *m/e* calc for $C_{18}H_{22}O_3S$ (MH^+), 319.138; found 319.137; 175 (42%); 105 (100%).

(±)-(1*S**, 2*R**, 3*R**, 4*S**)-3-*Methyl*-1-*phenyl*-2-[(*S**)-*phenylsulfinyl*]-1,4-*pentanediol* (**6**). R_f 0.21 (EtOAc–hexane 6:4); ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.34 (m, 10H), 5.02 (d, 1H, J = 10.6 Hz), 3.32 (m, 1H), 2.75 (d, 1H, J = 10.6 Hz), 2.23 (m, 1H), 1.15 (d, 3H, J = 7 Hz), 0.93 (d, 3H, J = 6 Hz); IR ($CHCl_3$) 3400, 3060, 2995, 1445, 1025, 700 cm^{-1}.

(±)-(1*R**, 2*S**, 3*R**, 4*S**)-3-*Methyl*-1-*phenyl*-2-[(*R**)-*phenylsulfinyl*]-1,4-*pentanediol* (**7**). R_f 0.28 (EtOAc–hexane 6:4); ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.63 (m, 2H), 7.55 (m, 3H), 7.30 (m, 3H), 7.16 (m, 2H), 4.84 (d, 1H, J = 5.5 Hz), 3.95 (m, 1H), 2.94 (dd, 1H, J = 5.5, 1.0 Hz), 2.23 (m, 1H), 1.19 (d, 3H, J = 7.4 Hz), 1.08 (d, 3H, J = 6.3 Hz); IR ($CHCl_3$) 3500, 3050, 2980, 1010, 700 cm^{-1}.

(±)-(1*R**, 2*R**, 3*R**, 4*S**)-3-*Methyl*-1-*phenyl*-2-[(*R**)-*phenylsulfinyl*]-1,4-*pentanediol* (**8**). R_f 0.30 (EtOAc–hexane 6:4); m.p. 165–166°; ^{1}H-NMR (220 MHz, $CDCl_3$) δ 8.10 (m, 1H), 7.40 (m, 9H), 5.36 (d, 1H, J = 7.5 Hz), 3.99 (m, 1H), 3.32 (dd, 1H, J = 7.5, 4.0 Hz), 1.85 (m, 1H), 1.16 (d, 3H, J = 7 Hz), 1.03 (d, 3H, J = 6 Hz); IR ($CHCl_3$) 3400, 3060, 2975, 1445, 1010, 695 cm^{-1}.

(±)-(1*S**, 2*S**, 3*R**, 4*S**)-3-*Methyl*-1-*phenyl*-2-[(*R**)-*phenylsulfinyl*]-1,4-*pentanediol* (**9**). R_f 0.24 (EtOAc–hexane 6:4); ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.34 (m, 10H), 5.42 (d, 1H, J = 1.8 Hz), 4.48 (m, 1H), 2.98 (m, 1H), 2.20 (m, 1H), 1.15 (d, 3H, J = 7 Hz), 0.95 (d, 3H, J = 6 Hz); IR ($CHCl_3$) 3400, 3060, 2965, 1445, 1010, 700 cm^{-1}.

(±)-(1*S**, 2*R**, 3*R**, 4*S**)-3-*Methyl*-1-*phenyl*-2-[(*R**)-*phenylsulfinyl*]-1,4-*pentanediol* (**10**). R_f 0.41 (EtOAc–hexane 6:4); ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.64 (m, 5H), 7.27 (m, 3H), 7.02 (m, 2H), 5.34 (s, 1H), 4.94 (m, 1H), 2.62 (dd, 1H, J = 5, 2 Hz), 2.21 (m, 1H), 1.22 (d, 3H, J = 6 Hz), 1.00 (d, 3H, J = 7 Hz); IR ($CHCl_3$) 3590, 3400, 1440, 1010, 695 cm^{-1}.

