

A Stereoselective Pummerer Rearrangement of an Optically Active Sulfoxide

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By a Pummerer type of rearrangement *o*-benzylsulfinylbenzoic acid (I) and α -phenylsulfinyl-*o*-toluic acid (III), when treated with *N,N'*-dicyclohexylcarbodiimide (DCC), were converted to 2-phenyl-3,1-benzoxathian-4-one (II) and 3-phenylthiophthalide (IV), respectively. The same transformations could be performed by the use of *p*-toluenesulfonic acid. Starting with optically active I the DCC reaction gave active II, while completely racemic II was obtained with *p*-toluenesulfonic acid. The optical purity of II was determined by NMR analysis utilizing the chiral shift reagent tris-(3-heptafluorobuturyl-*d*-camphorato)europium(III), Eu(hfbc)₃. The highest degree of stereoselectivity (30 %) and a high yield (91 %) was found with 1,2-dichloroethane as the solvent. In the presence of Eu(hfbc)₃, the enantiomeric shift difference (nonequivalence), $\Delta\delta$, of the enantiotopic 2-methine proton of II has been studied in chloroform and carbon tetrachloride solutions. On comparing II and the corresponding sulfone V in carbon tetrachloride solutions, a larger $\Delta\delta$ value was obtained for the sulfide.

In an earlier paper we reported the formation of 2-phenyl-3,1-benzoxathian-4-one (II) from *o*-benzylsulfinylbenzoic acid (I) with *N,N'*-dicyclohexylcarbodiimide (DCC) as a condensing agent.¹ Starting with optically active I the reaction was found to proceed stereoselectively with transfer of chirality from sulfur to carbon. This work has now been extended by studies of the solvent dependence of the reaction and the effect obtained by adding orthophosphoric acid as an external proton source. Furthermore, a new synthetic route leading to II and 3-phenylthiophthalide (IV), *viz.* treatment of I and α -phenylsulfinyl-*o*-toluic acid (III) with a catalytic amount of

p-toluenesulfonic acid (*p*-TsOH), is presented. The reactions can be referred to as Pummerer-type of rearrangements, as the sulfoxide is reduced to a sulfide and concomitantly oxidized at the α -position.²

A necessary condition for the stereoselectivity observed in the DCC reaction is the difference in reactivity between the diastereotopic methylene protons at the prochiral benzylic carbon atom in the initially formed DCC-substrate adduct and the retained configuration of the ylide intermediate. Evidence has been presented for a chemical nonequivalence of protons alpha to an asymmetric sulfur atom, especially in sulfoxide chemistry, where the generation and stereochemical preference of α -sulfinylcarbanions in hydrogen exchange reactions³ and the stereospecific hydroxyalkylation of chloromethyl phenyl sulfoxide⁴ have been studied. Diastereotopic reactivity of methylene hydrogens adjacent to a sulfonium center has been studied less, but demonstrated in the case of hydrogen-deuterium exchange.⁵ In view of both theoretical and experimental results, it is suggested that the reactions proceed *via* asymmetric carbanion and ylide intermediates and the stereochemical results are mainly interpreted in terms of the stability of the carbanion and ylide conformations.⁶

Sulfonium ylides are capable of exhibiting optical activity, which has been demonstrated by their resolution.⁷ Stabilizing substituents at sulfur have less effect upon the stability than an electron-withdrawing group at the α -carbon.⁸ Ylide formation will lower the barrier to inversion at sulfur relative to that in the parent sulfonium compound, while the

barrier to pyramidal inversion at carbon is higher in an ylide than that in a carbanion.^{8a} In the work of Johnson and Schroeck⁹, stable chiral oxosulfonium ylide reagents were used as alkylidene transfer reagents in the preparation of optically active oxiranes and cyclopropanes by asymmetric induction. Intramolecular transfer of chirality from sulfur to carbon *via* a chiral sulfonium ylide as an intermediate has been reported in the [2, 3] sigmatropic rearrangement of an optically active adamantylsulfonium compound with > 94% optical induction.¹⁰ The only reported stereoselective Pummerer rearrangement is the reaction of racemic 2,2-dialkyl-1,3-oxathiolan-5-one *S*-oxides with acetic anhydride.¹¹ However, the presently described conversion of I to II appears to be the only Pummerer type of reaction in which an intramolecular transfer of chirality has occurred with the formation of an optically active product.

