Chiral Acyl Anion and Enolonium Ion Equivalents. Asymmetric Synthesis of α-Methoxy-aldehydes

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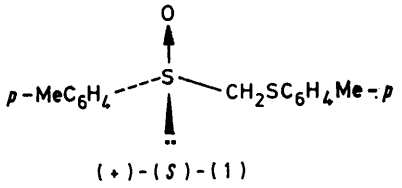
The reaction of the lithium derivative of (+)-(*S*)-*p*-tolyl *p*-tolylthiomethyl sulphoxide [(+)-(*S*)-(1)] with benzaldehyde and phenylacetaldehyde in tetrahydrofuran at −78 °C gives, after methylation of the hydroxy-group, reduction of the sulphoxide, and hydrolysis of the resulting dithioacetal, the corresponding α-methoxy-aldehydes, (−)-(*R*)-2-methoxy-2-phenylacetaldehyde and (+)-(*R*)-2-methoxy-3-phenylpropionaldehyde, enantiomeric excess 70 and 46%, respectively. The reaction of (+)-(*S*)-(1) with benzaldehyde in tetrahydrofuran at room temperature in the presence of Triton B gives the new optically pure reagent (*E*)-(+)-(*S*)-1-*p*-tolylsulphinyl-1-*p*-tolylthio-2-phenylethylene [(+)-(*S*)-(2)], which is a chiral enolonium equivalent. The addition of sodium methoxide to (+)-(*S*)-(2) in methanol gives, after reduction of the sulphoxide and hydrolysis of the resulting dithioacetal, (+)-(*S*)-2-methoxy-2-phenylacetaldehyde, enantiomeric excess 60%. The unfavourable equilibrium in addition of methoxide to (+)-(*S*)-(2) means that the latter is not very useful as a chiral enolonium equivalent in reactions of this type.

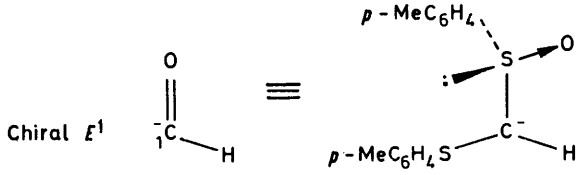
UMPOLUNG of the reactivity of carbonyl compounds by the application of sulphur-containing reagents has been well established for its synthetic usefulness.[1] Racemic methyl methylthiomethyl sulphoxide [2,3] and ethyl ethylthiomethyl sulphoxides,[4] as well as their derivatives, keten thioacetal mono-*S*-oxides,[4b,5] have been widely used as carbonyl equivalents.

The syntheses of chiral 1,3-dithian 1-oxide [6] and *p*-tolyl *p*-tolylthiomethyl sulphoxide (1) [7] have previously



(+)-(*S*)-(1)

been reported. Recently we developed a new one-step synthesis of (+)-(*S*)-(1).[8] The anion derived from (+)-(*S*)-(1), which is a chiral formyl anion equivalent (Scheme 1), permits chiral E^1 reactions [1a] to be per-

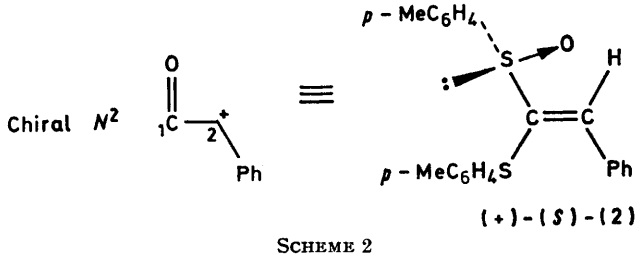


SCHEME 1

formed. We now report an E^1 reaction on both aromatic [9] and aliphatic aldehydes. We also describe the synthesis and use of (*E*)-(+)-(*S*)-1-*p*-tolylsulphinyl-1-*p*-tolylthio-2-phenylethylene [(+)-(*S*)-(2)], which is a chiral enolonium equivalent (Scheme 2) and can undergo chiral N^2 reactions.[1a]

α-Sulphinyl carbanions derived from optically active sulphoxides are known to react with carbonyl compounds,[10] but rarely with high direct β-induction. Somewhat better results have been achieved with nucleophilic addition to optically active αβ-unsaturated sulphoxides.[11,12]

The present method constitutes a new approach to optically active protected † α-hydroxy-aldehydes ‡ with an α-C–H bond in quite satisfactory optical yield.



