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Chiral sulfinyl-1,3-dienes. Synthesis and use in asymmetric reactions

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1. Introduction

The promising results obtained when racemic and, more recently, enantiopure sulfinyldienes are key partners in Diels–Alder (DA) reactions, the setting up of efficient methods for the asymmetric synthesis of a variety of sulfoxides, the general and well-accepted belief that sulfoxides represent an eclectic class of chiral auxiliaries, easy to remove and convertible into different functional groups without racemization, are the main reasons for increasing interest in the chemistry of conjugated diene sulfoxides. Recent years have witnessed an almost explosive development in their syntheses and a growing interest in their use in asymmetric reactions, but up to now these arguments have found restricted space in reviews[1] which provide great evidence of the synthetic usefulness of sulfoxides.

This report is mainly devoted to a survey of methodologies more frequently adopted in the synthesis of chiral[2] sulfinyldienes, paying special attention to the possibility of controlling their enantiomeric excess. The second part of the review illustrates the reactivity of chiral diene sulfoxides in DA reactions. A short account of stereocontrolled reactions, other than DA cycloadditions, is also given.

The report ends by Tables 1–3 and Schemes 34–39 (see Appendix A), showing an exhaustive listing of sulfinyldienes described in the literature: the absolute configuration of the sulfur centre is quoted only when the enantiomeric excess exceeds 90%; the registry numbers refer to racemate or isomeric mixtures, unless the configuration is explicitly stated. This review does not take into consideration sulfinyldiene systems involving heteroatoms in the basic diene skeleton, such as α,β-unsaturated sulfinylketones.[3]

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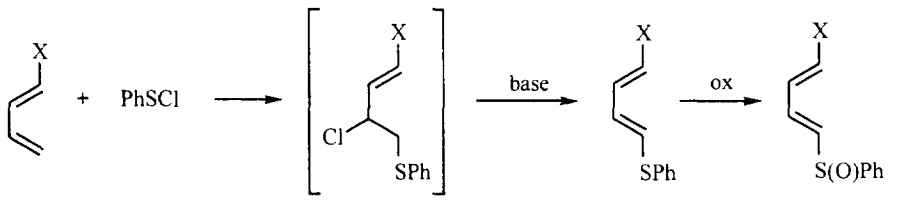
2. Synthesis of chiral sulfinyl-1,3-dienes

A comparative inspection of Tables 1–3 and Schemes 34–39 (see Appendix A) clearly evidences that a very large number of chiral 1-sulfinyldienes appears in the literature, compared to 2-sulfinyldienes. However, most 2-sulfinyldienes were obtained with high enantiomeric excesses. These trends are strictly related to the easier access to 1-sulfinyldienes, frequently by means of synthetic methodologies previously performed for vinylsulfoxides, and suitably modified. The syntheses of 2-sulfinyldienes are generally more recent, set up during the last few years when the interest in the preparation of enantiopure compounds notably increased.

2.1 Synthesis of 1-sulfinyl-1,3-dienes

Several methods for obtaining chiral sulfinyl-1,3-dienes, bearing the sulfoxide group on the first carbon atom of the diene moiety, are presently available, the more recent of which lead to enantiopure dienyl sulfoxides, but it is not always straightforward to gather them into a few general synthetic strategies.

The historically quoted synthetic approach to racemic 1-phenylsulfinyl-1,3-butadiene, described by Evans[4] in 1972, and used by Overman[5] for the preparation of 1,3-dienes possessing both sulfur and nitrogen substituents, is shown in Scheme 1.



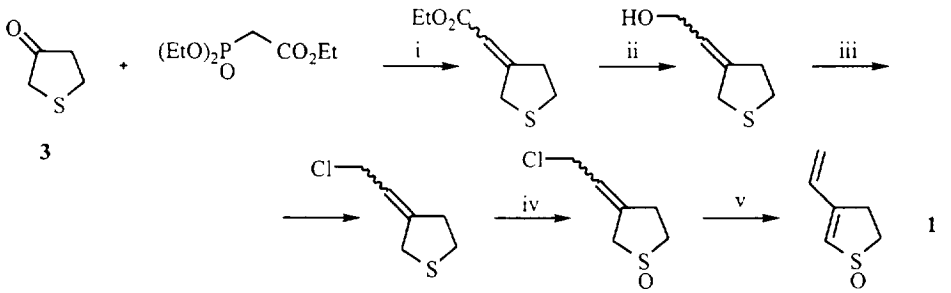
Scheme 1.