RESULTS AND DISCUSSION

DCC as a condensing agent. When I was treated with DCC at room temperature II was obtained. An excess of DCC which could make purification of II difficult was transferred into dicyclohexylurea (DCU) with acetic acid. DCU was filtered off, the filtrate was evaporated and the residue was purified by column chro-

matography (silica gel) with benzene as an eluent. The results are summarized in Table I. The reaction proceeds much faster in acetone and THF than in the more non-polar dichloroethane and benzene. Solvent polarity seems to have a minor influence upon the degree of stereoselectivity. Addition of 1/4 equivalent of orthophosphoric acid increased the rate of the reaction considerably. In THF and acetone solutions it was necessary to perform the reactions at 0 °C to avoid coloured by-products. Addition of the external proton source decreased the stereoselectivity with the exception of acetone as a solvent, where furthermore the sign of rotation surprisingly was changed. In order to investigate the influence of the concentration of orthophosphoric acid upon the reaction, a higher acid concentration (1 equivalent) was used in THF solution. No effect upon the optical purity of the product could be detected but the yield decreased from 89 to 33%. The reaction is only possible if the sulfoxide contains a carboxylic group in the *ortho* position. Starting with the methyl ester of I, this compound was recovered. In the investigation on the reactions of DCC-DMSO with carboxylic acids, Lerch and Moffatt¹² added orthophosphoric acid as an acidic catalyst and *p*-nitrobenzoic acid was in this manner converted into methylthiomethyl *p*-nitrobenzoate (V) (42%) and 1-*p*-nitrobenzoyl-1,3-

Table I. Conditions, optical rotations^a and yields of II obtained from I,^b

Pummerer reagent	Solvent	Temp. °C	Reaction time h	Yield %	$[\alpha]_D^{25}$	Optical purity %
DCC	(CH ₂ Cl) ₂	25	15	91	-46.3	29.9
DCC/H ₃ PO ₄ ^c	(CH ₂ Cl) ₂	25	2.5	73	-31.5	20.4
DCC	C ₆ H ₆	25	16	31	-19.4	12.5
DCC/H ₃ PO ₄ ^c	C ₆ H ₆	25	2.5	19	-8.7	5.6
DCC	THF	25	2	46	-46.0	29.8
DCC/H ₃ PO ₄ ^c	THF	0	0.5	89	-7.9	5.1
DCC/H ₃ PO ₄ ^d	THF	0	0.5	33	-7.5	4.9
DCC	(CH ₃) ₂ CO	25	2	60	-5.1	3.3
DCC/H ₃ PO ₄ ^c	(CH ₃) ₂ CO	0	0.5	64	+18.0	11.6
AA	C ₆ H ₆	80	5	91	-30.2	19.5
AA	AA	100	2	95	+17.3	11.2
AA	AA/NaOAc	100	2	98	+8.2	5.3
<i>p</i> -TsOH	CHCl ₃	62	3	51	0	0
<i>p</i> -TsOH	C ₆ H ₆	80	2	98	0	0

^a In ethanol, *c* = 1. ^b Optically pure, $[\alpha]_D^{25} = +451^\circ$.

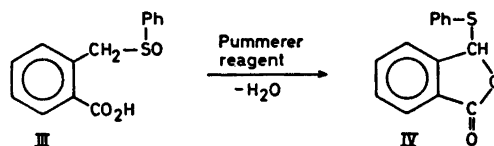
^c 1/4 equivalent of orthophosphoric acid. ^d 1 equivalent of orthophosphoric acid.

Table 2. Formation of IV with different methods.