(±)-(1*S**, 2*R**, 3*S**, 4*S**)-3-*Methyl*-1-*phenyl*-2-[(*R**)-*phenylsulfinyl*]-1,4-*pentanediol* (**15**). R_f 0.40 (EtOAc–hexane 1:1); m.p. 150–151°; ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.74 (m, 2H), 7.55 (m, 3H), 7.20 (m, 3H), 7.00 (m, 2H), 5.52 (s, 1H), 4.86 (s, OH), 3.84 (m, 1H), 3.16 (s, 1H), 1.94 (m, 1H), 1.59 (d, 3H, J = 7 Hz), 0.94 (d, 3H, J = 6 Hz); ^{13}C-NMR ($CDCl_3$) δ 132.2, 130.8, 129.7, 128.5, 126.8, 125.9, 73.0, 72.2, 69.2, 39.2, 22.9, 17.5; IR ($CHCl_3$) 3590, 3300, 1445, 1010, 695 cm^{-1}. (Found: C, 67.68; H, 6.91. Calc for $C_{18}H_{22}O_3S$: C, 67.89; H, 6.96%.)

(±)-(1*R**, 2*S**, 3*S**, 4*S**)-3-*Methyl*-1-*phenyl*-2-[(*R**)-*phenylsulfinyl*]-1,4-*pentanediol* (**16**). R_f 0.16 (EtOAc–hexane 1:1); ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.34 (m, 10H), 4.86 (d, 1H, J = 9 Hz), 3.78 (m, 1H), 2.93 (d, 1H, J = 9 Hz), 2.05 (m, 1H), 1.20 (d, 3H, J = 7 Hz), 0.61 (d, 3H, J = 7 Hz); IR ($CHCl_3$) 3590, 3400, 3055, 2965, 1445, 1010, 695 cm^{-1}; MS, *m/e* calc for $C_{18}H_{22}O_3S$ (MH^+), 319.138; found 319.139; 175 (10%), 126 (24%), 105 (57%).

(±)-(1*S**, 2*R**, 3*S**, 4*S**)-3-*Methyl*-1-*phenyl*-2-[(*S**)-*phenylsulfinyl*]-1,4-*pentanediol* (**17**). R_f 0.20 (EtOAc–hexane 4:6); m.p. 159–160°; ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.65 (m, 2H), 7.56 (m, 3H), 7.30 (m, 5H), 5.09 (d, 1H, J = 5.5 Hz), 4.63 (br s, OH), 3.74 (m, 1H), 3.27 (d, 1H, J = 5.5 Hz), 3.20 (br s, OH), 2.08 (m, 1H), 1.10 (d, 3H, J = 7 Hz), 0.96 (d, 3H, J = 6 Hz); IR ($CHCl_3$) 3585, 3500, 3040, 2985, 1080, 1060, 1010, 700, 690 cm^{-1}. (Found: C, 67.60; H, 6.86. Calc for $C_{18}H_{22}O_3S$: C, 67.89; H, 6.96%.)

(±)-(1*R**, 2*R**, 3*S**, 4*S**)-3-*Methyl*-1-*phenyl*-2-[(*S**)-*phenylsulfinyl*]-1,4-*pentanediol* (**18**). R_f 0.33 (EtOAc–hexane 4:6); ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.34 (m, 8H), 7.05 (m, 2H), 6.29 (s, OH), 5.46 (s, 1H), 3.69 (m, 1H), 3.04 (s, 1H), 2.24 (m, 1H), 1.33 (d, 3H, J = 6 Hz), 0.92 (d, 3H, J = 7 Hz); IR ($CHCl_3$) 3595, 3400, 3055, 2960, 1440, 1010, 700 cm^{-1}.

(±)-(1*R**, 2*S**, 3*S**, 4*S**)-3-*Methyl*-1-*phenyl*-2-[(*S**)-*phenylsulfinyl*]-1,4-*pentanediol* (**19**). R_f 0.22 (EtOAc–hexane 4:6); ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.59 (m, 5H), 7.14 (m, 3H), 6.86 (m, 2H), 5.23 (d, 1H, J = 3.4 Hz), 4.13 (m, 1H), 2.86 (m, 1H), 2.47 (m, 1H), 1.31 (d, 3H, J = 6 Hz), 1.16 (d, 3H, J = 7 Hz); IR ($CHCl_3$) 3400, 3065, 2970, 1455, 1445, 1025, 1010, 695 cm^{-1}.