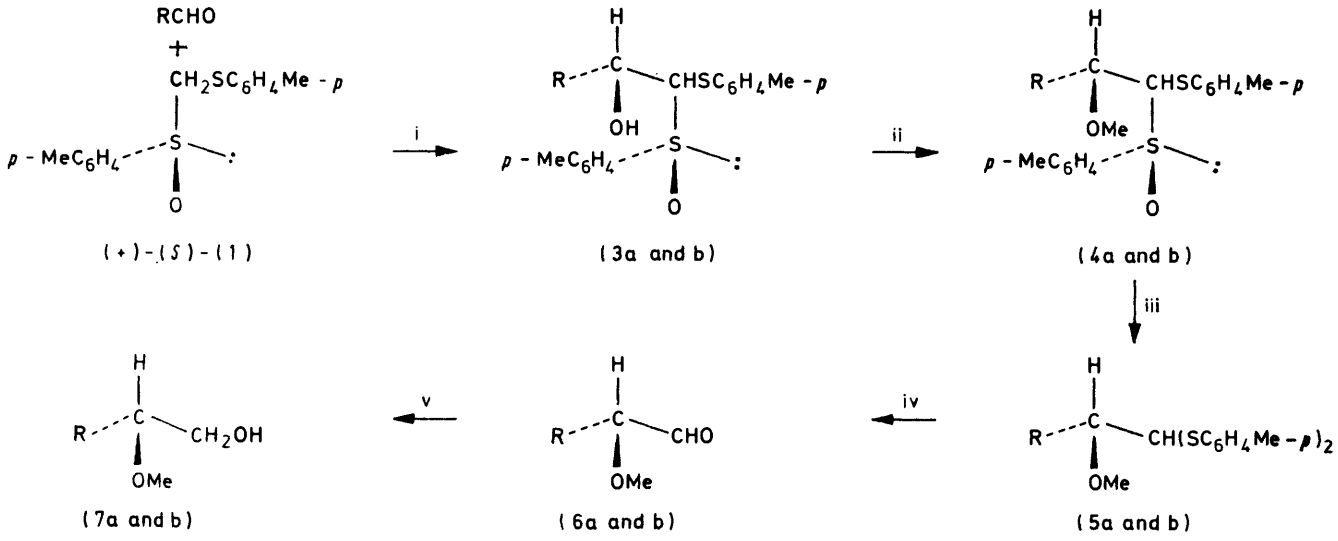
SCHEME 2

RESULTS AND DISCUSSION

To the anion prepared by treating (+)-(*S*)-(1) with n-butyl-lithium (Bu^nLi) in tetrahydrofuran (THF) at −20 °C, benzaldehyde or phenylacetaldehyde was added at −78°C. After a few minutes at −78 °C, the usual work-up gave (3) as a mixture of diastereoisomers (Scheme 3). A wide variety of procedures [13] was tried for selective *O*-methylation of (3a), but dehydration, retro-aldol condensation, and epimerization made all but one of these methods inefficient. Sodium hydride–methyl iodide in THF or dimethyl sulphoxide [2b] gave almost quantitatively the dehydration product, *i.e.*

† Non-protected α-hydroxy-aldehydes are known to be quite unstable and rapidly rearrange to α-hydroxy-ketones, dimerize, and polymerize (A. Hassner, R. H. Reuss, and H. W. Pinnick, *J. Org. Chem.*, 1975, **40**, 3427 and references therein).

‡ Recently, two different asymmetric syntheses of α-hydroxy-aldehydes with high optical purity have been reported, but these methods were only used to obtain α-hydroxy-aldehydes without α-C–H bonds (E. L. Eliel, J. K. Koshimies, and B. Lohri, *J. Am. Chem. Soc.*, 1978, **100**, 1614; E. L. Eliel and W. J. Frazee, *J. Org. Chem.*, 1979, **44**, 3598; T. Mukaiyama, Y. Sakito, and M. Asami, *Chem. Lett.*, 1978, 1253; 1979, 705).



