Tetrahedron Vol. 44, No. 16, pp 5243 to 5251, 1988
Printed in Great Britain

0040–4020/88 $3.00 + .00
Pergamon Press plc

ORGANOSULPHUR COMPOUNDS-LXIX[1]
OPTICALLY ACTIVE SULPHINATES: A NEW TYPE OF ENANTIOSELECTIVE ASYMMETRIC SYNTHESIS AND KINETIC RESOLUTION[2]

JÓZEF DRABOWICZ, SŁAWOMIR LEGĘDŹ and MARIAN MIKOŁAJCZYK*

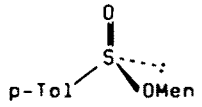
Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Department of Organic Sulphur Compounds, 90-362 Łódź, Boczna 5, Poland

(*Received in UK* 16 *May* 1988)

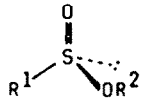
Abstract - Optically active sulphinates with the sulphur atom as a sole centre of chirality are prepared by two methods. The first involves the reaction of symmetrical sulphites with tert-butylmagnesium chloride in the presence of optically active aminoalcohols. This new asymmetric, enantioselective synthesis affords t-butylsulphinates with 40-70% enantiomeric excess values. The second approach is based on a new type of kinetic resolution taking place when racemic sulphinates are reacted with tert-butylmagnesium chloride complexed by optically active alkaloid bases. Both the recovered sulphinates and sulphoxides formed in this reaction show moderate optical purities.

INTRODUCTION

Chiral, non-racemic sulphinates have recently received considerable attention particularly as starting materials in the synthesis of sulphoxides[3] and as model compounds in the studies of nucleophilic substitution at sulphur[4]. The first optically active sulphinates were obtained by Phillips[5] as early as 1925. (-)-(S)--Menthyl p-toluenesulphinate (1) prepared by Phillips is up to now the most important precursor of chiral sulphoxides[6].



1



2

More recently, much effort has been devoted to the synthesis of optically active sulphinates (2) with the sulphur atom as a sole asymmetry centre. The first synthesis of such esters (2, R^1=Ar) involved asymmetric oxidation of the corresponding sulphenates with (+)-monoperoxycamphoric acid[7]. The optical purity of the sulphinates 2 obtained in this way was, however, very low[8]. In this regard, a more efficient and more general method to produce optically active sulphinates is the low temperature condensation of sulphinyl chlorides with achiral alcohols in the presence of optically active tertiary amines which affords the esters 2 (R^1=Alk,Ar) with optical purities up to 50%[10,11]. Kinetic resolution of racemic

sulphinates 2 upon treatment with chiral Grignard reagents[12] or their direct optical resolution via β-cyclodextrin inclusion complexes[13] give optically active sulphinates 2 with moderate to high enantiomeric excess only in specific cases. The recently developed asymmetric synthesis of 2, which involves esterification of arylsulphinic acids with achiral alcohols using optically active carbodiimides[14] as condensing agents or alkylation of arylsulphinic acids with optically active O-alkyl isoureas[15], results in the formation of the corresponding sulphinates (2, R^1=Ar) with optical purities below 10%.

From the point of view of availability of chiral esters 2 in a high state of optical purity, an important step toward obtaining these type of compounds was the first stereoselective synthesis of 2 based on the acid-catalysed alcoholysis of optically active sulphinamides[16]. However, even this approach to optically active sulphinates 2 has some serious limitations connected with the availability and optical stability of a chiral substrate and the fact that the reaction may proceed with diverse stereochemistry (inversion and/or retention) depending on various factors[4,17] such as the structure of both substrates, solvent and the presence of inorganic salts.