Method	Solvent	Reaction time h	Temp. °C	Yield %
DCC ^a	(CH ₂ Cl) ₂	16	84	32
<i>p</i> -TsOH ^a	C ₆ H ₆	11	80	81
AA	AA	3.5	110	89

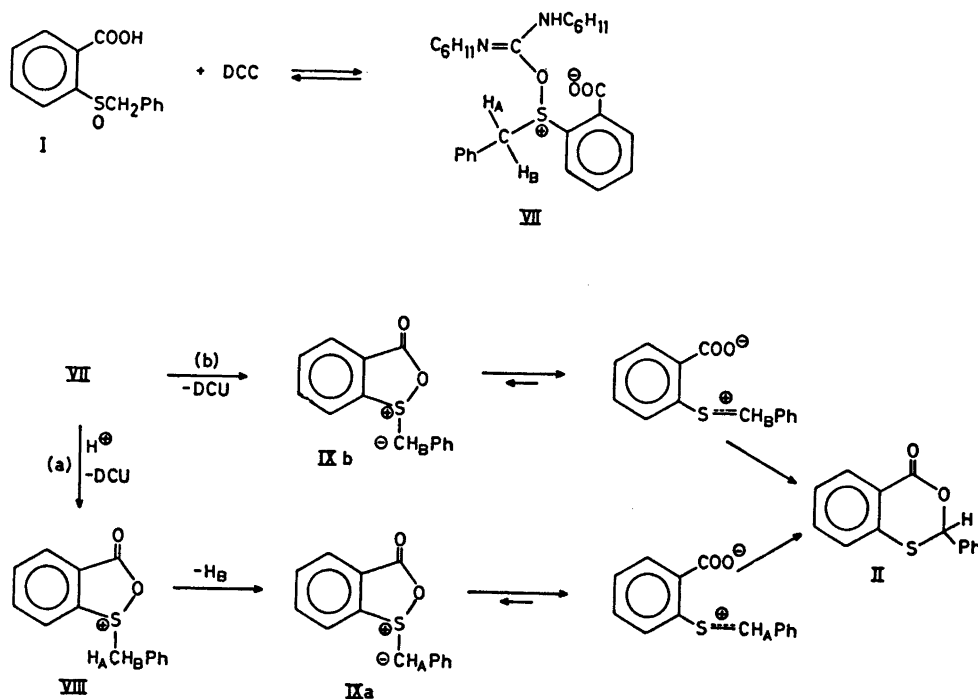
^a 2 equivalents.

dicyclohexylurea (VI) (40 %). As the results from our reactions show that the carboxylic group is an appropriate proton source, the reaction was reinvestigated in the absence of orthophosphoric acid. Otherwise the conditions were identical. V and VI were isolated in yields of 30 and 21 %, respectively. No attempt was made to optimize the yield but obviously this reaction is also insensitive to the proton source used. In summary, we can say that high yield and optical activity of II are favoured by (1) the use of 1,2-dichloroethane as solvent and (2) the absence of orthophosphoric acid.



Scheme 1.

The DCC-method was also tested on α -phenylsulfinyl-*o*-toluic acid (III). Analogously to the formation of II, III should be converted to 3-phenylthiophthalide (IV), Scheme 1. In this case it was found that more drastic conditions were needed to accomplish this reaction.



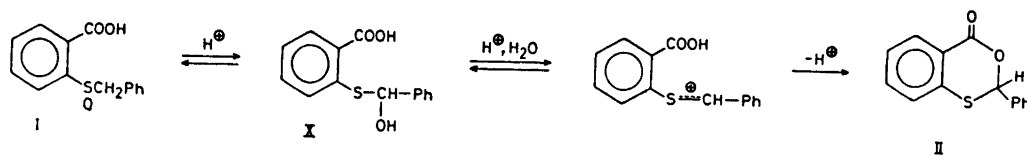
Scheme 2.

When III was subjected to the same treatment as I in 1,2-dichloroethane (with or without orthophosphoric acid), no trace of IV could be detected by TLC analysis. However, boiling under reflux for several hours yielded IV. The results of the preparation of IV with different methods are summarized in Table 2.