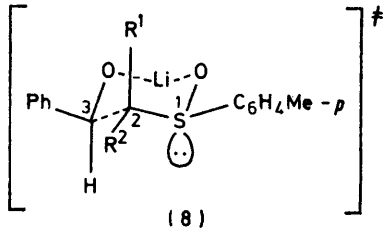
SCHEME 3 *Reagents:* i, Bu^nLi–THF, −78 °C; ii, Bu^n_4NOH–Me_2SO_4–H_2O–CH_2Cl_2; iii, NaI–I_2–Ph_3P when R = Ph, NaI–I_2–$(Me_2N)_3P$ when R = $PhCH_2$; iv, I_2–$NaHCO_3$–H_2O–dioxan; v, $NaBH_4$

PhCH=C(SOC_6H_4Me-*p*)SC_6H_4Me-*p*; n-butyl-lithium–methyl iodide in THF gave an uncharacterized mixture containing starting materials, benzaldehyde, and (1); and silver oxide–methyl iodide in *NN*-dimethylformamide led to the dehydration product together with the desired product (4a) in low yield. Accordingly, methylation of (3) was accomplished in good yield using dimethyl sulphate under phase-transfer conditions.[14] The diastereoisomeric ratio did not change under the mild conditions used.

Attempts to hydrolyse the thioacetal *S*-oxide (4a) directly into the aldehyde (6a) were unsuccessful: acidic hydrolyses [2,3a,4,5a,15] were ineffective; cerium(IV) ammonium nitrate,[16] methylfluorosulphonate,[17] and *O*-mesitylenesulphonylhydroxylamine [18] gave uncharacterized mixtures; copper(II) chloride in refluxing 1,2-dimethoxyethane [2b] gave a reaction mixture which appeared to contain the enol thio-ether PhC(OMe)=$CHSC_6H_4Me$-*p*.

Accordingly, the *S*-oxide (4) was reduced with NaI–I_2–R_3P [19] to provide the dithioacetal (5), which was in turn hydrolysed to the aldehyde (6) using I_2–$NaHCO_3$.[20] Reduction *in situ* of (6) with $NaBH_4$ gave the optically active alcohol (7) with *R*-configuration (Table 1). This reduction was performed because handling and purification of the alcohol (7) is easier than that of the aldehyde (6). Moreover, the alcohol (7) allows n.m.r. techniques to be used to check the enantiomeric excess.

The condensation of the anion of (1) with benzaldehyde under the above-mentioned conditions is a kinetically controlled irreversible process: the diastereoisomeric ratio of (3a) (*ca.* 55 : 30 : 15 : 0) did not change during the reaction, and a cross-over experiment which was attempted by adding *p*-chlorobenzaldehyde to the final reaction mixture produced no detectable cross-over product after 3 h. The observed diastereoisomeric ratio is probably due to cyclic transition states like (8), which are



(8)

a; R^1 = H, R^2 = SC_6H_4Me-*p*

b; R^1 = SC_6H_4Me-*p*, R^2 = H

stabilized by chelation.[21] A tentative assignment of absolute configuration to the observed diastereoisomers of (3a) is shown in Table 2. In any case, on the basis of

TABLE 1

Optical specific rotations of compounds obtained according to Scheme 3

Compound	$[\alpha]^{25}$ (°)	Absolute configuration	Enantiomeric excess (%)
(5a)	+45.1 [a,b]	*R*	≥70
(6a)	−66.0 [a,b]	*R*	≥70
(7a)	−92.5 [a,c]	*R*	70 [d]
(5b)	+9.2 [a,e]	*R*	≥46
(6b)	+28.9 [a,f]	*R*	≥46
(7b)	+2.0 [g]	*R*	46 [d]

[a] At 589 nm. [b] (*c*, 1 in $CHCl_3$). [c] (*c*, 1 in Me_2CO); $[\alpha]_D^{25}$ −132.0° (*c*, 1 in Me_2CO) is the value for optically pure (−)-(*R*)-(7a). [d] Confirmed by n.m.r. spectroscopy (see Experimental section). [e] (*c*, 3.7 in $CHCl_3$). [f] (*c*, 0.8 in $CHCl_3$). [g] At 365 nm (*c*, 3.3 in Me_2CO); $[\alpha]_{365}^{25}$ −4.3 °C (*c*, 3.3 in Me_2CO) is the value for optically pure (−)-(*S*)-(7b).

the absolute configuration and of the optical purity of the final compound (7a), C-3 of the two major diastereoisomers of (3a) must have *R*-configuration. The minor asymmetric induction obtained with phenylacetaldehyde compared with benzaldehyde (73 *vs.* 85%) can be due to the lower steric hindrance of a benzyl group in cyclic transition states like (8).