In this paper we wish to describe two novel approaches to optically active sulphinates 2. The first approach involves a new type of asymmetric synthesis of t-butylsulphinates while the second involves formation of optically active sulphinates together with optically active sulphoxides in a new kinetic resolution process. Both of the above methods are based on our earlier observation[18] that the reaction between dialkyl sulphites and bulky Grignard reagents (for example t-BuMgCl) is stopped at the mono-substitution step and leads to the corresponding sulphinates.

$$(RO)_2SO + Bu^tMgCl \longrightarrow Bu^tS(O)OR$$

RESULTS AND DISCUSSION

Asymmetric Synthesis of Alkyl t-Butylsulphinates (3). The reaction between dialkyl sulphites and t-butylmagnesium chloride mentioned above represents an interesting type of transformation in which a chiral product (sulphinate) is formed from a prochiral substrate (sulphite). Therefore, it was quite reasonable to expect that this reaction may be utilized in the synthesis of optically active sulphinates provided that it will be carried out under asymmetric conditions. It was gratifying to find that such a possibility existed because Grignard reagents are known to form chiral complexes with optically active amines[19]. Thus, a new asymmetric synthesis of optically active alkyl t-butylsulphinates (3) reported here involves the reaction between dialkyl sulphites (4) and t-butylmagnesium chloride (5) complexed by optically active amines (6) as chiral auxiliaries.

$$ROS(O)OR + Bu^tMgCl \xrightarrow{6} Bu^tS(O)OR \qquad \text{(eq.1)}$$

4 5 3

For 3,4
a, R=Me
b, R=Et
c, R=Pr^n
d, R=Pr^i
e, R=Bu^n

For 6
a, (-)-Quinine
b, (+)-Quinidine
c, (+)-Cinchonine
d, (-)-N-Methylephedrine
e, (-)-Brucine
f, (-)-Sparteine
g, (+)-N,N-Dimethyl-α-methylbenzylamine
h, (-)-N,N-Dimethylmyrtanylamine
i, (+)-N-Methylamphetamine

Optically active amines, 6a-i, used in this work were either commercially available alkaloids or were prepared from optically active α-methylbenzylamine and myrtanylamine. All condensation reactions were carried out according to the following standard procedure. The chiral complexes of 5 with 6 were obtained by addition of an appropriate amount of optically active amine 6 to a solution of t-butylmagnesium chloride (5) in ether followed by heating for a short time. Then, sulphite 4 was added dropwise to the resulting solution and the reaction mixture refluxed for a proper time (see Table I). After a typical Grignard work-up (hydrolysis with dilute hydrochloric acid, extraction with diethyl ether) optically active sulphinates 3 were isolated by distillation. The optical rotations, enantiomeric excess values and absolute configurations of 3 obtained as described above together with other experimental data are collected in Table I.

TABLE I. Asymmetric Synthesis of Optically Active Alkyl t-Butylsulphinates, t-BuS(O)OR, (3)

Exp.	Sulphite 4,R	Amine 6	Molar ratio 4:5:6	Reaction time (h)	Sulphinate 3	Yield[a] (%)	$[\alpha]_{589}$(°)	ee (%)	Abs. Conf.
1	4a,Me	6f	2:1:10	8	3a	65	-1.7	1.3	S
2	4a,Me	6g	2:1:1	9	3a	61	-0.9	0.7	S
3	4a,Me	6h	4:2:1	10	3a	62	+1.3	1.0	R
4	4a,Me	6i	4:2:1	10	3a	64	-0.8	0.6	S
5	4a,Me	6a	1:4:2	8	3a	62	+72.0	53.3[b]	R
6	4a,Me	6a	1:8:4	13	3a	66	+70.0	51.8	R
7	4b,Et	6a	1:5:2.5	9	3b	62	+100.0	69.0	R
8	4b,Et	6a	1:8:4	14	3b	60	+96.2	66.4	R
9	4b,Et	6f	2:1:10	12	3b	71	-0.8	0.6	S
10	4c,Pr^n	6a	1:2:1	14	3c	50[c]	+62.0	46.2	R
11	4c,Pr^n	6a	1:3:1	14	3c	79	+63.2	47.1	R
12	4c,Pr^n	6a	1:4:2	14	3c	77	+81.7	60.8	R
13	4c,Pr^n	6a	1:8:4	12	3c	79	+97.7	72.7	R
14	4c,Pr^n	6a	1:16:8	12	3c	79	+99.7	74.2	R
15	4c,Pr^n	6f	1:2:1	12	3c	68	-1.3	1.0	S
16	4c,Pr^n	6b	1:8:4	12	3c	69	-25.2	20.0	S
17	4c,Pr^n	6c	1:8:4	12	3c	63	-37.9	28.2	S
18	4c,Pr^n	6d	1:8:4	12	3c	67	+15.9	11.8	R
19	4c,Pr^n	6e	1:8:4	12	3c	69	+3.3	2.5	R
20	4d,Pr^i	6a	1:8:4	14	3d	70	+54.3	43.0	R
21	4d,Pr^i	6b	1:8:4	14	3d	69	-25.3	20.0	S
22	4e,Bu^n	5a	1:8:4	18	3e	84	+83.3	62.4	R