The fundamental feature of the mechanism can be formulated based upon the well-known DMSO-DCC reactions developed by Moffatt *et al.*¹³ By addition of DMSO to protonated DCC, they propose the initial formation of a DMSO-DCC adduct, a sulfonium isourea, from which the highly insoluble DCU is displaced by an attack from a variety of nucleophilic functional groups with formation of a sulfonium compound, which can readily lose a proton giving a sulfonium ylide. The latter can then directly rearrange or undergo further reactions. The mechanism applied to our system is outlined in Scheme 2 with I as a substrate. We have suggested the formation of the adduct VII as an attack by the sulfoxide oxygen upon protonated DCC. This would lead to an oxysulfonium intermediate well adapted for an intramolecular attack by the carboxylate anion upon the positive sulfur atom. Such a step is supported by the data which illustrate the ease with which alkoxy-sulfonium salts undergo nucleophilic attack, such as their ready hydrolysis to sulfoxides.¹⁴ Formation of the ylide can occur either directly *via* a concerted cyclic process where the attack by the carboxyl group is accompanied by intramolecular abstraction of a proton from the methylene group by the incipient DCU nitrogen (path b), or in two steps by loss of a proton from the corresponding sulfonium compound, VIII (path a). In this way two enantiomeric ylides, IXa and IXb, may be obtained. Conversion to the product should take place *via* an ion pair with restricted rotation around the partially double C-S-bond. Furthermore, the observed stereoselectivity is consistent with a nonplanar ylide and a carbanion moiety with retained stereochemistry. Preservation of carbanion configuration in an ylide can be assumed, since hydrogen exchange experiments¹⁵ with 1-methylcyclopropylide show no loss of the stereochemical integrity at the carbon atom. The optical rotations of the product II we have obtained, can be reason-

ably explained if path b is the preferred route in the absence of orthophosphoric acid. Addition of the external acid increases the contribution of path a in 1,2-dichloroethane, benzene, and THF solutions, but with acetone as a solvent path a is now predominant. It has been found that the relative rates of exchange of the diastereotopic methylene hydrogens in benzyl methyl sulfoxide¹⁶ and 1,3-dihydrobenzo[c]thiophene-2-oxide¹⁷ are altered by changing base or solvent. Therefore, one can question if our two-way mechanism is needed to interpret the results. However, it is difficult to realize why a catalytic amount of orthophosphoric acid would have an influence on the medium and cause a change of the stereochemistry.

p-Toluenesulfonic acid as a condensing agent. The transformation I to II could also be performed using *p*-TsOH as a proton source to catalyze the reaction. The reaction was carried out in refluxing solutions of benzene (water separator connected) or chloroform and the product was purified by column chromatography affording 96 and 51 % yields of II. Starting with optically active I we obtained II with no optical rotation. Under the same conditions the optically active methyl ester of I did neither react nor racemize. The same result was obtained with (+)-I in acetone solution. Therefore, the inactivity of II cannot be explained by racemization of I prior to reaction and a mechanism quite different from that of the DCC-method seems to operate, Scheme 3. The first step involves an acid catalyzed rearrangement of I with the formation of an α -hydroxysulfide (hemithioacetal) X. Support for this assumption is given by the reaction of sulfoxides containing a β -carbonyl function or an other electron-withdrawing group with acidic reagents. Such reactions have been the subject of much mechanistic speculation. Pummerer found that phenylsulfanylacetic acid is cleaved to thiophenol and glyoxylic acid, tentatively *via* the hemithioacetal, in the presence of mineral acids.¹⁸ A mechanism involving a primary cleavage into a mercaptan and a carbonyl fragment followed by hemithioacetal formation has been proposed.¹⁹ However, this cleavage-recombination mechanism is in disagreement with chemical and spectroscopic results.²⁰ Thus, the mechanism first



Scheme 3.

suggested by Pummerer on intuitive grounds is most consistent with presently available data.