(±)-(1*S**, 2*S**, 3*S**, 4*S**)-3-*Methyl*-1-*phenyl*-2-[(*S**)-*phenylsulfinyl*]-1,4-*pentanediol* (**20**). R_f 0.15 (EtOAc–hexane 4:6); ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.61 (m, 2H), 7.45 (m, 3H), 7.25 (m, 5H), 5.43 (d, 1H, J = 9 Hz), 4.77 (br s, OH), 3.71 (d, 1H, J = 9 Hz), 3.18 (m, 1H), 1.70 (m, 1H), 1.04 (d, 3H, J = 6 Hz), 0.94 (d, 3H, J = 7 Hz); IR ($CHCl_3$) 3390, 3055, 2960, 1445, 1010, 695 cm^{-1}.

Condensation of the carbanion from (*R*)-**21a** with benzaldehyde gave four distinct spots on TLC at R_f 0.58, 0.41, 0.35 and 0.20 (EtOAc–hexane 2:3). Each was determined to contain only a single diastereoisomer. Preliminary purification of the crude reaction mixture using column chromatography (silica gel; EtOAc–hexanes 5:95 by volume) cleanly afforded isomers **22** and **25**. Subsequently the intermediate fractions were combined and applied to TLC plates for separation of isomers **23** and **24** using two elutions of EtOAc–hexanes (1:1 by volume). The total yield of purified products was routinely 80–85%.

(±)-(α*R*)-α-[(1*S*,2*R*)-2-*Methyl*-1-[(*R*)-*p*-*tolylsulfinyl*]-*butyl*]*benzyl alcohol* (**22**). R_f 0.58 (EtOAc–hexane 4:6);

$[\alpha]_D^{23}+110°$ (*c* 1.22, $CHCl_3$); m.p. 100–102°; ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.59 (d, 1H, J = 7 Hz), 7.45 (d, 1H, J = 7 Hz), 7.27 (m, 6H), 7.05 (d, 1H, J = 7 Hz), 5.50 (s, 1H), 4.86 (br s, OH), 2.48 (s, 3H), 2.46 (s, 1H), 2.00 (m, 1H), 1.68 (d, 3H, J = 6 Hz), 1.39 (m, 2H), 0.66 (t, 3H, J = 6 Hz); IR ($CHCl_3$) 3390, 2995, 2950, 1490, 1450, 1010, 810, 700 cm^{-1}; MS, *m/e* calc for $C_{19}H_{24}O_2S$ (MH^+), 317.158; found 317.159; 246 (22%), 158 (100%).

(+) - (αS) - α - [(1*S*, 2*R*) - 2 - *Methyl* - 1 - [(*R*) - *p* - *tolylsulfinyl*]*butyl*]*benzyl alcohol* (**23**). R_f 0.41 (EtOAc–hexane 4:6); m.p. 102–103°; $[\alpha]_D^{23}-52.7°$ (*c* 1.02, $CHCl_3$); ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.61 (m, 2H), 7.34 (m, 7H), 5.30 (d, 1H, J = 10 Hz), 4.75 (br s, OH), 3.36 (d, 1H, J = 10 Hz), 2.42 (s, 3H), 1.32 (m, 3H), 1.14 (d, 3H, J = 6 Hz), 0.68 (t, 3H, J = 6 Hz); IR ($CHCl_3$) 3350, 2992, 2950, 1490, 1450, 1380, 1230, 1050–990, 805 cm^{-1}.

(+) - (αS) - α - [(1*R*, 2*R*) - 2 - *Methyl* - 1 - [(*R*) - *p* - *tolylsulfinyl*]*butyl*]*benzyl alcohol* (**24**). R_f 0.35 (EtOAc–hexane 4:6); m.p. 118–119°; $[\alpha]_D^{23}+75.1°$ (*c* 2.16, $CHCl_3$); ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.32 (m, 9H), 5.17 (d, 1H, J = 7 Hz), 2.84 (dd, J = 7 Hz), 2.59 (br s, OH), 2.37 (s, 3H), 2.00 (m, 1H), 1.55 (m, 1H), 1.41 (m, 1H), 1.11 (d, 3H, J = 6 Hz), 0.66 (t, 3H, J = 6 Hz); IR (film) 3400, 3025, 2950, 1490, 1450, 1050–1015, 805 cm^{-1}. (Found: C, 72.15; H, 7.41. Calc for $C_{19}H_{25}O_2S$: C, 72.12; H, 7.64%.)

