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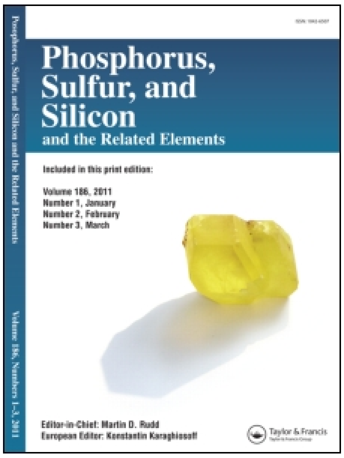

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Asymmetric Reactions of High-Symmetry Chiral Organosulfur Reagents

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ASYMMETRIC REACTIONS OF HIGH-SYMMETRY CHIRAL ORGANOSULFUR REAGENTS

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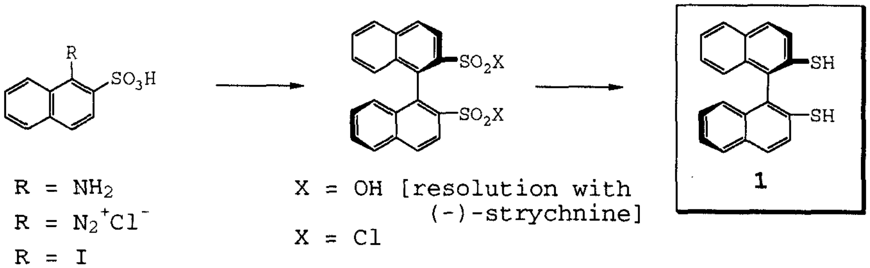
Abstract The utility of high-symmetry, doubly substituted organosulfur compounds as chiral auxiliaries in asymmetric reactions is described.

INTRODUCTION

It is standard practice in asymmetric synthesis to use optically active chiral auxiliaries derived from the "natural pool". Indeed, a large number of enantioselective syntheses are based on chiral auxiliaries such as camphor, menthol, tartaric acid, ephedrine, *etc.* which are obtained from nature. These auxiliaries can be modified to some extent in order to improve their ability to transmit the chiral information. Well-known examples are 8-phenyl menthol and several substituted camphor derivatives. However, by resorting exclusively to the chiral pool for auxiliaries, one is limited by the range of structural architectures available and sometimes limited by the possible future chemistry due to functional groups that the natural chiral auxiliary brings with it. The recent advances on the separation of enantiomers now make it possible to suggest synthetic chiral auxiliaries that can be planned in such a way to meet the desired requirements of simplicity, crystallinity, suitability for NMR and UV detection, *etc.* With these reagents, the extra steps required in resolution offset the drawbacks cited for the natural reagents. In other words, it might now be legitimate to design with indefinite freedom artificial chiral auxiliaries with a certain specific architecture for maximal chiral transmission. Imperative in this strategy is the achievement of high efficiency, high yield of products and general simplicity of operations. In this lecture, the results obtained with a reagent of this type and a few modification that can enlarge the potentiality of the synthetic concept, will be described. We have decided to investigate a chiral dithiol because it allows to prepare chiral variants of several synthons already well defined in the achiral domain.

1,1'-BINAPHTHALENE-2,2'-DITHIOL

1,1'-Binaphthalene-2,2'-dithiol was chosen because it possesses C_2-symmetry and its aromatic character simplifies detection and especially reductive removal at the end of the planned sequence of reactions. Furthermore, upon reduction, the dithiol **1** would be returned with its chirality intact and such reusable chiral auxiliaries are rare in the arena of organosulfur chemistry. In addition, **1** was inspiring because of the very important results obtained with its oxygen analogue **2**. Dithiol **1** was known since 1928[1a] and it was prepared in optically pure form in 1957.[1b]



R = NH_2
R = $N_2^+Cl^-$
R = I

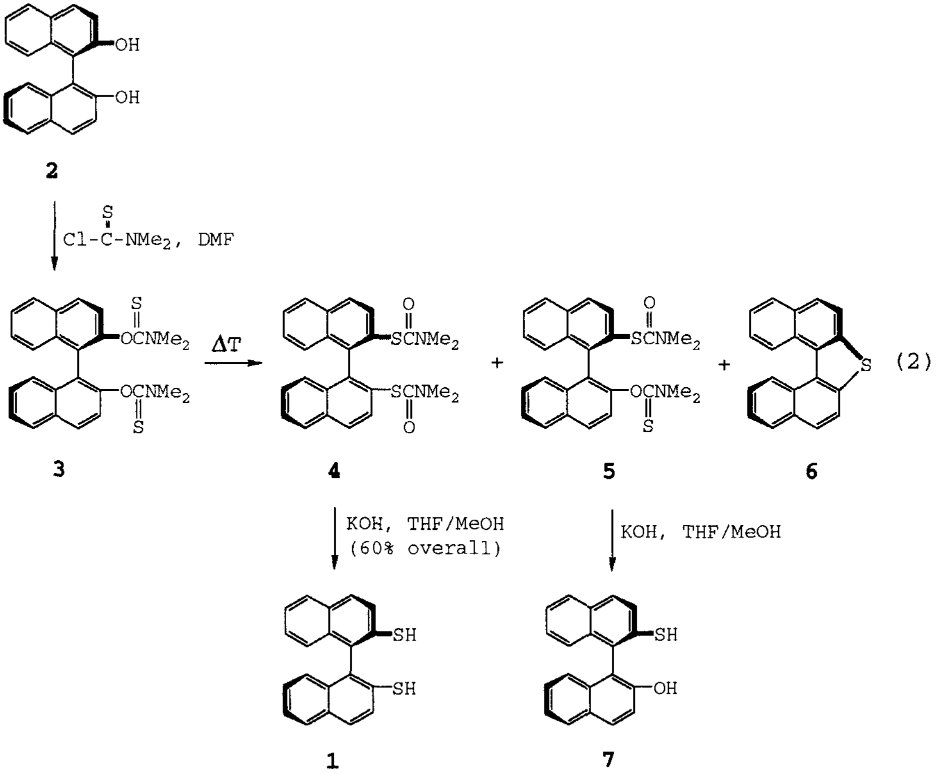
X = OH [resolution with (-)-strychnine]
X = Cl