The source of the hydroxyl group in the hemithioacetal is still obscure. Undoubtedly, the first step in the reaction is protonation of the sulfoxide oxygen. An intramolecular migration of the hydroxyl group, attached to the positive sulfur atom, to the adjacent carbon atom has been proposed.^{20b} An alternative mechanism to hemithioacetal involving loss of a proton from protonated sulfoxide and a final attack of water upon a reactive ylide intermediate was suggested by Becker.^{20a} The formation of α -hydroxysulfides in organic media^{19,20b} can be explained according to this consideration as catalytic amounts of water should be sufficient. However, such a mechanism involving a nucleophilic attack upon a carbanionic site of an ylide appears unlikely, as stated by Johnson and Phillips in their investigations of the Pummerer rearrangement of sulfonium salts.²¹ Evidence was found for an initial ylide formation and a subsequent α -migration of an alkoxy group by an intermolecular process *via* a sulfur-stabilized carbonium ion. Focusing our attention on the close relationship between this rearrangement and α -hydroxysulfide formation, an attractive thought is to rationalize the latter reaction in terms of the above discussion.²¹ As our reaction in benzene solution was performed under anhydrous conditions, the role of water is irrelevant, and the mechanism suggested by Johnson and Phillips is consistent with our results. The last step to II is a lactonization responsible for the racemization. Elimination of water is a reversible process with the equilibrium far shifted to the hydroxy compound, as no formation of II was obtained in the water-soluble solvents acetone, DMSO, THF, acetonitrile, or ethanol.

The carboxyl group of I can also serve as the sole source of protons necessary for catal-

ysis. Heating I under reflux for 4 h in benzene gave II in 16% yield. No attempts were made to optimize the yield.

Upon treatment with *p*-TsOH in boiling benzene, III was converted to IV. By increasing the amount of *p*-TsOH from 0.15 to 2 equivalents, the yield was raised from 13 to 81%. The preparation of IV is summarized in Table 2.

Acetic anhydride as a condensing agent. Numata and Oae have reported that I, when treated with a large excess of acetic anhydride, gave II.²² Utilizing their method with optically active I, we have found this reaction also to be stereoselective.¹ II was obtained with a sign of rotation opposite to that obtained by the DCC-method. However, a small amount of acetic anhydride in benzene gave the same result as with DCC. From the lack of steric effects Numata and Oae formulated the mechanism, different from that of the normal Pummerer reaction, as an initial acetylation of the carboxyl group. The following intramolecular attack of the sulfoxide oxygen upon the anhydride group afforded a cyclic acyloxysulfonium salt, which after removal of an α -proton was rearranged to II. However, we feel that a mechanism analogous to that of the DCC-method (Scheme 2) cannot be ruled out. We found that treatment of optically active I with acetic anhydride at 100 °C and quenching the solution after 3 min, 37% of the starting sulfoxide was recovered with 38% of the original activity. In the same way the methyl ester of I was found to racemize much slower than the acid and no formation of II could be detected. The first step in the racemization of sulfoxides by acetic anhydride²³ is the formation of an intermediate acetoxy-sulfonium compound followed by a rapid acetoxy interchange.²⁴ As this mechanism accounts for the racemization of the ester of I it could also be valid for I. This implies the formation of an acetoxy-sulfonium salt of I, which can serve

as the entrance to II according to the mechanism outlined in Scheme 2.

It was found that this method was the best one to prepare IV. By boiling III in acetic anhydride and removing excess acetic anhydride high yield of IV was obtained after recrystallization, Table 2.

Determination of enantiomeric composition. As the rotation of optically pure II is not known, the optical yields of the DCC-reactions cannot immediately be estimated from available data. We have considered the possibility to obtain optically pure II with chemical methods as fruitless. The NMR method based on chemical shift non-equivalence of enantiomers in optically active solvents is limited by the small magnitude of the chemical shift differences induced between corresponding resonances of enantiomers.²⁵ However, after the discovery²⁶ and in connection with development²⁷ of lanthanide shift reagents (LSR), the problem

of direct determination of optical purity has been solved in a satisfactory way by the use of chiral LSR.²⁸ This method was found to be applicable to our system.