(−) - (αR) - α - [(1*R*, 2*R*) - 2 - *Methyl* - 1 - [(*R*) - *p* - *tolylsulfinyl*]*butyl*]*benzyl alcohol* (**25**). R_f 0.20 (EtOAc–hexane 4:6); m.p. 129–130°; $[\alpha]_D^{23}+159.5°$ (*c* 1.23, $CHCl_3$); ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.32 (m, 9H), 5.30 (d, 1H, J = 6 Hz), 4.32 (br s, OH), 2.95 (dd, 1H, J = 6.3, 2.7 Hz), 2.39 (s, 3H), 1.87 (m, 1H), 1.09 (d, 3H, J = 7 Hz), 0.91 (m, 2H), 0.54 (t, 3H, J = 7 Hz); IR (film) 3450, 3020, 2960, 1495, 1460, 1050–1020, 810, 700 cm^{-1}.

The condensation of racemic sulfoxides **21a,b** with benzaldehyde yielded four distinct spots on TLC at R_f 0.53, 0.34, 0.28 and 0.19 (EtOAc–hexanes 2:3 by volume). Each band was determined to contain two diastereomers in identical 1:1 ratios. Preliminary purification by preparative TLC using two elutions of EtOAc–hexanes (2:3) provided separation of the most mobile pair of adducts from the other three bands. These isomers (R_f 0.53) were separable by preparative TLC with four elutions of EtOAc–hexanes (2:3). The other six diastereoisomers were separated into their distinct pairs using preparative TLC (two elutions with EtOAc–hexanes 1:1). Two adducts at R_f 0.34 were separated by HPLC on a LiChrosorb Si 60 column (10 mm × 25 cm) at 100 psi using hexanes–isopropanol (99:1 by volume). The remaining two sets of diastereomers were each cleanly separated by TLC with three elutions of EtOAc–hexanes (1:1). The total yield of isolated adducts was 77% after all purifications. Characterizations are described below.

(αR^*) - α - [(1*S**, 2*R**) - 2 - *Methyl* - 1 - [(*R**) - *phenylsulfinyl*]*butyl*]*benzyl alcohol* (**22**). R_f 0.53 (EtOAc–hexanes 4:6); ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.67 (m, 5H), 7.26 (m, 3H), 7.02, (m, 2H), 5.45 (s, 1H), 4.81 (d, OH, J = 1.4 Hz), 2.48 (s, 1H), 2.01 (m, 1H), 1.55 (d, 3H, J = 6.9 Hz), 1.41 (m, 2H), 0.68 (t, 3H, J = 7.4 Hz); IR (KBr) 3440, 3240, 3050, 2950, 1440, 1005, 995, 700 cm^{-1}.

(αS^*) - α - [(1*R**, 2*R**) - 2 - *Methyl* - 1 - [(*R**) - *phenylsulfinyl*]*butyl*]*benzyl alcohol* (**23**). R_f 0.34 (EtOAc–hexane 4:6); ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.69 (m, 2H), 7.53 (m, 3H), 7.30 (s, 5H), 5.33 (d, 1H, J = 10.4 Hz), 4.71 (d, OH, J = 2 Hz), 3.37 (d, 1H, J = 10.4 Hz), 1.38 (m, 3H), 1.19 (d, 3H, J = 5.7 Hz), 0.72 (t, 3H, J = 7 Hz); IR (film) 3455, 3040, 2960, 1445, 1055–1000, 745, 700 cm^{-1}.

(αS^*) - α - [(1*R**, 2*R**) - 2 - *Methyl* - 1 - [(*R**) - *phenylsulfinyl*]*butyl*]*benzyl alcohol* (**24**). R_f 0.28 (EtOAc–hexane 4:6); ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.48 (s, 5H), 7.38 (m, 5H), 5.28 (d, 1H, J = 7.2 Hz), 2.88 (dd, 1H, J = 7, 3.6 Hz), 2.02 (m, 1H), 1.80 (br s, OH), 1.47 (m, 2H), 1.16 (d, 3H, J = 7 Hz), 0.64 (t, 3H, J = 7 Hz); IR (film) 3450, 3025, 2975, 1445, 1060–1000, 745, 700 cm^{-1}.