Later on, Overman et al.[6] reported the syntheses of sulfinyldienes **1** and **2** where the sulfinyl group is included in a five-membered ring (Scheme 2). These products were prepared following two different synthetic approachs: the first one starts from tetrahydrothiophen-3-one **3**, and 4,5-dihydro-3-ethenylthiophene-S-oxide **1** is obtained in a five-step sequence, while the second approach uses the Johnson procedure[7] for the cyclization of the ylide **4** in the presence of anhydrous $CuSO_4$, to yield 5-vinyl-1,3-oxathiole-3-oxides **2** (see Scheme 36).

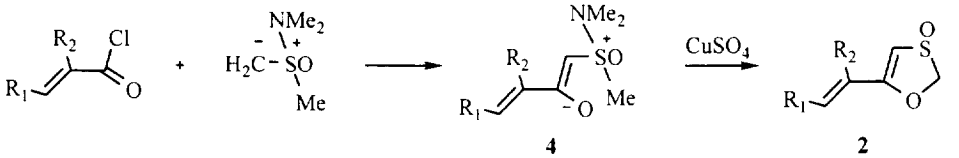
Thermal isomerization of sulfur substituted allene systems leads to the corresponding 1-sulfinyl-1,3-dienes.[8] The method has been successfully applied by Okamura in the synthesis of sensitive polyenes bearing useful functional groups. For instance, triene sulfoxides **5** and **6** (Scheme 3) are formed *via* the intermediacy of vinylallenes **7**, which are obtained in turn from [2,3]-sigmatropic shift of sulfenate esters **8**. The influence of phenylsulfinyl group on the course of the vinylallene variant of the [1,5]-sigmatropic hydrogen shift is emphasized:[8f] the sulfoxide group is an useful substituent which not only accelerates the [1,5]-shift but also can effect good control of π-facial stereoselection in the triene synthesis shown in Scheme 3 [**5**:**6** ratio ranges from ~4:1 to >98:2 (63–91%)].[8d]

Recent papers report the synthetic approach to a new class of 4-alkoxy-1-(phenylsulfinyl)-1,3-butadienes **9**,[9] characterized by an enantiopure alkoxy residue, coming from (L)-menthol or (−)-8-phenylmenthol. *trans*-Acetalization of methyl acetal **10** in acidic medium, followed by γ-elimination of methanol, affords sulfides **11**, easily oxidized to 1-sulfinyldienes **9** (Scheme 4). The elimination process leads to total control of the enol ether 3–4 bond without any stereoselectivity for the thioenol ether 1–2 double bond (1E,3E:1Z,3E=50:50). Furthermore, sulfur oxidation of asymmetric enol ethers **11** occurs without any diastereoselectivity.

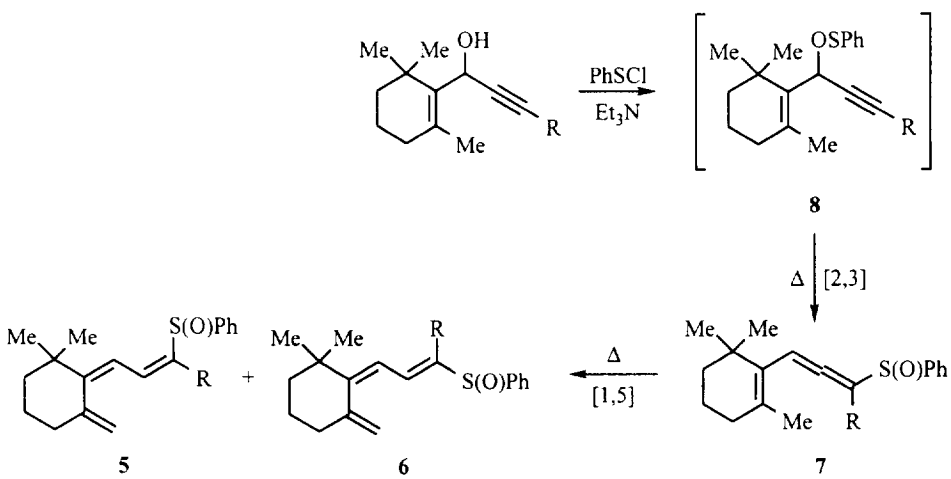
Coupling of a carbonyl compound with a sulfur containing ylide or anion represents a general