Fig. 1 illustrates the influence of tris-(3-heptafluorobutyl-*d*-camphorato)europium (III), $\text{Eu}(\text{hfbc})_3$, on the NMR spectrum of II. Addition of successive small quantities of LSR to a carbon tetrachloride solution of II produces marked modifications in the original spectrum. The lanthanide induced shifts (LIS) of the H_2 and H_3 protons increase with an increase in the LSR/substrate ratio. In esters and lactones the carbonyl oxygen is the preferred coordination site of LSR and therefore II has two potential coordinating groups. However, with one exception,²⁹ thioethers have been found to complex much less strongly than carbonyl or ether groups with LSR in the vast majority of cases.³⁰ Therefore, competition between the two functionalities in II

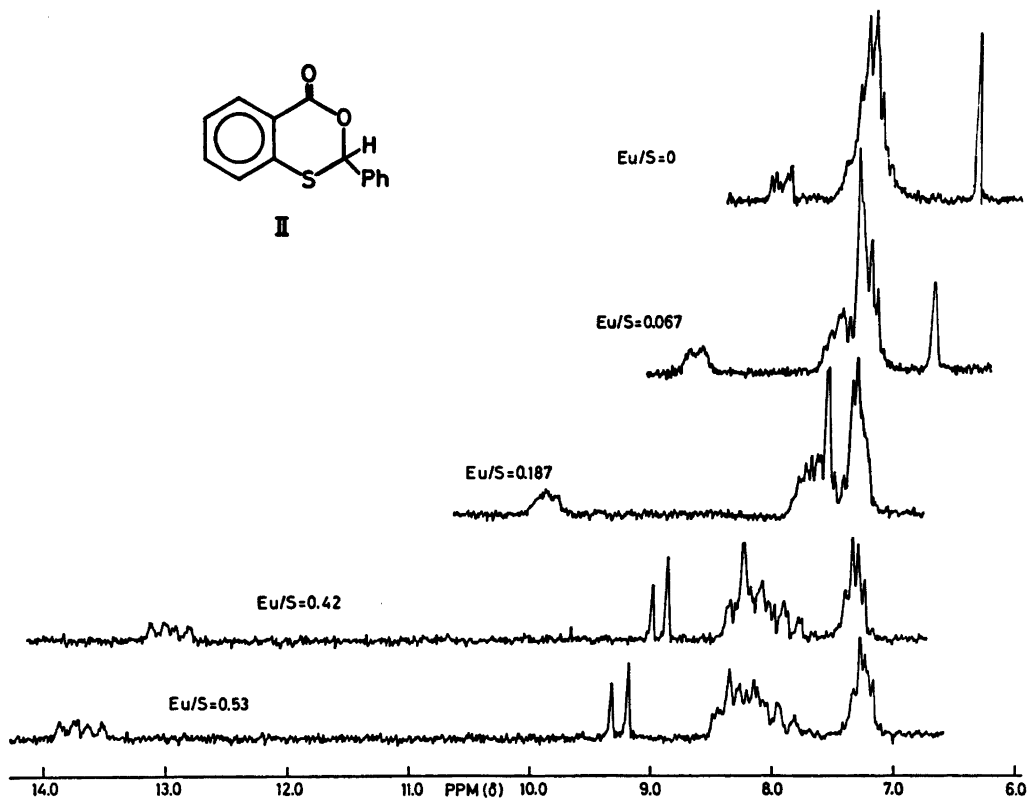


Fig. 1. The NMR spectrum of partially resolved II ($[\alpha]_D^{25} = -28.1^\circ$) as a function of the LSR/substrate molar ratio.

for the shift reagent need not be considered. The latter observations are consistent with our results as the close proximity of H_a to the coordinating carbonyl group is reflected in the great response of the LIS by addition of LSR.