(αS^*) - α - [(1*R**, 2*R**) - 2 - *Methyl* - 1 - [(*R**) - *phenylsulfinyl*]*butyl*]*benzyl alcohol* (**25**). R_f 0.19 (EtOAc–hexane 4:6); ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.49 (m, 5H), 7.35 (m, 5H), 5.34 (d, 1H, J = 6.3 Hz), 3.81 (br s, OH), 2.95 (dd, 1H, J = 6.3, 2.7 Hz), 1.89 (m, 1H), 1.12 (d, 3H, J = 7 Hz), 0.93 (m, 2H), 0.53 (t, 3H, J = 7 Hz); IR (film) 3440, 3030, 2970, 1445, 1050–1005, 745, 695 cm^{-1}.

(αS^*) - α - [(1*R**, 2*R**) - 2 - *Methyl* - 1 - [(*S**) - *phenylsulfinyl*]*butyl*]*benzyl alcohol* (**26**). R_f 0.53 (EtOAc–hexane 4:6); ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.67 (m, 5H), 7.26 (m, 3H), 7.02 (m, 2H), 5.40 (s, 1H), 4.71 (d, OH, J = 1.9 Hz), 2.47 (d, 1H, J = 2 Hz), 2.36 (m, 1H), 2.15 (m, 1H), 1.66 (m, 1H), 0.98 (t, 3H, J = 6.4 Hz), 0.94 (d, 3H, J = 6.9 Hz); IR (KBr) 3450, 3050, 2950, 1445, 1055, 1005, 995, 750, 700 cm^{-1}.

(αR^*) - α - [(1*R**, 2*R**) - 2 - *Methyl* - 1 - [(*S**) - *phenylsulfinyl*]*butyl*]*benzyl alcohol* (**27**). R_f 0.34 (EtOAc–hexane 4:6); ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.69 (m, 2H), 7.53 (m, 3H), 7.30 (s, 5H), 5.35 (d, 1H, J = 9.3 Hz), 4.82 (d, OH, J = 3 Hz), 3.27 (dd, 1H, J = 9.3, 1.2 Hz), 1.39 (m, 1H), 1.04 (d, 3H, J = 6.3 Hz), 0.77 (t, 3H, J = 7 Hz); IR (film) 3430, 3025, 2960, 1490, 1445, 1060–1000, 745, 695 cm^{-1}.

(αR^*) - α - [(1*S**, 2*R**) - 2 - *Methyl* - 1 - [(*S**) - *phenylsulfinyl*]*butyl*]*benzyl alcohol* (**28**). R_f 0.28 (EtOAc–hexane 4:6); ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.65 (m, 2H), 7.50 (m, 3H), 7.30 (m, 5H), 5.02 (d, 1H, J = 3.8 Hz), 2.92 (m, 1H), 2.03 (m, 1H), 1.62 (m, 1H), 1.38 (m, 1H), 1.24 (d, 3H, J = 7 Hz), 0.64 (t, 3H, J = 7.2 Hz); IR (film) 3460, 3060, 2970, 1060–1000, 745, 695 cm^{-1}.

(αS^*) - α - [(1*S**, 2*R**) - 2 - *Methyl* - 1 - [(*S**) - *phenylsulfinyl*]*butyl*]*benzyl alcohol* (**29**). R_f 0.19 (EtOAc–hexane 4:6); ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.54 (m, 2H), 7.46 (m, 3H), 7.39 (m, 5H), 5.35 (d, 1H, J = 6.6 Hz), 4.34 (br s, OH), 3.05 (dd, 1H, J = 6.6, 3.5 Hz), 1.81 (m, 2H), 1.34 (m, 1H), 0.80 (t, 3H, J = 7 Hz), 0.64 (d, 3H, J = 7 Hz); IR (film) 3445, 3055, 2960, 1055–1000, 745, 695 cm^{-1}.