1

(1)

Except for being used by Cram in macrocyclic ligands,[1c] dithiol **1** has not been used in synthesis. Beside the original method described in Eq. (1), dithiol **1** can be prepared in other ways. We have optimised the method described by Cram[1c] that makes use of the Newman-Kwart rearrangement of the thioester **3** which is itself obtained in high yield from binaphthol and dimethylthiocarbamoyl chloride as shown in Eq. (2). The rearrangement occurs in a reasonably high yield but always gives the monorearranged compound **5** and thiophene **6** in addition to the dsesired product **4**, irrespective to the changing of reaction conditions.[2] Indeed, on forcing the reaction conditions, higher quantities of **6** are produced, while on the other hand, shorter reaction times or lower temperatures lead to partial conversion with recovery of starting material and higher formation of monotransposed compound **5**. It should be noted that **5** is a precursor to the valuable atropisomeric hydroxythiol **7**[3] and that **6** does not have a planar geometry as shown by diffractometric studies.[4] Both these molecules have been investigated in different contexts.

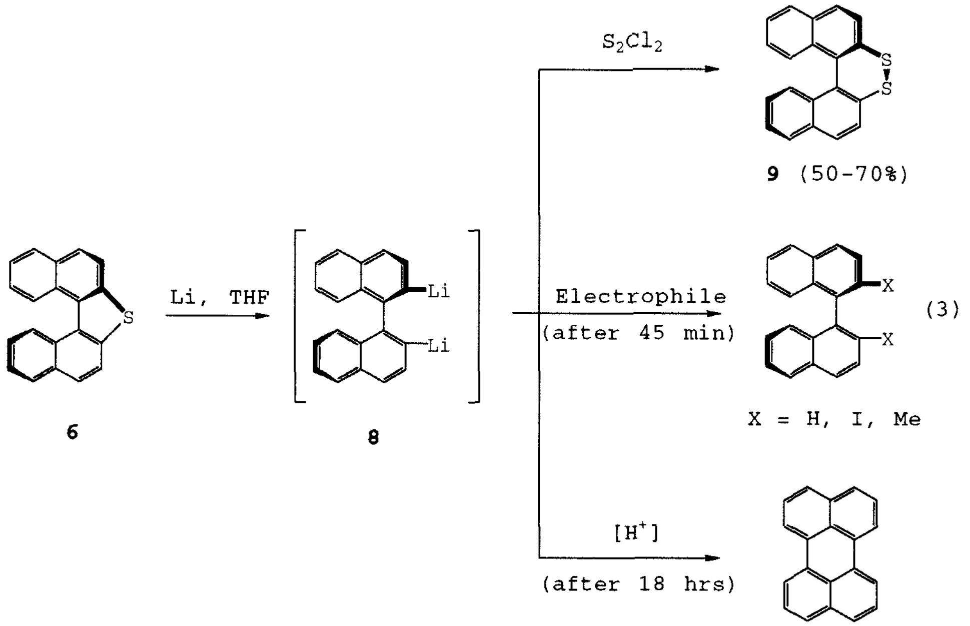
The binaphthothiophene **6** that accumulates after a few preparative runs can be transformed into the desired dithiol **1** by the



sequence of reactions shown in Eq. (3). The postulated dilithium compound **8** that is generated from the addition of lithium metal to **6** is quenched with sulfur dichloride to produce disulfide **9** which is readily converted into dithiol **1**.[5]

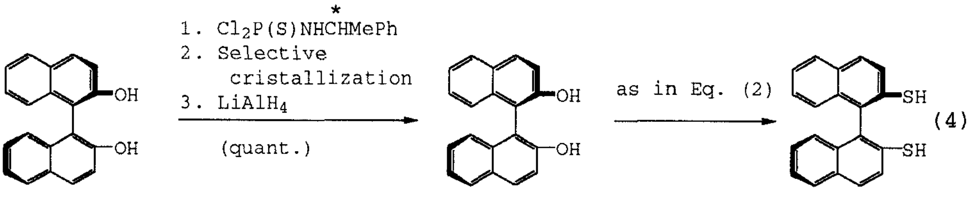
This alternative generation of 2,2'-dilithium-1,1'-binaphthyl (**8**) can de used for the preparation of other valuable binaphthyls including binaphthalene itself, upon quenching with a proton source, the diiodo and the dimethyl derivatives on quenching with iodine or methyl iodide respectively. On longer exposure of the thiophene to metallic lithium, perylene was produced essentially quantitatively, as shown in the lower part of Eq. (3).[6]

The preparation of **1** in optically pure form can be achieved by classical resolution of the sulfonic acid with strychnine, following the original method by Armarego and Turner[1b] as illustrated in Eq. (1). Alternatively, the enantioselective oxidation of appropriate sulfides that can be further transformed into **1** constitutes a valuable method for the preparation of **1** in optically pure form.[7]



6 **8** **9** (50-70%)

The use of enantiomerically pure **2** as starting material in the sequence of reactions shown in Eq. (2) is a further possibility for the preparation of enantiomerically pure **1**. Careful optimization of the reaction conditions in the thermolysis of the thiocarbamoyl chloride **3** allowed us to minimize or even suppress racemization.[8] With this method enantiomerically pure **1** can be obtained in rather large quantities with little extra effort over the racemic procedure. It should be noticed that methods of preparation of diol **2** in optically pure form are numerous, some of which can be accomplished on large scale. In the course of these studies we have developed our own method of resolution of diol **2** which is represented in Eq.(4).[8a]

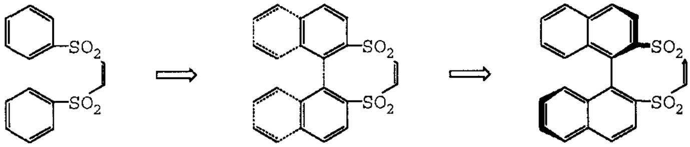


2 **2*** **1***

We recommend this method especially for the low cost of the materials involved and the simplicity of the required operations. A similar resolution has been recently reported by Hu.[8b]