In the presence of chiral shift reagents enantiomers have non-equivalent NMR spectra, demonstrated in Fig. 1 by the significant splitting of the H_a proton. This enantiomeric shift difference ($\Delta\delta$) increases over the range investigated. The resonances are sufficiently separated for direct determination of the enantiomeric composition. This was performed with a partially resolved sample of II ($[\alpha]_D^{25} = -28.1$). A 0.30 M solution of this compound in carbon tetrachloride containing 0.53 equivalents of $\text{Eu}(\text{hfbc})_3$ was used. Peak areas of the expanded signals ($\Delta\delta = 0.15$ ppm) corresponded to 18.2% optical purity of II. In order to investigate the influence of solvent and substrate concentration on the induced shifts and $\Delta\delta$, spectra were recorded for solutions in carbon tetrachloride and chloroform and at two different concentrations of II in carbon tetrachloride. By plotting the chemical shifts of the enantiomeric H_a proton

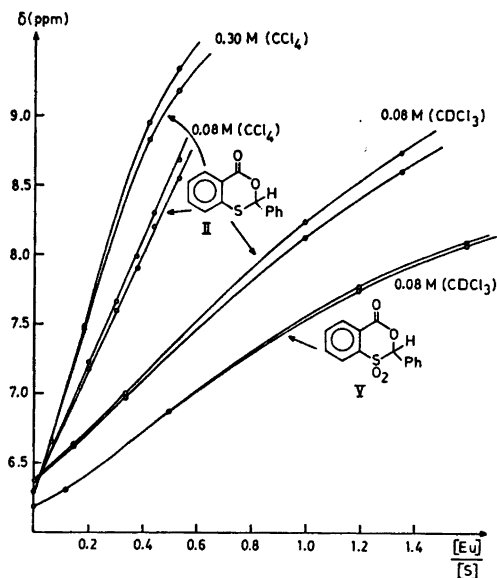


Fig. 2. Illustration of the enantiomeric shift differences obtained for the methine proton with varying solution and concentration conditions.

vs. the $\text{Eu}(\text{hfbc})_3$ /substrate ratios, straight lines are obtained with different slopes at lower concentrations, but deviation from linearity is apparent at higher ratios in two of the cases, Fig. 2. The slope of a line is a measure of the shifting power of LSR. As can be seen in Fig. 2, this is influenced both by the solvent and by the concentration of the substrate. For comparable concentrations of II (0.08 M), carbon tetrachloride gives significantly larger values for the induced shift as well as $\Delta\delta$ than does chloroform. The induced shift, but not the magnitude of non-equivalence, is increased by increasing substrate concentration. Fig. 2 also shows the effect of adding $\text{Eu}(\text{hfbc})_3$ to a chloroform solution of the sulfone of II. Within the range investigated, the frequency separation between the enantiomeric shifts is less than 0.02 ppm. The sulfone group is a weak donor toward LSR.²¹ Therefore, one can expect the interaction of this molecule with the shift reagent to occur at the carbonyl group. The validity of this assumption is supported by a comparison of the induced shift obtained for a 0.08 M solution of II in chloroform. Inspection of Fig. 2 reveals about the same slope for the two compounds, which indicates the LSR/substrate complexes to be very similar.

EXPERIMENTAL

General. All melting points are uncorrected. The optical activity was measured at 589 nm (D-line) using a Perkin-Elmer model 141 photoelectric polarimeter and 1 ml microcells of 10 cm length with ethanol as a solvent. The IR spectra were recorded on a Perkin-Elmer model 157 spectrophotometer. NMR spectra were obtained with a Varian A-60 D NMR spectrometer. The $\text{Eu}(\text{hfbc})_3$ was purchased from Willow Brook Labs., Inc., USA. The shift reagent was stored *in vacuo* over P_2O_5 until just before use, but no extraordinary precautions were taken to exclude water or air during the addition. The chemical shift differences were followed by incremental addition of $\text{Eu}(\text{hfbc})_3$, thereby shifting the signals progressively downfield from TMS. Thin layer and column chromatographic procedures were accomplished using silica gel F_{254} plates (Merck) and silica gel 60, 70–230 mesh (Merck), respectively. The column chromatographic separation was followed by the use of a LDC model 1522 ultraviolet detector operating at 280 nm. Elemental analyses were performed by the Analytical Department, Institute of Chemistry,

University of Uppsala. Most of the experimental data are summarized in Tables 1 and 2.