Reagents: i) NaH; ii) DIBAL; iii) $MeSO_2Cl$, collidine, LiCl; iv) $NaIO_4$; v) $(Me_3Si)_2NLi$



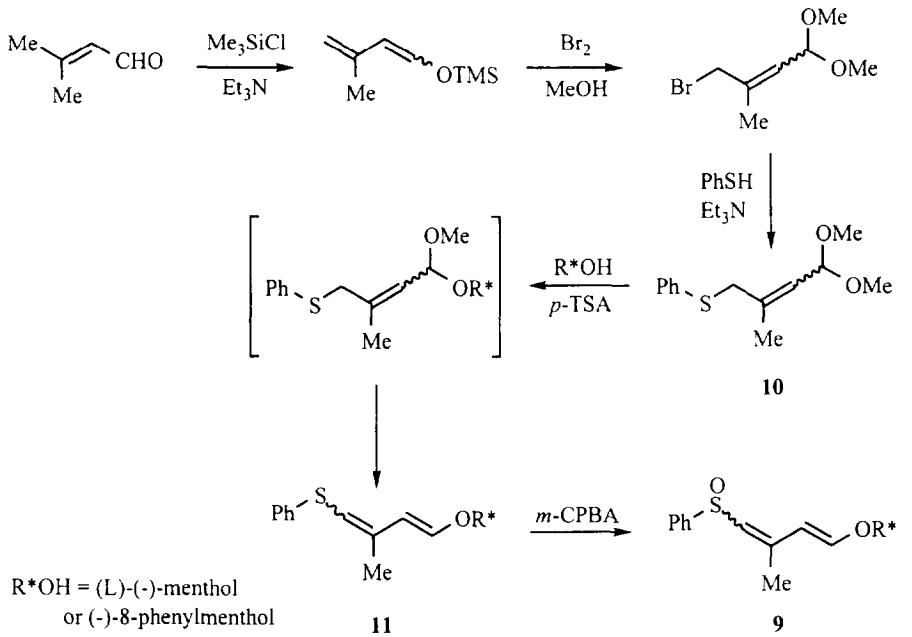
Scheme 2.



Scheme 3.

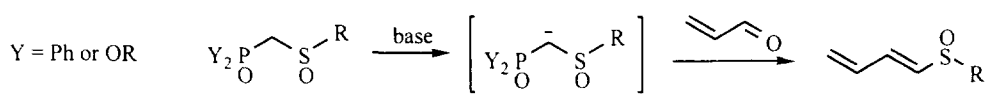
procedure for the generation of vinylsulfoxides, and has been widely exploited as an approach to 1-sulfinyldienes.

The Horner–Wittig or Horner–Wadsworth–Emmons reaction, successfully applied to the preparation of α,β-unsaturated sulfoxides,[10] can be easily extended to the synthesis of 1-sulfinyldienes by adding a sulfinyl diaryl or dialkoxy phosphine oxide anion to an α,β-unsaturated carbonyl compound (Scheme 5). Sulfinyldienes are obtained in good yields as a mixture of geometrical isomers where the (E)-isomer is prevalent. Generally, diarylsulfinylphosphine oxides and dialkyl arenesulfinylmethanephosphonates[11] have been used in the synthesis of racemic sulfinyldienes,[12] although enantiomerically pure α-phosphoryl sulfoxides can be easily obtained by reaction of enantiopure menthyl *p*-toluenesulfinate with dialkylphosphorylmethyllithium.[13] After the pioneering paper of Hoffmann,[14] describing the synthesis of (R_S)-1-(4-tolylsulfinyl)-1,3-butadiene from (S_S)-4-toluenesulfinylmethanephosphonate and acrolein, no further reports appeared in the literature, until the recent synthesis[15] of enantiopure 2- and 3-vinylindoles bearing a sulfoxide group at the β-vinyl positions. The Horner–Wadsworth–Emmons reaction was performed on indole 2- and 3-carbaldehydes



Scheme 4.