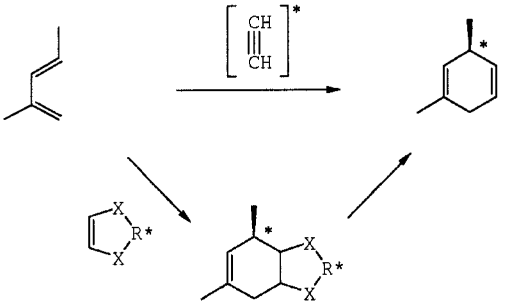
DINAPHTHO[2,1-*e*:1',2'-*g*][1,4]DITHIOCIN, 1,1,4,4-TETROXIDE

The original reasoning that led us to the binaphthyl system and to the whole chemistry described here is represented in Eq. (5).



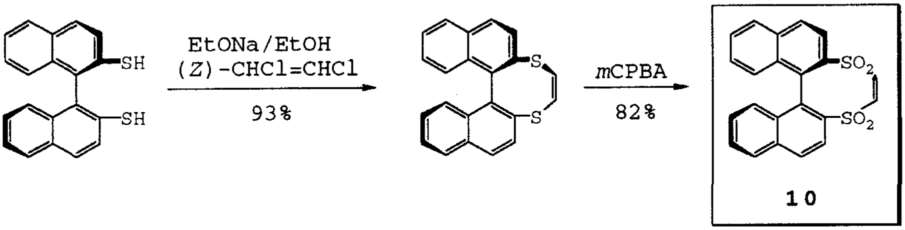
(5)

We wanted to prepare a chiral acetylene equivalent and the binaphthyl group allowed us to design a chiral dienophile with minimum structural change over the known bis(phenylsulfonyl)-ethylenes. These latter compounds have proved to be useful acetylene equivalents in a number of cases.[9] Indeed, a chiral acetylene equivalent would allow the preparation of optically active hydrocarbons which would be difficult to prepare by classical methods.



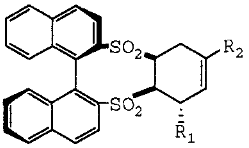
(6)

The preparation of dithiocin **10** is shown in Eq. (7).[2]

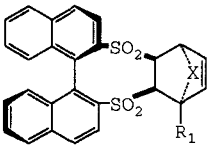


(7)

Dienophile **10** was reacted with a number of non-symmetric dienes and in each case a single diastereomeric adduct was observed. Compound **10** was a highly reactive dienophile and the corresponding Diels-Alder adducts formed immediately at room temperature as crystalline solids. The following adducts were obtained from acyclic and cyclic dienes.



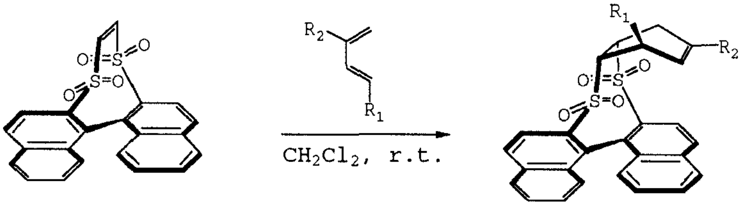
R_1= OMe R_2= OTMS (mp 185-6°C)
R_1= OMe R_2= H (mp 250°C)
R_1= OTMS R_2= H (mp 266-8°C)
R_1= Me R_2= H (mp 311-3°C)
R_1= H R_2= OTMS (mp 230°C)
R_1= H R_2= Me (8:2 mixture)



R_1= OMe X= O (mp 180°C)
R_1= OMe X= $-(CH_2)_2-$ (mp 307°C)

In one case only (*i.e.* with isoprene) did the cycloaddition result in a 8:2 mixture of diastereoisomers suggesting that a single methyl group in the C-2 dienic carbon is not sufficient to provide an efficient diastereomeric bias. Thus far, however, this is the only case in which two diastereoisomers were formed.

The stereochemistry of addition was determined by NMR and X-ray structure analysis and it is shown in Eq. (8). It should be noted that there are four possible modes of addition, and only one (that indicated) was observed.



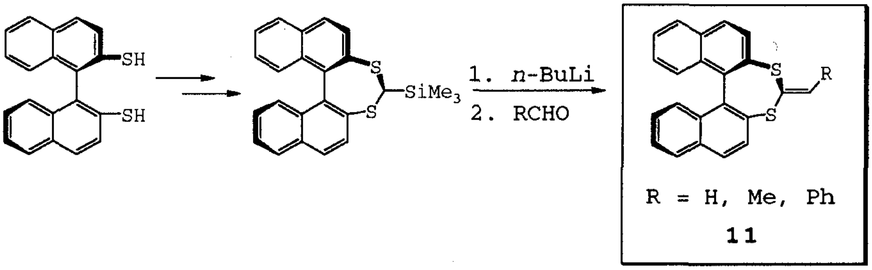
10

(8)

Sodium-amalgam reduction in buffered methanol, removed the binaphthyl residue to afford the hydrocarbon and eventually the starting dithiol.[2] The process is equivalent to the Diels-Alder addition of acetylene in a chiral form.