TABLE 2

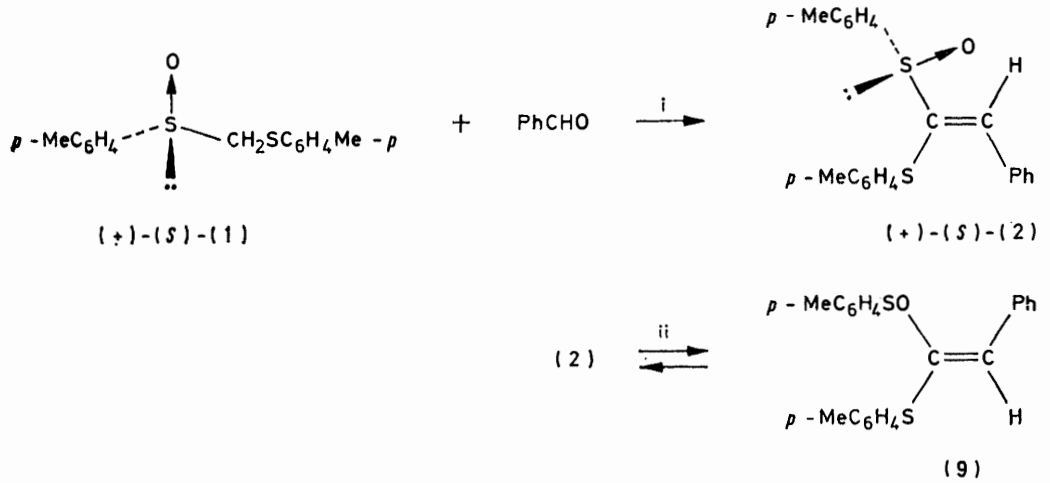
Diastereoisomeric mixture of (3a) obtained from reaction of the lithium derivative of (+)-(*S*)-(1) and PhCHO

Diastereoisomer of (3a) (absolute configuration) [a]	Diastereoisomeric relative ratio (%)
(1*S*,2*S*,3*R*)	55
(1*S*,2*R*,3*R*)	30
(1*S*,2*S*,3*S*)	15
(1*S*,2*R*,3*S*)	0

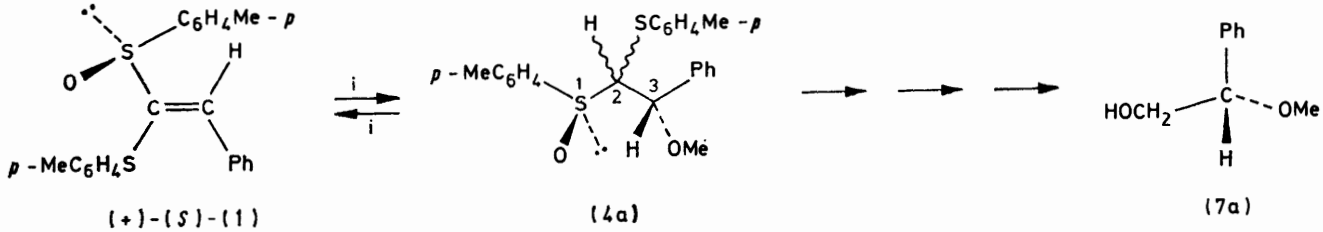
[a] For numbering of chiral centres see (8).

occurs at higher fields than in (2), and the LIS for the latter is much more pronounced than for the former. Moreover, the olefinic proton in racemic (2) is very clearly split in the presence of $Eu(tfc)_3$, while in racemic (9) it is not. Optical purity of (+)-(*S*)-(2) obtained according to Scheme 4 was confirmed by n.m.r. spectroscopy in the presence of $Eu(tfc)_3$, under conditions pre-established on a racemic sample of (2).