[a]Yield refers to the product with purity higher than 98% (GLC assay); [b]52% from ^{1}H-NMR; [c]In mixture with 35% of 4c

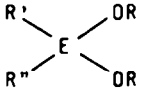
It is evident from the results given in Table I that the new asymmetric synthesis of sulphinates 3 is efficient in terms of both chemical and optical yield. The enantiomeric excess values of 3 were often found to be in the range 40 to 75%. Only in the case of experiments with optically active tertiary amines, 6f - i as asymmetric complexing agents were the values of ee very low (entries 1 to 4 and 9,15). Far better results were obtained with aminoalcohols as chiral auxiliaries and the highest ee values (~70%) of 3 were observed for

the reactions with quinine 6a. It should be pointed out that the highest value of optical purity (74%) observed for 3c (entry 14) is much better than those obtained by any other known method of asymmetric synthesis of sulphinates.

An inspection of the results in Table I reveals also an interesting relationship between the enantiomeric excess values of sulphinates 3 and the stoichiometry of reagents. Usually, a high degree of asymmetric induction is observed when the chiral Grignard reagent is prepared from t-butylmagnesium chloride (5) and amine 6 in a 2:1 molar ratio and it is used in a large molar excess with respect to sulphite 4 - the third reaction component. For example, the reaction of di-n-propyl sulphite (4c) with t-butylmagnesium chloride (5) and quinine (6a) used in a 1:2:1 molar ratio affords the corresponding sulphinate 3c with 46.2% ee. When the ratio of the same reagents is 1:16:8, the sulphinate 3c with 74.2% ee is obtained.

Although the present experimental data do not allow us to propose a detailed structural model for the asymmetric reaction in question, it should be emphasized that there is a clear relationship between the chirality at sulphur in sulphinates 3 formed and the chirality at the carbon atom bearing the hydroxy group in the aminoalcohols, 6a-d, used as chiral auxiliaries. For example, whereas the reaction of diisopropyl sulphite (4d) with the complex of 5 and quinine (6a) affords (+)-(R)-isopropyl t-butylsulphinate (3d), the use of quinidine (6b) promotes the formation of (-)-(S)-enantiomer of 3d. Similarly, the reaction of di-n-propyl sulphite (4c) with 5 in the presence of cinchonine (6c) and (-)-N-methylephedrine (6d), having also opposite configurations at the carbon atom connected with the hydroxy group, results in the formation of n-propyl t-butylsulphinate (3c) with (-)-(S) and (+)-(R)-chirality at sulphur, respectively.

Finally, one should note that the asymmetric synthesis of sulphinates from prochiral sulphites exemplifies a rather general type of asymmetric synthesis of heteroorganic compounds from a prochiral substrates of a general formulae shown below.

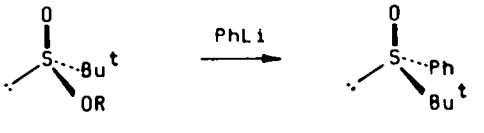


E=P,Si,As etc

Our current studies are directed towards the asymmetric synthesis of phosphorus and silicon compounds using this approach.

Optical Purity and Absolute Configuration of Alkyl t-Butylsulphinates (3)[20]

To determine the extent and direction of asymmetric induction the esters 3 obtained as described above were converted into optically active t-butyl phenyl sulphoxide (7a) as a configurational standard. It was assumed that the reaction of phenyllithium with 3 leading to 7 (see eq.2) proceeds stereospecifically with inversion of configuration at the sulphinyl sulphur atom. The results of these experiments are summarized in Table II.