2-ALKYLIDENE-DINAPHTHO[2,1-*d*;1',2'-*f*][1,3]DITHIEPINE

Ketenedithioacetals **11** are chiral variants of a large class of reagents whose synthetic utility is well recognized.[10,11] Similarly useful are the monoxides, bisoxides and tetroxides derived therefrom.[10]

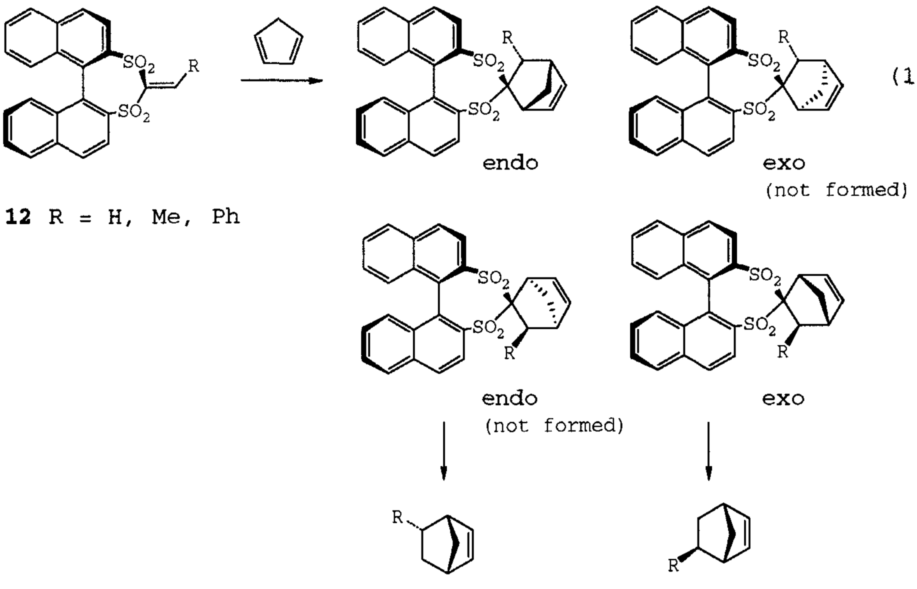


R = H, Me, Ph

11

(9)

The preparation of the chiral ketenedithioacetals of type **11** could be readily accomplished by the Peterson olefination methodology as shown in Eq. (9). Among the several applications that can be envisaged for these reagents, the cycloaddition of the sulfones **12** to cyclopentadiene is representative. The cycloaddition afforded one single exo and one single endo adduct as shown in Eq. (10). The two adducts could be readily separated by flash chromatography and desulfonylated to the norbornenes **13** using sodium amalgam.



12 R = H, Me, Ph

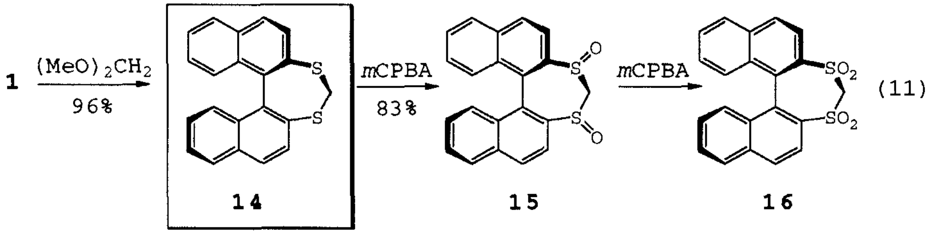
(10)

endo-**13** exo-**13**

^{1}H-NMR studies and especially n.O.e. experiments allowed the assignment of the stereochemistry of the adducts represented in the Eq. (10). If performed with optically pure starting material, one can anticipate the preparation of both the endo and the exo isomers of norbornenes **13** in optically pure form (for R ≠ H).

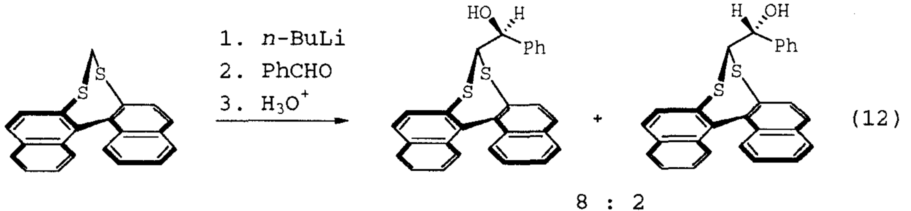
DINAPHTHO[2,1-*d*:1',2'-*f*][1,3]DITHIEPINE

The dithiepine **14** is a chiral version of a class of reagents that are well-known formyl anion synthons.[12] The C_2 symmetry is shared also by the bisoxide **15** (it forms stereoselectively as single pseudoequatorial isomer) and by the bis-sulfone **16**.



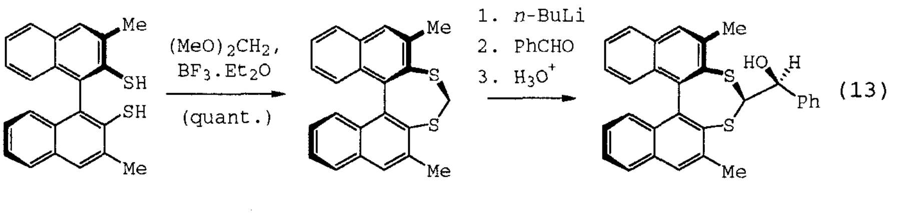
14 **15** **16** (11)

Reaction of the anion of **14** with benzaldehyde gave only a 8:2 mixture of diastereoisomers **17**.[13]



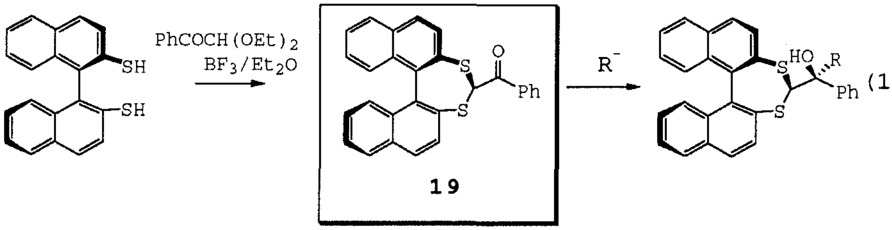
14 **17** 8 : 2 **17'** (12)

In contrast, the anion of **18** gave a single diastereoisomer with benzaldehyde.[14] This result convincingly establishes the importance of the 3,3' positions of the binaphthyl group for efficient diastereomeric bias.



18 1 diastereoisomer (13)

A single diastereoisomer (corresponding to the major diastereoisomer obtained in the reaction of the anion of **14** with benzaldehyde, *i.e.* **17**) was also obtained in the reduction of ketone **19** with lithium aluminium hydride as illustrated in Eq. (14).[15] The addition of other nucleophiles such as methyl magnesium iodide also gave a single adduct.