The addition of sodium methoxide to (+)-(*S*)-(2) in methanol at reflux led to a reaction mixture containing starting material and four diastereoisomers of (4a) (relative ratio *ca.* 65 : 15 : 12 : 8) in 15% total yield (Scheme 5). According to the previously discussed Scheme 3, (4a) gave the alcohol (−)-(*S*)-(7a) with 60% enantiomeric excess. This Michael addition to (+)-(*S*)-(2) is a thermodynamically controlled reversible process. The isolated product (4a), under the reaction conditions, gave the same reaction mixture: (2) (85%) and (4a) (15%, relative ratio *ca.* 65 : 15 : 12 : 8). On the basis of the absolute configuration and of the optical purity of the final com-



SCHEME 4 *Reagents:* i, Triton B–THF, room temperature; ii, *hν*, MeOH



SCHEME 5 *Reagents:* i, MeONa–MeOH, reflux

The reaction of (+)-(*S*)-(1) with benzaldehyde in THF in the presence of Triton B (*N*-trimethylbenzylammonium hydroxide) at room temperature led, after 24 h, to the new optically pure reagent (+)-(*S*)-(2), with *E*-configuration at the double bond (Scheme 4). The stereoisomer (9), with *Z*-configuration, was obtained by irradiation of (2) in methanol. The stereochemistry at the double bond of (2) and (9) was confirmed by comparison of the n.m.r. spectra and of lanthanide-induced shifts (LIS) of their olefinic protons in the presence of tris[3-(2,2,2-trifluoro-1-hydroxyethylidene)-(+)-camphorato]europium(III) [$Eu(tfc)_3$]. The resonance of the olefinic proton in (9)

TABLE 3

Diastereoisomeric mixture of (4a) obtained from reaction of (+)-(*S*)-(2) and MeONa

Diastereoisomer of (4a) (absolute configuration) [a]	Diastereoisomeric relative ratio (%)
(1*S*,2*R*,3*S*)	65
(1*S*,2*S*,3*S*)	15
(1*S*,2*R*,3*R*)	12
(1*S*,2*S*,3*R*)	8

[a] For numbering of chiral centres see (4a) in Scheme 5.

pound (7a), C-3 of the two more stable, and therefore major, diastereoisomers of (4a) must have *S*-configuration.[12a] Table 3 shows a possible assignment of the absolute configuration of diastereoisomers of (4a), based on molecular models, taking into account unfavourable 1,3-interactions.

Thus, from a single chiral origin [(+)-(*S*)-(1)], asymmetric synthesis of both enantiomers (*R*)- and (*S*)-(7a) was realized, by performing either an E^1 or an N^2 reaction on a chiral carbonyl equivalent.

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded with Varian A-60 (60 MHz) or FT-80 (80 MHz) instruments, using tetramethylsilane as internal standard. I.r. spectra were recorded with a Perkin-Elmer 257 spectrophotometer. Optical rotations were measured at 25 °C on a Perkin-Elmer 141 polarimeter, using a 1-dm tube.

All reactions involving organolithium reagents were carried out in dry tetrahydrofuran (THF) under dry oxygen-free argon, in a semi-closed system by injection through a rubber cap. THF was freshly distilled from $LiAlH_4$.

Organic extracts were dried (Na_2SO_4) and filtered before removal of the solvent at <40 °C under reduced pressure. Silica gel 60—230 mesh (Merck) was used for column chromatography. Distillations were evaporative bulb-to-bulb distillations, at the pressure and oven temperature indicated.

The sulphoxide (+)-(*S*)-(1) was prepared as described.[8] The conditions for each reaction involved in Schemes 3, 4, and 5 were pre-established using racemic (1).

Benzaldehyde was treated with $NaHCO_3$–H_2O, and the products were decanted from the slurry, dried (K_2CO_3), filtered, and distilled under reduced pressure in an atmosphere of dry oxygen-free nitrogen before use. Phenylacetaldehyde was dried (K_2CO_3), filtered, and distilled as described for benzaldehyde.

Typical procedures are fully described for benzaldehyde.

General Procedure for Metallation of p-*Tolyl* p-*Tolylthiomethyl Sulphoxide* (1).—A solution of (1) in dry THF [11 ml per mmol of (1)] was cooled to −40 °C and a solution of 1.6N-Bu^{n}Li in n-hexane (1.1 equiv.) added. The resulting pale yellow solution was stirred at −20 °C for 20 min to ensure complete metallation.