(±) - (αS^*) - α - [(1*R**, 2*R**) - 2 - *Methyl* - 1 - [(*R**) - (1 - *methylimidazol* - 2 - *yl*)*sulfinyl*]*butyl*]*benzyl alcohol* (**31**). R_f 0.23 (70% EtOAc–hexane, 2 elutions); m.p. 128–129.5°; ^{1}H-NMR (360 MHz, $CDCl_3$) δ 7.49 (m, 2H), 7.35 (m, 2H), 7.25 (m, 2H), 7.06 (s, 1H), 5.91 (s, 1H), 4.34 (d, J = 2.1 Hz, OH), 4.01 (s, 3H), 3.92 (dd, 1H, J = 4.5, 1.9 Hz), 2.18 (m, 2H), 1.65 (m, 1H), 0.92 (t, 3H, J = 7.2, 3 Hz), 0.85 (d, 3H, J = 6.9 Hz); IR ($CHCl_3$) 3420, 3000, 2970, 2935, 2880, 1465, 1455, 1275, 1125, 1090, 1060, 1000, 700, 670 cm^{-1}. High resolution MS, calc for $C_{16}H_{23}N_2O_2S$ ($M^+ + 1$), 307.1480; found 307.1427.

(±) - (αR^*) - α - [(1*S**, 2*R**) - 2 - *Methyl* - 1 - [(*S**) - (1 - *methylimidazol* - 2 - *yl*)*sulfinyl*]*butyl*]*benzyl alcohol* (**33**). R_f 0.29 (70% EtOAc–hexane, 2 elutions); m.p. 120–122°; ^{1}H-NMR (360 MHz, $CDCl_3$) δ 7.48 (m, 2H), 7.35 (m, 2H), 7.25 (m, 2H), 7.07 (s, 1H), 5.98 (s, 1H), 4.43 (br s, OH), 4.01 (s, 3H), 3.99 (m, 1H), 2.04 (sextet of d, 1H, J = 7.4, 2.6 Hz), 1.45 (d, 3H, J = 7.2 Hz), 1.25 (quintet of d, 2H, J = 7.4, 1.4 Hz), 0.62 (t, 3H, J = 7.2 Hz); IR ($CHCl_3$) 3420, 3000, 2960, 2930, 2880, 1465, 1450, 1375, 1280, 1120, 1060, 1000, 875, 630 cm^{-1}. High resolution MS, calc for $C_{16}H_{23}N_2O_2S$ ($M^+ + 1$), 307.1480; found 307.1495.

Procedure for the Raney nickel desulfurization of sulfoxide adducts

To a soln of β-hydroxysulfoxide or β-hydroxysulfide (0.15–0.3 mmol) in EtOH (3–5 ml) at 22° was added Raney Ni in portions.[17] The Raney Ni was freshly prepared, kept under EtOH, and could be stored for 2 months at −20°. Usually approximately 0.5–1.0 g of reagent were used per 100 mg of substrate. The suspension was vigorously stirred for 15–30 min, and filtered through a small pad of Florisil, which was subsequently washed with abs EtOH (50 ml) and then dry THF (50 ml). Solvent evaporation *in vacuo* afforded crude alcohols, which were purified by preparative TLC using EtOAc–hexane mixtures. Yields were generally 70–96%. Raney Ni desulfurizations of cyclic ethers (Table 1 of the following paper) also occurred in excellent yields, illustrating the accessibility of 2,3,5-trisubstituted tetrahydrofurans.

(±) - (1*R**, 3*R**, 4*S**) - 3 - *Methyl* - 1 - *phenyl* - 1,4 - *pentanediol*. ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.27 (m, 5H), 4.76 (dd, 1H, J = 10, 3 Hz), 3.62 (m, 1H), 1.91 (m, 1H), 1.75 (m, 1H), 1.45 (m, 1H), 1.19 (d, 3H, J = 6 Hz), 0.96 (d, 3H, J = 6 Hz); IR (film) 3400–3200, 1600, 1085, 1050, 1000 cm^{-1}; MS (70 eV), *m/e* 194.1 (M^+), 176.2 (M − 18), 120.1 (41), 117.1 (29), 107.1 (79), 105.1 (27), 91.1 (22), 79 (100), 77 (70). (Found: C, 73.70; H, 9.37. Calc for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34%.)