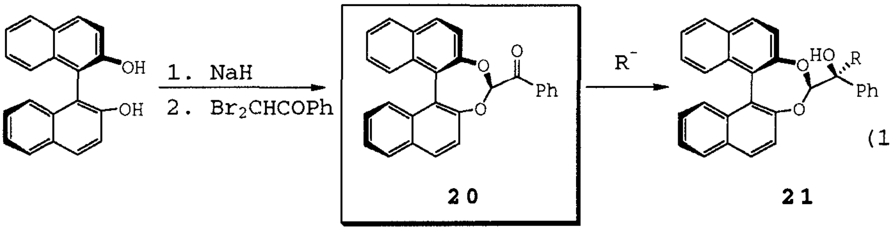


19

(14)

Nucleophile	Reaction conditions	Diastereomeric Ratio	Yield (%)
$LiAlH_4$	Et_2O, -78°C, 45 min	100:-	98
$NaBH_4$	$EtOH/H_2O$, Et_3N, 20°C, 4h	86:14	99
MeMgI	THF/Et_2O, 0°C, 40 min	100:-	98

The addition of hydrides and carbon nucleophiles to the corresponding oxygen analogue **20** was also very diastereoselective.[16]



20

21

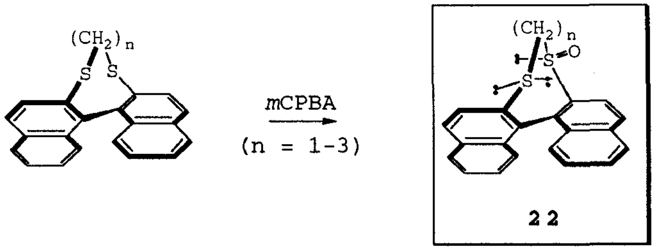
(15)

Nucleophile	Reaction Conditions	Diastereomeric Ratio	Addition: Reduction	Yield (%)
$LiAlH_4$	Et_2O, -78°C, 2h	98:2	-	97
MeMgI	several conditions	-	-	-
MeMgBr	THF, -78°C, 2h	100:-	100:-	99
MeLi	Toluene, -83°C, 2h	57:43	100:-	97
$ZnMe_2$	Et_2O, -20°C, 2h	97:3	93:7 (93:7)	60
EtMgBr	THF, -78°C, 2h	100:-	93:7	96
$ZnEt_2$	Et_2O, -20°C, 2h	92:8	93:7	80
i-PrMgBr	THF, -78°C, 2h	69:31	36:64 (83:17)	80
n-BuMgBr	THF, -78°C, 2h	100:-	81:19	97
n-BuLi	Toluene, -83°C, 2h	62:38	100:-	96
PhMgBr	THF, -78°C, 2h	-	92:8	99
p-$Me_2NPhMgBr$	THF, -78°C, 2h	100:-	100:-	98
p-FPhMgBr	THF, -78°C, 2h	100:-	100:-	98

The products **21**, upon hydrolysis furnished aldehydes that are valuable synthetic intermediates and precursors to arylpropionic acids.

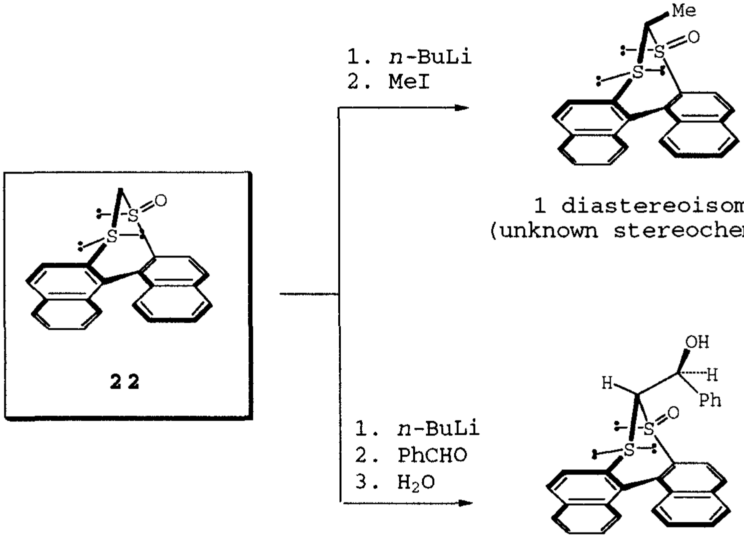
DINAPHTHO[2,1-*d*;1',2'-*f*][1,3]DITHIEPINE *S*-OXIDE

Oxidation of **14** and of similar compounds possessing different chain size between the two sulfur atoms invariably gave single diastereomeric sulfoxides with pseudoequatorial configuration as determined by X-ray analysis.[13]



(16)

In general, the oxides exhibit increased distereoselectivity with respect to the unoxidised substrates as in the examples of Eq. (17).[13]

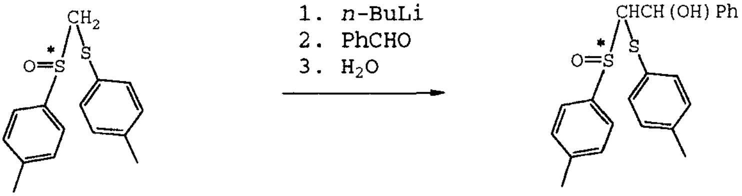


1 diastereoisomer
(unknown stereochemistry)

(17)

23
1 diastereoisomer

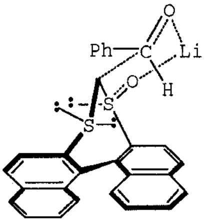
These results compare well with the modest diastereoselectivity achieved with the open-chain structures represented in Eq. (18).[17]



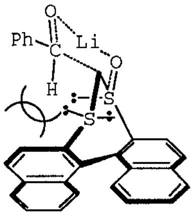
(18)

diastereomeric ratio: 50:35:15:0[17a]
" " 50:26:15:9[17b]

To rationalise the stereoselectivity observed, the transition states **24** and **24'** need to be considered. The commonly accepted mechanism involves the formation of a six-membered, chair-like conformation. Of the two that possess the phenyl group in an equatorial position, **24** is preferred because in **24'** the benzaldehyde proton approaches the naphthyl edge too closely. One can see the importance of the 3,3' positions in the binaphthyl system in disfavouring transition state **24'** and this has already been described in Eq. (13).