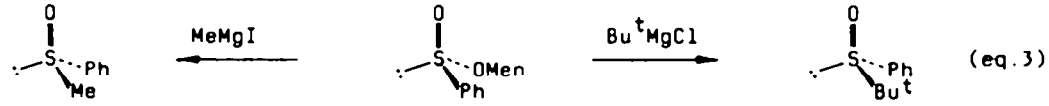


(+)-(R)-3 (+)-(R)-7a (eq.2.)

TABLE II. Conversion of Optically Active Alkyl t-Butylsulphinates, t-BuS(O)OR,(3) into Optically Active t-Butyl Phenyl Sulphoxide, tBuS(O)Ph, (7a)

Sulphinate 3			Sulphoxide 7a		
3, R	$[\alpha]_{589}$(c,MeOH) (°)	Abs. Conf.	$[\alpha]_{589}$(c,$CHCl_3$) (°)	ee [%]	Abs. Conf.
3a, Me	+72.0 (5.0)	R	+93.1 (1.7)	53.3	R
3b, Et	+100.0 (3.9)	R	+120.5 (2.0)	69.0	R
3c, Pr^n	+95.5 (4.9)	R	+124.1 (3.0)	71.1	R
3d, Pr^i	-25.3 (2.0)	S	-34.9 (1.7)	20.0	S
3e, Bu^n	+82.8 (2.0)	R	+108.2 (2.1)	62.0	R

The enantiomerically pure, dextrorotatory t-butyl phenyl sulphoxide (7a) was obtained by Montanari et al.[21] in the reaction of (-)-(S)-menthyl benzenesulphinate (8) with t-butylmagnesium chloride. The absolute configuration of 7a was established as shown below.



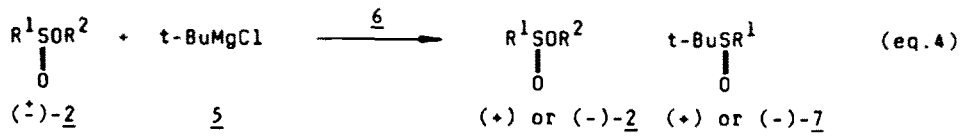
(+)-(R)-9 $[\alpha]_{589}$+178.3° (-)-(S)-8 $[\alpha]_{589}$-206.0° (+)-(R)-7a $[\alpha]_{589}$+174.6°

Since (-)-(S)-8 was found to give (+)-(R)-methyl phenyl sulphoxide (9) on treatment with methylmagnesium iodide and (+)-t-butyl phenyl sulphoxide (7a) on treatment with t-butylmagnesium chloride, the R-configuration was assigned to the latter based on the very reasonable assumption that both reactions follow the same steric course. With regard to the optical rotation of t-butyl phenyl sulphoxide (7a), it is worthy of mention that the recent determination of optical purity of 7a[22] using ^{1}H-NMR spectroscopy and chiral shift reagent gave a value which is in excellent agreement (±1%) with that reported by Montanari.

In the present study the optical purity of (+)-(R)-methyl t-butylsulphinate (3a) determined by chemical method was also checked by ^{1}H-NMR techniques using tris-[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]-europium (TFMC) as a chiral shift reagent. The ^{1}H-NMR spectrum of racemic 3a consists of two singlets at 1.13 and 3.69 ppm due to the t-butyl and methyl protons, respectively. The ^{1}H-NMR spectrum of optically active 3a, $[\alpha]_{589}$+72.0°, recorded in the presence of TFMC shows two pairs of singlets of unequal intensity at 1.37, 1.40 and 4.15, 4.20 ppm. The enantiomeric excess in the sample studied determined by integration of the singlets corresponds to 52% which is in very good agreement with the value (53.3%) obtained from the chemical correlation.