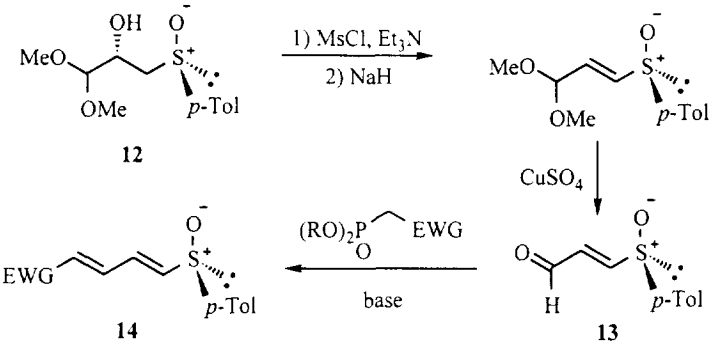
with (R)- or (S)-4-toluenesulfinylmethanephosphonate. There was no discrimination towards the E/Z configuration of the obtained 2-(*p*-tolylsulfinyl)vinylindoles with respect to the absolute configuration of the employed phosphonate, but the (E)-diastereomer represented generally the main product. These sulfinylvinylindoles are regarded as 1-sulfinyldienes because they act as 4π-components bearing the chiral auxiliary in asymmetric DA reactions (see section 3.1).



Scheme 5.

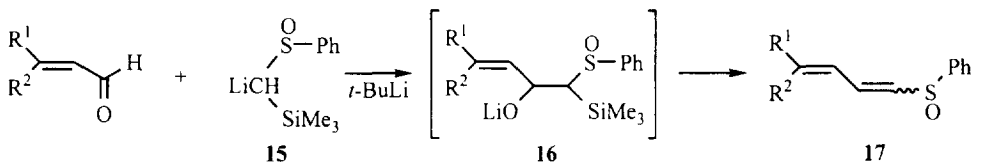
A different synthetic strategy, in any case based on the general Horner–Wadsworth–Emmons method, was described by the Cantoblanco researchers.[16] The α,β-unsaturated carbonyl compound, including a resolved chiral sulfinyl group, was condensed with readily available phosphonates, substituted with electron-withdrawing groups (Scheme 6). Starting from the easily accessible (S,R$_S$)-2-hydroxy-3-(*p*-tolylsulfinyl)propionaldehyde dimethyl acetal **12**, the (R$_S$,E)-3-(*p*-tolylsulfinyl)-2-propenal **13** was obtained in two steps, and then reacted with commercially available or easily obtainable phosphonates. The enantiomeric excess of sulfinyldienes **14**, range between 8% and 98%, reflect that of the starting aldehydes which often undergo partial racemization in the desacetalization step. The Horner–Wadsworth–Emmons approach appears especially reliable for introducing electron withdrawing substituents on the diene framework.

The nucleophilic attack of a trimethylsilyl carbanion onto an α,β-unsaturated carbonyl system affords an intermediate species which provides a new carbon–carbon double bond *via* a four-centre elimination process, similar to the conclusive step of a Wittig coupling reaction. Thus, 1-trimethylsilyl-1-(phenylsulfinyl)methyllithium (**15**) adds to α,β-unsaturated aldehydes or ketones to give intermediates **16** which fragment to 1-sulfinyldienes **17** and Me$_3$SiOLi under extremely mild conditions (Scheme 7).[17] Yields are generally good. The formation of these racemic sulfoxides is



Scheme 6.

not stereoselective at the double bond, mixtures of *cis* and *trans* isomers being formed from the different carbonyl compounds. Conjugate addition did not occur when acrolein, cinnamaldehyde, or cyclohexenone was used, exclusive 1,2-addition being observed.