24



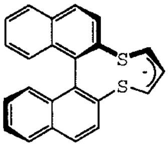
24'

The stereochemistry of addition was firmily established by an X-ray structure determination that confirmed the prediction based on the transition state **24**. The reduction of the sulfoxide oxygen gave a sulfide identical to **17** confirming also the stereochemistry of the latter.

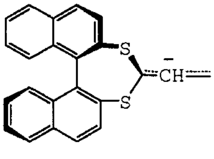
DINAPHTHO[2,1-*f*;1',2'-*h*][1,5]DITHIONIN

The allyl anions generated from 1,3-(bismethylthio)- or 1,3-(bisphenylthio)propene **25** have been shown to be useful synthetic equivalents of the β-acyl vinyl anion.[18] The chiral molecules **26** and **27** represent chiral allyl anions with C_2 symmetry.[19]

25 R = Me, Ph

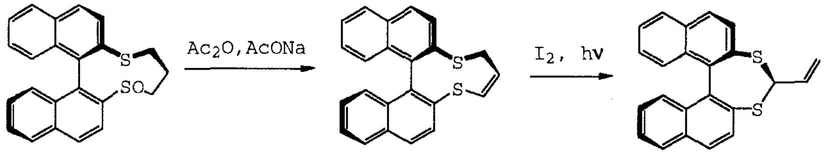


26



27

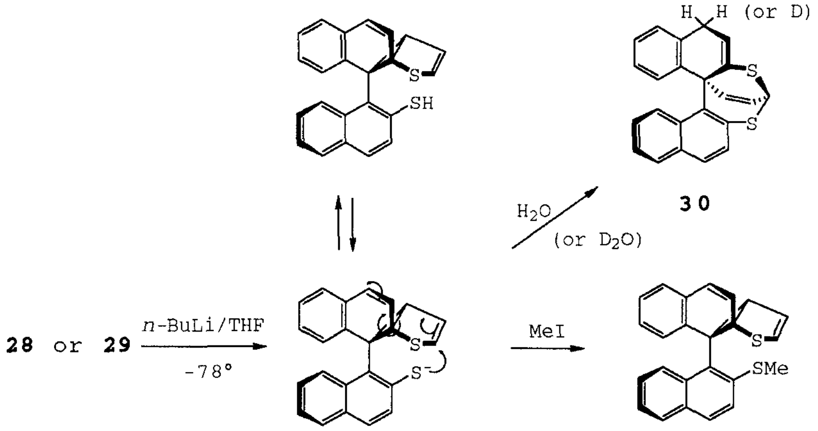
The preparation of suitable precursors to **26** and **27** is illustrated in Eq. (19). Olefin **28**, which is readily available via a Pummerer reaction,[20] rearranged in the presence of light to the isomeric olefin **29**, probably through radical intermediates.



(19)

28 **29**

Unfortunately, generation of the anion either from **28** or **29** with *n*-buthyllithium in THF at -78 C°, followed by quenching of the anion with water, did not give back the expected starting material, but the highly rearranged isomer **30**. Quenching of the anion with deuterated water afforded **30** deuterated stereoselectively at the methylenic carbon while quenching of the anion with methyl iodide afforded **31** in high yield.



30

(20)

31

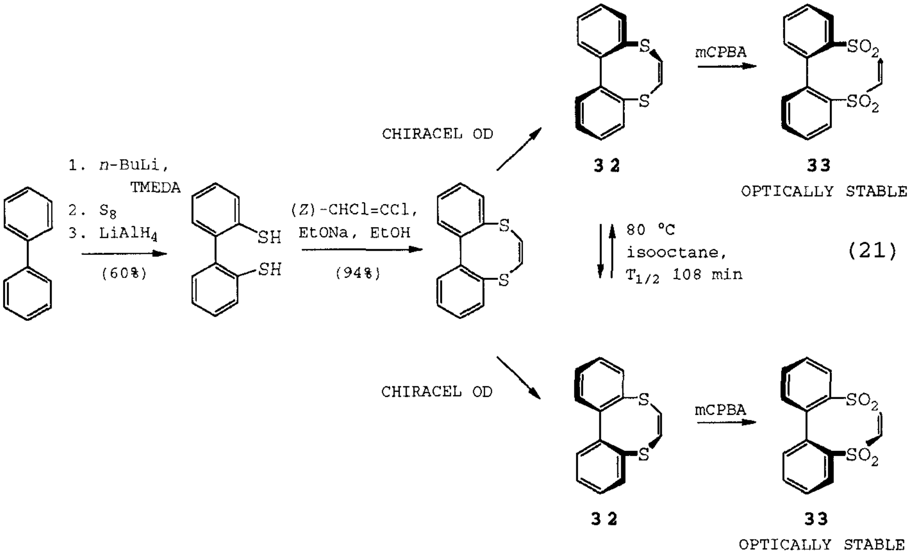
On the basis of the results obtained so far, there is no evidence of charge delocalization in the allyl anion **26** probably because of the peculiar geometry of this molecule that precludes a correct orbital allignment of the allyl system.

BIPHENYL DERIVATIVES

As already mentioned, the preparation of all the compounds described here in optically pure form can be achieved with the use of optically pure dithiol **1**. Alternatively, resolution can be performed by chromatographic separation either of the reagents (*e.g.* **10**, **12**, **14** *etc.*) or of the products.[21] The successful chromatographic separation of the binaphthyl compounds turned our attention to the chemistry of the biphenyl derivatives.