Kinetic Resolutiion of Sulphinates (2). Although the new enantioselective, asymmetric synthesis of alkyl t-butylsulphinates (3) is quite satisfactory from the point of view of chemical and optical yield, it may only be applied to the preparation of optically active sulphinates which contain a bulky group attached to the sulphinyl sulphur atom. This limitation should be, in principle, easily overcome if instead of prochiral sulphites 4, racemic sulphinates 2 are subjected to treatment with the complexes of Grignard reagent and optically active amines 6. In such a case kinetic resolution of racemic 2 would be expected to occur leading

simultaneously to optically active 2 and optically active sulphoxides 7 (eq.4). Preliminary experiments fully confirmed our expectations.



For 2
a, R^1=p-Tol, R^2=Me
b, R^1=p-Tol, R^2=Et
c, R^1=p-Tol, R^2=Pr^i
d, R^1=p-Tol, R^2=Bu^t
e, R^1=p-Tol, R^2=CH_2Bu^t
f, R^1=Ph, R^2=Pr^h
g, R^1=Me, R^2=Pr^n
h, R^1=Me, R^2=CH_2Bu^t

For 6
a, (-)Quinine
b, (-)Quinidine

For 7
a, R^1=Ph
b, R^1=p-Tol
c, R^1=Me

A typical experimental procedure for kinetic resolution of sulphinates 2 is as follows. To a solution of t-butylmagnesium chloride (5) in ether a half molar equivalent of quinine is added and the resulting solution is heated for a short time. Then, racemic ester 2 (one equivalent) is added dropwise and the reaction mixture refluxed for 30 min. The typical work-up consisting of quenching with diluted hydrochloric acid and extraction with ether affords a mixture of optically active sulphinate 2 and sulphoxide 7 which are separated by column chromatography. The optical rotations, enantiomeric excess values and absolute configurations of sulphinates 2 and sulphoxides 7 are given in Table III.

TABLE III. Kinetic Resolution of Racemic Sulphinates, $R^1S(O)OR^2$, in the Reaction with t-Butylmagnesium Chloride (5) Complexed by Quinine (6a)

Sulphinate 2							Sulphoxide, 7, t-BuS(O)R^1				
2, R^1	R^2	Yield[a] [%]	$[\alpha]_{589}$ (EtOH)	ee[b] [%]	Abs. Conf.	7, R^1	Yield[a] [%]	$[\alpha]_{589}$ (EtOH)	ee [%]	Abs. Conf.
2a, p-Tol	Me	25	-11.0	5.0	S	7b, p-Tol	75	-39.0	18.4	S
2b, p-Tol	Et	30	-22.0	10.5	S	7b, p-Tol	65	-56.0	30.2	S
2c, p-Tol	Pr^i	90	-9.2	5.0	S	7b, p-Tol	8	-124.3	64.7	S
2c, p-Tol	Pr^i	33	-64.3	33.0	S	7b, p-Tol	66	-25.2	13.1	S
2c, p-Tol	Pr^i	40	-54.1	28.0	S	7b, p-Tol	60	-77.9	40.5	S
2c, p-Tol	Pr^i	88	+15.3[d]	8.0	S	7b, p-Tol	12	+75.6[d]	39.3	R[d]
2d, p-Tol	Bu^t	80	-3.0	2.0	R[d]	7b, p-Tol	20	-15.7	8.2	S
2e, p-Tol	CH_2Bu^t	60	-32.5	7.5	S	7b, p-Tol	40	-38.3	19.3	S
2f, Ph	Pr^h	25	-46.5	27.0	S	7a, Ph	75	-38.6[e]	21.8	S
2g, Me	Pr^n	50	-10.0	6.0	S	7c, Me	38	0.0		
2h, Me	CH_2Bu^t	50	-16.0	10.2	S	7c, Me	31	0.0		