2-Phenyl-3,1-benzoxathian-4-one (II). Method A. (+)-I + DCC. To 0.130 g (0.5 mmol) of finely powdered (+)-I (slightly soluble in benzene and 1,2-dichloroethane) in 5 ml of solvent was added with stirring 0.206 g (1 mmol) of DCC and in some cases 1/4 equivalent of anhydrous orthophosphoric acid. To destroy excess DCC, 0.25 g of acetic acid was added and after stirring for an additional 30 min, the precipitated *N,N'*-dicyclohexylurea (DCU) was removed by filtration and the remaining filtrate evaporated to dryness. The product was then purified by column chromatography on silica gel with benzene as the eluent. TLC-examination showed only a single spot and the optical activity was determined.

Method B. (+)-I + p-TsOH. 0.5 mmol of (+)-I and 1/8 mmol of *p*-TsOH was heated under reflux in benzene (water separator connected) or chloroform. The reaction mixture was cooled, washed with a diluted sodium bicarbonate solution and water and dried over anhydrous calcium chloride. The product was purified in the same way as above. The obtained II was found to be racemic. After 2 h a white solid began to precipitate from the chloroform solution. The IR spectrum of this product was identical with that for 2,2'-dithiodibenzoic acid.

If (+)-I or its methyl ester were subjected to the same treatment in acetone for 2 h or benzene for 1 h, no formation of II was detected and the recovered acid and ester had retained optical activities.

Method C. (+)-I + AA. According to Oae and Numata,²² treatment of I with an excess of acetic anhydride afforded II. Starting with optically pure I, partially active II was obtained.

By this method a quenching study was performed as follows. 0.5 mmol of (+)-I was heated at 100 °C with 1 ml of acetic anhydride. After 3 min, the reaction was quenched by cooling in an ice-bath and 10 ml of 2 M sodium hydroxide solution was added. The solution was extracted repeatedly with chloroform whereupon the water layer was acidified with dilute sulfuric acid. The acid which had precipitated was filtered off and dried. 0.045 g of (+)-I was recovered with $[\alpha]_D^{25} = 171^\circ$.

3-Phenylthiophthalide (IV). Starting with α -phenylsulfinyl-*o*-toluic acid (III),²³ IV was obtained by the methods A, B, and C. The product was recrystallized from benzene-ligroin. M.p. 100–102 °C, lit.²³ 102–103 °C. Experimental data are given in Table 2.

2-Phenyl-3,1-benzoxathian-4-one-1,1-dioxide (V). To 0.97 g (4 mmol) of II dissolved in 40 ml of glacial acetic acid was added a warm solution (50 °C) of potassium permanganate (1.28 g) in 15 ml of water. The reaction mixture was stirred for 15 min. Then a solution

of sodium disulfite (1.50 g) in 15 ml of water was added to destroy excess permanganate and manganese dioxide. Ice water was added to the mixture and the precipitated solid collected by filtration. The product was recrystallized from ethanol and the yield of sulfone, melting at 184–185.5 °C, was 1.00 g (91 %). (Found: C 61.34; H 3.71; S 11.66. Calc. for $C_{14}H_{10}O_4S$: C 61.30; H 3.67; S 11.69).

Methyl (-)-*o*-benzylsulfinylbenzoate. 0.52 g (2 mmol) of (-)-I was suspended by stirring in 10 ml of methanol. After cooling to 0 °C an excess of diazomethane in ether was added. The solvent was then allowed to evaporate at room temperature. Recrystallization from ligroin-acetone yielded 0.42 g (77 %) ester with m.p. 143–144 °C and $[\alpha]_D^{25} = -423.1^\circ$ ($c = 0.8$, ethanol).

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