(±) - (1*S**, 3*R**, 4*S**) - 3 - *Methyl* - 1 - *phenyl* - 1,4 - *pentanediol*. ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.27 (m, 5H), 4.87 (dd, 1H, J = 8, 5 Hz), 3.71 (m, 1H), 1.90 (m, 1H), 1.82 (m, 1H), 1.57 (m, 1H), 1.18 (d, 3H, J = 6 Hz), 0.98 (d, 3H, J = 6 Hz); IR (film) 3420–3200, 1085, 1050, 1000 cm^{-1}.

(±) - (1*S**, 3*S**, 4*S**) - 3 - *Methyl* - 1 - *phenyl* - 1,4 - *pentanediol*. ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.36 (m, 5H), 4.75 (dd, 1H, J = 10, 2.5 Hz), 3.86 (m, 1H), 2.72 (br s, OH), 1.92 (m, 2H), 1.71 (m, 1H), 1.50 (m, 1H), 1.16 (d, 3H, J = 6 Hz), 0.94 (d, 3H, J = 7 Hz); IR ($CHCl_3$) 3595, 3350, 2960, 2920, 1450, 1380, 1080, 1045, 1010, 700 cm^{-1}; MS (70 eV), *m/e* 176 (M − 18), 120 (27), 117 (20), 107 (68), 105 (27), 91 (21), 79 (100), 77 (82).

(±) - (1*R**, 3*S**, 4*S**) - 3 - *Methyl* - 1 - *phenyl* - 1,4 - *pentanediol* (**12**). ^{1}H-NMR (220 MHz, $CDCl_3$) δ 7.36 (m, 5H), 4.87 (dd, 1H, J = 8, 5 Hz), 3.85 (m, 1H), 2.76 (br s, OH), 1.89 (m, 1H), 1.75 (m, 2H), 1.16 (d, 3H, J = 6 Hz), 0.94 (d, 3H, J = 7 Hz); IR (film) 3400–3210, 2965, 1450, 1085, 1045, 1010, 700 cm^{-1}. Mass spectral data were indistinguishable from the diastereomer listed above.

(±) - (1*S**, 3*R**) - 3 - *Methyl* - 1 - *phenyl* - 1 - *pentanol*. This alcohol, bearing a 1,3-*anti* relationship of hydroxy and methyl substituents, was produced by reduction of products **22**, **25**, **27**, **28** and **33**. Moreover, the stereochemical features of sulfoxide **33** had been assigned by X-ray diffraction studies. The *anti*-3-methyl-1-phenylpentan-1-ol was characterized as a colorless oil: ^{1}H-NMR (360 MHz, $CDCl_3$) δ 7.35 (m, 5H), 4.87 (dd, 1H, J = 9.3, 4 Hz), 1.83 (m, 1H), 1.68 (m, 1H), 1.59 (m, 1H), 1.40 (m, 1H), 1.25 (m, 1H), 0.95 (d, 3H, J = 6.5 Hz), 0.89 (t, 3H, J = 7.5 Hz); IR (film) 3380, 3045, 2970, 1450, 1360, 1045, 1030, 995, 750, 700 cm^{-1}.

(±) - (1*R**, 3*R**) - 3 - *Methyl* - 1 - *phenyl* - 1 - *pentanol*. This alcohol, bearing a 1,3-*syn* arrangement of hydroxy and methyl substituents, was obtained from the Raney Ni reductions of **23**, **25**, **26**, **29** and **31**. Furthermore, the stereochemistry of sulfoxide **31** had been confirmed by X-ray crystallography. The *syn*-3-methyl-1-phenylpentan-1-ol was characterized as a colorless oil: ^{1}H-NMR (360 MHz, $CDCl_3$) δ 7.34 (m, 5H), 4.76 (t, 1H, J = 7, 7 Hz), 1.82 (br s, OH), 1.67 (t, 2H, J = 7 Hz), 1.40 (m, 2H), 1.18 (m, 1H), 0.93 (d, 3H, J = 7 Hz), 0.85 (t, 3H, J = 7 Hz); IR (film) 3360, 3050, 3025, 2965, 2930, 2880, 2860, 1495, 1457, 1378, 1057, 1028, 993, 770, 751, 698 cm^{-1}.

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