Reaction of the Lithium Derivative of (1) *with Aldehydes.*—To a solution of the lithium derivative of optically pure (+)-(*S*)-(1) (18 mmol) cooled to −78 °C, benzaldehyde (3.7 ml, 36 mmol) was added. After 15 min at −78 °C the reaction was quenched by aqueous NH_4Cl and extracted with Et_2O. The crude product obtained from usual work-up was chromatographed on silica gel (CH_2Cl_2–MeOH) to give a mixture of three diastereoisomers * of (3a) (3.6 g, 91%); $\nu_{max.}$ ($CHCl_3$) 3 450 and 1 035 cm^{-1}; δ ($CDCl_3$) 1.6 (br s, disappeared with D_2O).

In another experiment, the reagents were mixed as before, and aliquots of reaction mixture were withdrawn over a 4 h period, worked up as above, and assayed by a u.v. spectrodensitomer on t.l.c. plates.* No variation in the diastereoisomeric relative ratio of (3a) was observed within experimental error.

In another experiment, compound (1) (3.6 mmol) and PhCHO (7.2 mmol) were allowed to react as before, and *p*-chlorobenzaldehyde (3.6 mmol) was added to the final reaction mixture. No cross-over product was detectable after 3 h at −78 °C.

Phenylacetaldehyde was treated with (+)-*S*-(1) as described above for benzaldehyde to give a diastereoisomeric mixture of (3b) in 85% yield.

O-*Methylation of* (3a).—To a solution of compound (3a) (5.0 g) and Me_2SO_4 (7.5 ml) in CH_2Cl_2 (250 ml), 40% aqueous tetrabutylammonium hydroxide (17.0 g) was added at room temperature. After 3 min, the reaction mixture was made acidic by dropwise addition of 2N-HCl. The reaction mixture was extracted with CH_2Cl_2. Usual work-up and column chromatography on silica gel (CH_2Cl_2–MeOH) gave a mixture of three diastereoisomers * of (4a) (4.7 g, 90%).

Under the same conditions, (3b) gave (4b) in 76% yield.

Reduction of (4a).—Ph_3P (27.7 g) and I_2 (26.8 g) were stirred together in dry MeCN (200 ml) under dry nitrogen until a yellow slurry was obtained. A solution of (4a) (3.0 g) in MeCN (35 ml) was added, followed by addition of powdered NaI (27 g). After stirring for 10 min at room temperature the reaction mixture was taken up in Et_2O and then washed with aqueous $Na_2S_2O_3$, aqueous $NaHCO_3$, and brine. After usual work-up the residue was taken up in n-hexane and filtered from most of the Ph_3P and Ph_3PO. n-Hexane was removed under reduced pressure and the residue chromatographed on silica gel (n-hexane–ethyl acetate) to give (5a) (2.3 g, 68%); $[\alpha]_D$ +45.1° (*c*, 1 in $CHCl_3$); δ ($CDCl_3$) 2.27 and 2.31 (each 3 H, s, *p*-*Me*Ar), 3.31 (3 H, s, OMe), 4.36, 4.47 (AB system, 2 H, *J* 4.2 Hz, CHCH), and 6.91—7.40 (13 H, m, ArH).

Reduction of (4b).—I_2 (3.7 g) was suspended in MeCN (15 ml) under nitrogen. To this suspension, $(Me_2N)_3P$ (2.7 ml) was slowly added at room temperature. To the resulting clear solution, a solution of (4b) (3.0 g) in MeCN (15 ml) was added dropwise followed by addition of NaI (1.1 g). After stirring at room temperature overnight, the reaction mixture was taken up in Et_2O and washed with aqueous $Na_2S_2O_3$, aqueous $NaHCO_3$, and brine. Usual work-up and column chromatography on silica gel (n-hexane–ethyl acetate) gave (5b) (1.6 g, 55%); $[\alpha]_D$ +9.2° (*c*, 3.7 in $CHCl_3$); δ ($CDCl_3$) 2.30 (6 H, s, 2 × *p*-*Me*Ar), 3.01—3.05 (2 H, m, CH_2), 3.31 (3 H, s, OMe), 3.60—3.80 (1 H, m, C*H*OMe), 4.40 [1 H, d, *J* 2.7 Hz, C*H*(SAr)$_2$], and 6.87—7.29 (13 H, m, ArH).

Hydrolysis of (5a).—To solution of (5a) (0.9 g) in dioxan (15 ml) were added water (15 ml), I_2 (0.74 g), and $NaHCO_3$ (0.23 g) under nitrogen. After 10 min at room temperature a second portion of I_2 (0.39 g) and $NaHCO_3$ (0.12 g) was added and the reaction mixture was stirred for an additional 10 min.