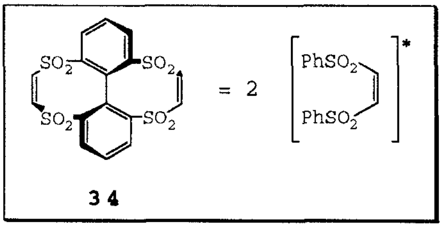
Indeed, a drawback that is intrinsic to the binaphthyl reagents is that the binaphthyl residue has a large molecular weight and that in the diastereomerically pure products most of the weight is due to the chiral auxiliary. A substantial reduction in molecular weight can be obtained using biphenyl derivatives. The use of these lighter auxiliaries is possible because the biphenyl reagents exhibit similar reactivity as the binaphthyl homologues and because they are optically stable.

The dibenzo-2,2'-dithiol precursor is readily available by direct metallation of biphenyl as shown in Eq. (21).[22] The 1,4-dithiocine **32** derived therefrom could be racemised in boiling isooctane with $T_{1/2}$ of *ca.* 2 h. The corresponding tetroxide **33** could not be racemised even after prolonged heating. It is hence possible to prepare a single enantiomer from the racemate and store it indefinitely in optically active form after oxidation.[21]

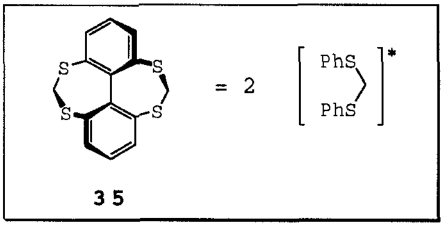


(21)

A further reduction in molecular weight of the auxiliary can be achieved by including a second reactive unit per auxiliary. The two reactive sites need to possess homochirality as in **34** and **35**. These two molecules correspond to more synthons assembled in a single reagent in a chiral form.

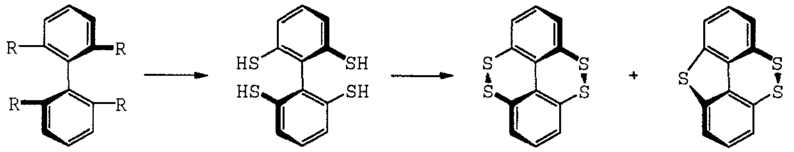


34



35

The preparation of **34** and **35** entails a synthesis of the corresponding tetrathiol **35**. The latter oxidises very readily in the air and could be isolated only as the bis-disulfide **36** with the sequence of reactions of Eq. (22). In the same reaction larger quantities of the unusual compound **37** are also produced.[23]



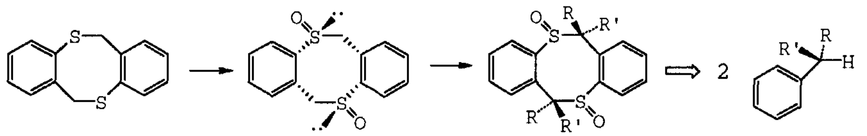
35 **36** **37** (22)

R= OMe -> OH -> OCSNMe$_2$ -> SCONMe$_2$ -> SH

It should be noted that in recent times reagents containing more homochiral reactive sites have been proposed by Davies et al. also.[24]

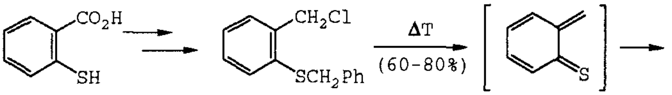
6*H*,12*H*-DIBENZO[*b*,*f*][1,5]DITHIOCIN

We reasoned that a further improvement could be obtained if it would prove possible to assemble more prochiral fragments in a chiral form by means of conjunctive atoms which can eventually be removed. Sulfur is particularly suited as a conjunctive atom because it can be made asymmetric by enantioselective oxidation to the sulfoxide, because it imparts efficient activation to the vicinal carbon and because it can be readily removed at the end. In this strategy it is important to devise a system capable of giving high diastereoselectivity in order to avoid complex mixtures of stereoisomers. Along these lines, the oxidised 1,5-dithiocin **39** corresponds to the assembling of two reactive benzyl units in a chiral form.[25]



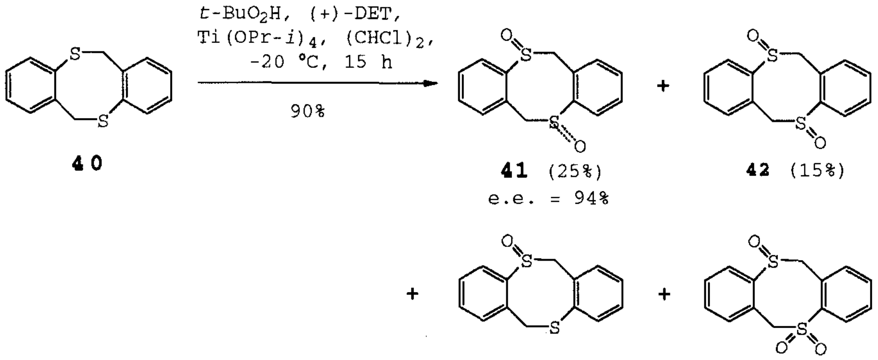
40 **39** (23)

6*H*,12*H*-Dibenzo[*b*,*f*][1,5]dithiocin **40** was obtained in up to 80% yield optimizing the reported[26] pyrolysis of *o*-benzylmercaptobenzyl chloride as shown in Eq. (24).



40 (24)

Asymmetric oxidation[27] of **40** with *t*-butylhydroperoxide in 1,2-dichloroethane in the presence of (+)-diethyltartrate and titanium tetraisopropoxide[28] at -20 °C for 15 h afforded a mixture of four products as represented in Eq. (25).