[a] Based on the isolated product by column chromatography; [b] Calculated based on the following data: $[\alpha]_{589}$=218.9°(EtOH) for (S)-2a; $[\alpha]_{589}$=-208.4° (EtOH) for (S)-2b; $[\alpha]_{589}$=-202.4°(EtOH) for (S)-2c; $[\alpha]_{589}$=-129.8°(EtOH) for (S)-2d from ref.16; $[\alpha]_{589}$=-185.9°(EtOH) for (S)-2e; $[\alpha]_{589}$=-172.2°(EtOH) for (S)-2f; $[\alpha]_{589}$=-166.6°(EtOH) for (S)-7g; $[\alpha]_{589}$=-156.9°(EtOH) for (S)-7h from ref.10.; [c] Calculated based on the following data: $[\alpha]_{589}$=+190.0°(EtOH) for (R)-7b from K.Mislow et.al., J.Am.Chem.Soc., 87, 1958 (1965); $[\alpha]_{589}$=+174.6°($CHCl_3$) for (R)-7a from ref.21; [d] These data refer to the reaction carried out in the presence of quinidine (6b); [e] In $CHCl_3$ solution.

In spite of the fact that sulphinates 2 obtained in this way show only moderate enantiomeric excess, this type of kinetic resolution represents a general and simple approach to optically active sulphinates with the sole chiral centre at sulphur. As expected, one observes in this type of reaction a strong dependence of the ee-values of esters 2 and sulphoxides 7 on their chemical yield. For example, when the reaction of isopropyl p-toluenesulphinate 2c with the complex of 5 and 6a was stopped at an early stage, the recovery of 2c and yield of 7b were 90 and 8%, respectively, and the optical purity of the recovered sulphinate 2c was only 5% and that of the sulphoxide 7b formed was 64.7%. However, when the reaction was carried out for a longer time, 2c and 7b were isolated in 33 and 66% yield, with optical purities of 33 and 13.1%, respectively. Similarly as in the asymmetric synthesis case, the use of quinine (6a) and quinidine (6b) as complexing agents leads to the formation of sulphinates 2 and consequently sulphoxides 7 with opposite configurations at sulphur. This result reflects once again the important influence of the aminoalcohol moiety configuration in 6 on the direction of asymmetric induction in our reactions.

EXPERIMENTAL PART

Infrared spectra were recorded on a Perkin-Elmer 437 Spectrophotometer using liquid films. ^{1}H-NMR spectra were obtained with a Perkin-Elmer R-20 spectrometer (60 MHz) and Tesla spectrometer (80 MHz) in $CDCl_3$ solutions using Me_4Si as an internal standard. The optical activity measurements were done on a Perkin-Elmer 241 MC photopolarimeter. Mps and Bps are not corrected. Diethyl ether and tetrahydrofuran were distilled from lithium aluminium hydride before use. Petroleum ether and benzene were distilled from sodium.

The following optically active amines 6 were used in the present work: 6a, (-)-quinine, $[\alpha]_{589}$-145.2° (ethanol), mp 172-173°C; 6b, (+)-quinidine, $[\alpha]_{589}$+262.0° (ethanol), mp 169-170°C; 6a, (+)-cinchonine, $[\alpha]_{589}$+229°(ethanol), mp 259-261°C; 6d, (-)-N-methylephedrine, $[\alpha]_{589}$-29.5° (methanol), mp 87-88°C; 6e, (-)-brucine, $[\alpha]_{589}$-120.5° (chloroform), mp 174-176°C; 6f, (-)-sparteine, $[\alpha]_{589}$-5.9° (benzene), mp 30-31°C; 6g, (+)-N,N-dimethyl-α-methylbenzylamine, $[\alpha]_{589}$+65.3° (neat); 6h, (-)-N,N-dimethylmyrtanylamine, $[\alpha]_{589}$-28.6° (chloroform); 6i, (+)-N-methylamphetamine, $[\alpha]_{589}$+3.32° (neat).

Symmetrical sulphites 4 were prepared from thionyl chloride and the corresponding alcohols and were purified by distillation.
Dimethyl sulphite (4a): bp. 65°/60 mmHg (lit.[23] bp 124-127°/760 mmHg);
diethyl sulphite (4b): bp 55°/15 mmHg (lit.[23] bp 158°/760 mmHg);
di-n-propyl sulphite (4c): bp 52°/1.5 mmHg (lit.[23] bp. 89°/15 mmHg);
di-i-propyl sulphite (4b): bp 60°/7 mmHg (lit.[23] bp. 78°/20 mmHg);
di-n-butyl sulphite (4e): bp 81°/4 mmHg (lit.[23] 114-118°/15 mmHg)

Racemic sulphinates 2 were obtained from the corresponding sulphinyl chlorides and alcohols according to the method of Douglass[24]. They were purified by simple distillation with the exception of 2d which undergoes decomposition under distillation conditions (0.01 mmHg). This compound was virtually pure (^{1}H-NMR and TLC assay) after simple removal of ether following extractive work-up.