(a) *Isolation of aldehyde* (6a). To the reaction mixture cooled to 0 °C was added an excess of $Na_2S_2O_3$. Extraction with Et_2O, usual work-up, and column chromatography on silica gel (CH_2Cl_2) gave crude 2-methoxy-2-phenylacetaldehyde (6a) (67%); $[\alpha]_D$ −66.0° (*c*, 1 in $CHCl_3$) [lit.,[22] −95° (*c*, 3.7 in $CHCl_3$)]; $\nu_{max.}$ (film) 1 730 cm^{-1}.

Under the same conditions, (5b) gave 2-methoxy-3-phenylpropionaldehyde (6b) in 43% yield; $[\alpha]_D$ +28.9° (*c*, 0.8 in $CHCl_3$); δ (CD_3COCD_3) 2.79—3.19 (2 H, m, CH_2), 3.37 (3 H, s, OMe), 3.79—3.97 (1 H, m, C*H*OMe), 7.26 (5 H, s, Ph), and 9.65 (1 H, d, *J* 1.5 Hz, CHO).

* Diastereoisomeric relative ratios of both (3a) and (4a) were determined by a K. Zeiss PMQ III Stahl spectrodensitometer ($\lambda_{max.}$ 250 nm), after application of samples (crude mixture of stereoisomers) on t.l.c. silica gel 60 F_{250} plates (Merck) and elution with CH_2Cl_2–MeOH (98 : 2 v/v).

(b) *Reduction* in situ *to alcohol* (7a). To the reaction mixture cooled to 0 °C was added an excess of $NaBH_4$; 2N-HCl was added to neutral pH and the reaction mixture was extracted with Et_2O. Usual work-up and column chromatography on silica gel (CH_2Cl_2–MeOH) gave crude 2-methoxy-2-phenylethanol (7a) in 66% yield, which was distilled at 65 °C and 0.1 Torr (lit.,[23] 82—85 °C at 3 Torr); $[\alpha]_D$ −92.5° (*c*, 1 in Me_2CO); δ ($CDCl_3$) 2.48br (1 H, s, OH), 3.30 (3 H, s, OMe), 3.50—3.75 (2 H, m, CH_2), 4.22—4.37 (1 H, m, CH), and 7.32 (5 H, s, Ph).

To a solution of (7a) in $CDCl_3$ (*ca.* 50 mg ml^{-1}), $Eu(tfc)_3$ [0.07 mmol per mmol of (7a)] was added: the n.m.r. spectrum of the resulting solution showed that the parent OMe singlet (δ 3.30) in (7a) was split into two signals (δ 4.19 and 4.27), relative ratio *ca.* 85 : 15 [under the same conditions, relative ratio is 1 : 1 for racemic (7a)].

Following the above described procedure, (5b) gave 2-methoxy-3-phenylpropan-1-ol (7b) (48%), which was distilled at 100 °C and 2 Torr; $[\alpha]_{365}$ +2.0° (*c*, 3.3 in Me_2CO); δ ($CDCl_3$) 1.94br (1 H, s, OH), 2.74—2.89 (2 H, m, PhCH_2), 3.39 (3 H, s, OMe), 3.43—3.71 (3 H, m, CH_2OH and CH), and 7.27 (5 H, s, Ph).

Enantiomeric excess (e.e.) of (7b) was confirmed by n.m.r. ($CDCl_3$) spectroscopy according to Mosher's procedure [24] in the presence of $Eu(fod)_3$ [25] (0.7 mmol per mmol of Mosher's ester): the parent overlapped *Me*OCCF_3 quartets (δ 3.51—3.59) were split into two separate signals (δ 5.86 and 5.98), relative ratio *ca.* 3 : 1.

(−)-(R)-2-*Methoxy*-2-*phenylethanol* (−)-(R)-(7a).—(−)-(*R*)-2-Methoxy-2-phenylacetic acid (Fluka) was methylated (CH_2N_2) and reduced ($LiAlH_4$). Distillation at 65 °C and 0.1 Torr gave pure (−)-(*R*)-(7a); $[\alpha]_D$ −132.0° (*c*, 1 in Me_2CO) [lit.,[26] $[\alpha]_D^{29}$ −127.0 (*c*, 6.4 in EtOH)], e.e. 100% confirmed by n.m.r. spectra in the presence of $Eu(tfc)_3$.