40

41 (25%)
e.e. = 94%

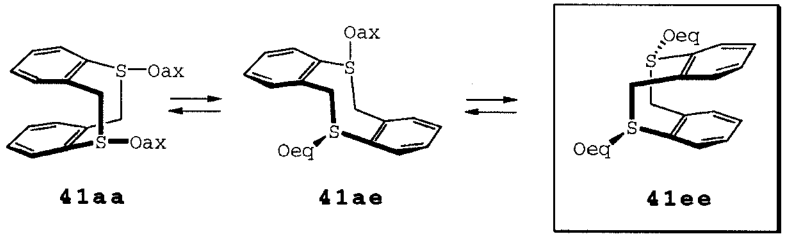
42 (15%)

43 (40%)
e.e. = 40%

44 (10%)
e.e. = 60%

(25)

The products were separated by flash chromatography and charachterized. The enantiomeric purity of each sulfoxide was determined by ^{1}H-NMR by addition of trifluoroanthracenyl ethanol. In a reaction performed on 2 grams scale the enantiomeric purity of the "non-meso" bis-sulfoxide **41** was 96%. It should be noted that the ^{1}H-MNR spectrum shows in the aliphatic region a sharp AB system suggesting the exclusive formation of the syn-bisequatorial conformer **41ee**.

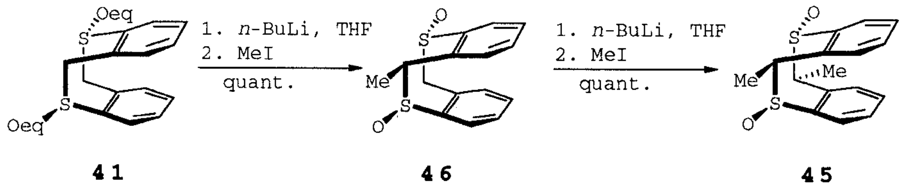


(26)

The anti-conformer **41ae**, in which one oxygen is axial and the other equatorial, is not consistent with the observed NMR spectrum (it does not change even at low temperatures), while the bis-axial conformer **41aa** is supposedly of higher energy.

The other products of Eq. (25) were characterized as the meso dioxide **42**, the monoxide **43** and the sulfone-sulfoxide **44**. It should be noted that the NMR spectrum of **43** at room temperature is quite broad suggesting that the molecule is very flexible. The conformations of the the bis-sulfoxides **41** and **42** and of the sulfoxide-sulfone **43** appear to be much less labile.

Representatively, a THF solution of **41** was treated with *n*-butyllithium and quenched with methyl iodide. The reaction gave rise to a single diastereomeric bis methylated product **45**.

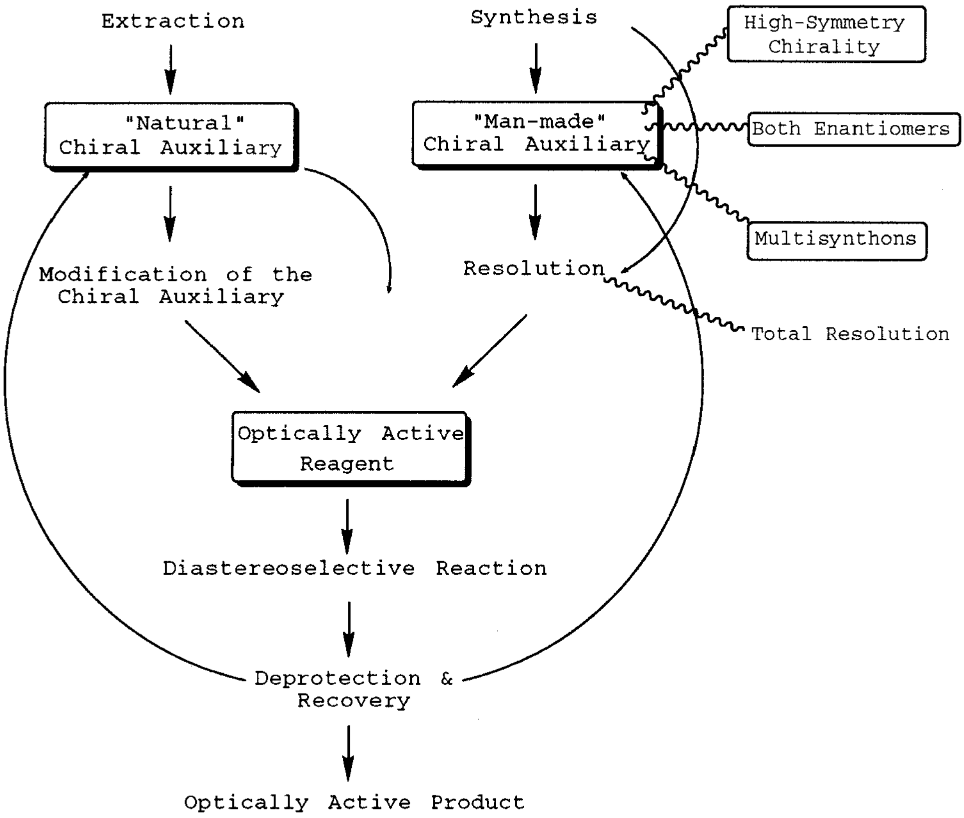


(27)

Stepwise deprotonation-methylation with one equivalent of base afforded the monosubstituted derivative **46** as single diastereoisomer. The stereochemistry shown has been determined by X-ray diffractometry. These results attest the feasibility of **41** to act as a chiral modification of the benzyl group with the minimum addition of molecular weight. Work is now in progress to determine the diasteroselectivity in the reaction with aldehydes which will be followed by the recovery of the substituted benzyl units.

CONCLUDING REMARKS

The following Scheme summarises the general reasoning that was followed during this research. We believe that now it may be legitimate to put forward non-natural chiral reagents and that the limited drawbacks of the resolution may sometime offset the obvious advantages of using common auxiliaries derived from the natural chiral pool. Most remarkably are the extra-features that can be introduced in non-natural chiral reagents such as the high-symmetry chirality and the possibility to include several reactive units per auxiliary. The latter concept can be achieved assembing synthons in a chiral form or linking prochiral fragment by sulfinyl groups. Furthermore, with non-natural chiral auxiliaries both enantiomers are available and "total resolution" can be obtained in some case. We are confident that future work will lead to more conclusive results and thus will make this strategy more attractive.



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