Asymmetric Synthesis of Sulphinates 3: General Procedure. To a three-necked flask equipped with a mechanical stirrer and a water cooling system containing a solution of t-butylmagnesium chloride (prepared from 0.02 mol of t-butyl chloride and 0.02 mol of magnesium) in ether (40 ml) a solution of the appropriate amine 6 (0.04 mol) in ether (~100 ml) is added. Formation of a precipitate and the tendency toward rapid rise in temperature during addition indicate that the formation of a complex is occurring. The mixture is stirred and refluxed for

20 min. To this stirred mixture is added dropwise, over a 20 min period, a solution of the corresponding sulphite 4 (in amounts given in Table I) in ether (10--20 ml). The mixture is stirred under reflux for the appropriate time (see Table I) and after cooling to room temperature quenched with a 10% solution of hyrochloric acid. After being stirred the layers are separated and the ether phase is extracted twice with 5% solution of sulphuric acid and washed twice with 5% solution of potassium carbonate and water and than dried over magnesium sulphate. After evaporation of ether, the crude sulphinate 3 are purified by distillation. Physical properties and spectroscopic data (^{1}H-NMR and IR) of optically active sulphinates 3 were in good agreement with the literature data for racemic esters 3. The yields and optical rotations of sulphinates 3 obtained in this way are collected in Table I.

Kinetic Resolution of Sulphinates 2. General Procedure. To a three-necked flask equipped with a mechanical stirrer and a water cooling system containing a solution of t-butylmagnesium chloride in ether (50 ml/100 mmol) a solution of the appropriate amine 6 (in amounts which allow to keep the ratio of reagents given in Table III) in ether is added. The mixture is refluxed with stirring for 20 min. Next, to the stirred mixture is added dropwise at room temperature, over a 20 min period, a solution of racemic sulphinates 2 in ether (in a ratio given in Table III). The tendency toward rapid rise in temperature during addition indicates that the reaction is occurring. The mixture is stirred for 30 min at room temperature and worked up by addition of 10% solution of hydrochloric acid. After being stirred the layers are separated and the water phase is extracted twice with methylene chloride (30 ml). The combined organic solutions are extracted with 5% solution of sulphuric acid and washed successively with 5% sodium bicarbonate solution, and water and than dried over magnesium sulphate. The solvents are removed at reduced pressure to give a mixture of the partially resolved sulphinate 2 and the corresponding sulphoxide 7. This mixture is chromatographed on silica gel (Merck 60-230 mesh). Sulphinates 2 are eluted with a hexane-ether mixture. Careful removal of the solvent under reduced pressure gives the virtually pure, optically active sulphinate 2 (TLC, ^{1}H-NMR and IR assay). Elution with methanol affords the corresponding sulphoxides 7. Removal of the solvent gives material exhibiting ^{1}H-NMR and IR spectra consistent with the assigned structure. The yields and optical rotations of sulphinates 2 and sulphoxides 7 obtained in this way are collected in Table III.

Conversion of Optically Active Alkyl t-Butylsulphinates (3) into Optically Active t-Butyl Phenyl Sulphoxide (7a). General Procedure. To a solution of phenyllithium |prepared from 0.471 g (0.003 mol) of bromobenzene and lithium (0.042 g, 0.003 mol)| in ether (20 ml) a solution of optically active sulphinate 3 (0.0015 mol) in ether (5 ml) is added at room temperature. The mixture is refluxed for 20 min. Next, the reaction mixture is cooled to room temperature and worked up by quenching with saturated aqueous ammonium chloride solution (20 ml). The organic layer is than separated and the water solution is extracted with chloroform (2 x 15 ml). The combined organic solutions are washed successively with 5% solution of sodium bicarbonate (5 ml) and water (15 ml) and dried over magnesium sulphate. Evaporation of the solvent gives the crude product in yields over 70%. Thin layer chromatography of the crude sulphoxide 7a afforded pure (TLC,IR,^{1}H-NMR assay) optically active t-butyl phenyl sulphoxide (7a) spectroscopic data of which were identical with an authentic sample of racemic mixture. Optical rotations and optical purities of t-butyl phenyl sulphoxide (7a) obtained in these reactions are collected in Table II.