(−)-(S)-2-*Methoxy*-3-*phenylpropan*-1-*ol* (−)-(S)-(7b).—(−)-(*S*)-3-Phenyl-lactic acid (Fluka) was methylated (MeI–Ag_2O–DMF) and reduced ($LiAlH_4$). Distillation (at 100 °C and 2 Torr) gave pure (−)-(*S*)-(7b); $[\alpha]_{365}$ −4.3° (*c*, 3.3 in Me_2CO) e.e. 100% confirmed by n.m.r. spectra according to Mosher's procedure in the presence of $Eu(fod)_3$.

Synthesis of (E)-(+)-(S)-1-p-*Tolysylphinyl*-1-p-*tolylthio*-2-*phenylethylene* (+)-(S)-(2).—To a solution of (+)-(*S*)-(1) (1.0 g) in THF (3 ml), PhCHO (0.55 ml) and Triton B (40% in MeOH; 0.4 ml) were added and the mixture was stirred at room temperature for 24 h. Acetic acid (55 μl) and water (0.5 ml) were added. Extraction with Et_2O, usual work-up, and column chromatography on silica gel ($CHCl_3$) gave the crude product, which was recrystallized from MeOH to give pure (+)-(*S*)-(2) (0.86 g, 66%), m.p. 86—87 °C; $[\alpha]_D$ +368.0° (*c* 1, in $CHCl_3$,); $\nu_{max.}$ ($CHCl_3$) 1 041 cm^{-1}; δ ($CDCl_3$) 2.26 (3 H, s, *p*-*Me*C_6H_4S), 2.34 (3 H, s, *p*-*Me*C_6H_4SO), 6.95—7.93 (13 H, m, ArH), and 8.08 (1 H, s, CH).

To a solution of racemic (2) in $CDCl_3$ (*ca.* 45 mg ml^{-1}), aliquots of $Eu(tfc)_3$ were added, in the range 0.06—0.22 mmol per mmol of (2). Under these conditions, the parent singlet of the olefinic proton of (2) (δ 8.08) was split into two signals: plotting LIS *vs.* mg of added $Eu(tfc)_3$, two straight lines with the same intercept (8.08) and different slope (0.15, 0.16) were obtained. Under the same conditions, (+)-(*S*)-(2), $[\alpha]_D$ +368.0°, showed only a signal due to the olefinic proton, fitting the line with slope 0.15. This indicates that (+)-(*S*)-(2) obtained as above described is optically pure within experimental error.

(Z)-1-p-*Tolysulphinyl*-1-p-*tolythio*-2-*phenylethylene* (9).—Irradiation of a solution of (2) in MeOH and chromatography on silica gel–$AgNO_3$ afforded pure (9); δ ($CDCl_3$) 2.25 (3 H, s, *p*-*Me*C_6H_4S), 2.33 (3 H, s, *p*-*Me*C_6H_4SO), 6.83—7.46 (14 H, m, CH and ArH); δ{$CDCl_3$, in the presence of $Et(tfc)_3$ [0.22 mmol per mmol of (9)]}: LIS of *ca.* 0.3 p.p.m. for the olefinic proton and no chiral LIS.

Addition of MeONa *to* (+)-(S)-(2) *in Methanol*.—Sodium (50 mg) was dissolved in absolute MeOH (10 ml) under dry oxygen-free argon. A solution of (+)-(*S*)-(2) (0.76 g) in absolute MeOH (5 ml) was added and the reaction mixture was refluxed for 2 h. AcOH (125 μl) was added and the solvent was removed under reduced pressure. The residue was taken up with CH_2Cl_2–H_2O and the organic layer was separated and worked up as usual. After column chromatography on silica gel (CH_2Cl_2), (4a) (0.12 g, 15%) was obtained as a mixture of four diastereoisomers (relative ratio *ca.* 65 : 15 : 12 : 8).*

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* Diastereoisomeric relative ratios of both (3a) and (4a) were determined by a K. Zeiss PMQ III Stahl spectrodensitometer ($\lambda_{max.}$ 250 nm), after application of samples (crude mixture of stereoisomers) on t.l.c. silica gel 60 F_{250} plates (Merck) and elution with CH_2Cl_2–MeOH (98 : 2 v/v).

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