Acknowledgement: The financial support of this work by the Polish Academy of Sciences within the research project CPBP 01.13 is gratefully acknowledged.

REFERENCES AND NOTES

1. Part XLIX of the series of Organosulphur Compounds; part XLVIII see: M.Mikołajczyk and P.Bałczewski, Synthesis, sent for publication.
2. For preliminary report of this work see: J.Drabowicz, S.Legędź and M.Mikołajczyk, J.C.S.Chem.Commun., 1985, 1670.
3. M.Mikołajczyk and J.Drabowicz in Topics in Stereochemistry, 13, 333 (1982).
4. M.Mikołajczyk in Perspectives in the Organic Chemistry of Sulfur, eds. B.Zwanenburg and A.H.J.Klunder, Elsevier, 1987 p.23.
5. H.J.Phillips, J.Chem.Soc., 127, 2552 (1925).
6. G.Solladie, Synthesis, 1981, 185.
7. L.Sagramora, P.Koch, A.Garbesi and A.Fava, J.C.S.Chem.Commun., 1967, 985.
8. Recently, asymmetric oxidation of sulphenic esters by chiral titanium complexes[9] was found to occur with higher degree of asymmetric induction.
9. C.W.Nemecek, E.Dunach and H.B.Kagan, Nouv.J.Chem., 10, 761 (1986).
10. M.Mikołajczyk and J.Drabowicz, J.C.S.Chem.Commun., 1974, 547.
11. J.Drabowicz and M.Mikołajczyk, unpublished results.
12. W.H.Pirkle and M.E.Hoekstra, J.Am.Chem.Soc., 98, 1832 (1976).
13. M.Mikołajczyk and J.Drabowicz, J.Am.Chem.Soc., 100, 2510 (1978).
14. J.Drabowicz and M.Pacholczyk, Phosphorus and Sulfur, 29, 257 (1987).
15. P.Kiełbasiński, R.Żurawiński, J.Drabowicz and M.Mikołajczyk, J.Org.Chem., sent for publication.
16. a) M.Mikołajczyk, J.Drabowicz and B.Bujnicki, J.C.S.Chem.Commun., 1976, 568; b) M.Mikołajczyk, B.Bujnicki and J.Drabowicz, Bull.Acad.Pol.Sci., Ser.Sci. Chem., 25, 267 (1977); c) K.Hiroi, R.Kitayama and S.Sato, Synthesis, 1983, 1040.
17. M.Mikołajczyk, J.Drabowicz and B.Bujnicki, Tetrahedron Letters, 26, 5699 (1985).
18. M.Mikołajczyk and J.Drabowicz, Synthesis, 1974, 124.
19. a) J.Toney and G.D.Stucky, J.C.S.Chem.Commun, 1967, 1169; b) A.L.Speak, P.Voorbergen, G.Schat, C.Blomberg and F.Bickelhaupt, J.Organomet.Chem., 77. 147 (1974).
20. In our preliminary communication all the prefixes (R,S) to specify the absoluty configuration of sulphinates 3 are erroneously reversed.
21. U.Folli, F.Montanari and G.Torre, J.Chem.Soc.,C, 1968, 1317.
22. F.A.Davis, R.H.Jenkins Jr., S.B.Awad, O.D.Stringer, W.H.Watson and J.Galloy, J.Am.Chem.Soc., 104, 5412 (1982).
23. W.Voss and E.Blanke, Liebigs Ann.Chem., 485, 258 (1931).
24. J.B.Douglass, J.Org.Chem., 30, 633 (1965).