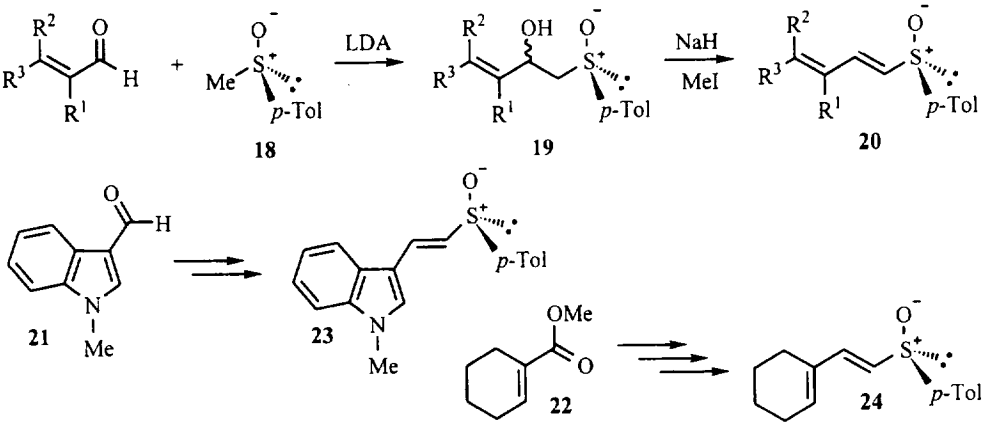


Scheme 7.

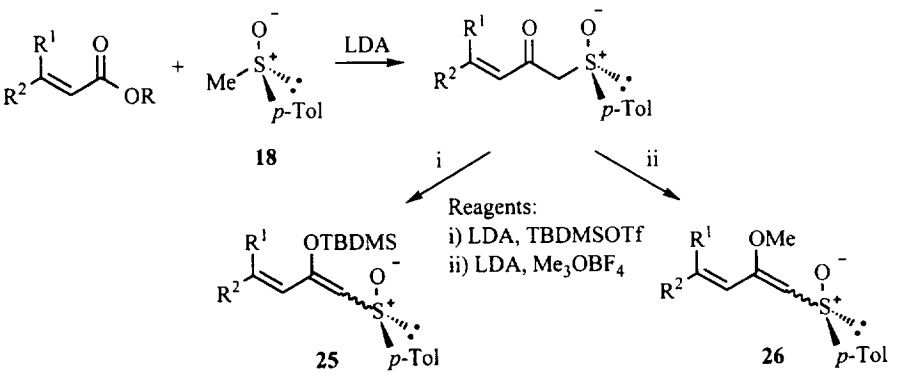
Condensation of an α-sulfinyl anion with a carbonyl group, followed by dehydration of the corresponding aldol compound, can be regarded as an efficient counterpart of the Wittig double bond generation. Strasbourg and Madrid researchers have successfully applied this methodology to the synthesis of a series of enantiomerically pure 1-sulfinyldienes.[18] Addition of the (R_S)-methyl-*p*-tolylsulfoxide **18** anion to α,β-unsaturated aldehydes afforded in all cases a mixture of diastereomeric carbinols **19** (Scheme 8).[18b,e] Subsequent dehydration in the presence of NaH/MeI produced the (E,E)-dienes **20** in high yields and, in most cases, as crystalline solids. Recently, the same methodology has been applied to the synthesis of enantiopure 1-sulfinyldienes with an endocyclic double bond.[18d] The anion of **18** was added to cyclic α,β-unsaturated aldehydes or esters, *i.e.* 3-formyl-1-methylindole **21** and 1-methoxycarbonylcyclohexene **22**: in this last case the obtained β-ketosulfoxide was reduced with DIBAL/$ZnBr_2$ to give enantiomerically pure β-hydroxysulfoxide (analogue of **19**) which was further dehydrated to the corresponding sulfinyldiene **24**. The obtainment, by this way, of N-methylindole **23** and cyclohexene **24**, bearing (R_S,E)-2-(*p*-tolylsulfinyl)vinyl substituents, would give access to polycyclic systems, otherwise not easily achievable.[18d] Sulfoxide **23** pertains to the group of 1-sulfinyldienes synthesized by Pindur[15] following the Horner–Wadsworth–Emmons methodology, but the synthesis performed by the French and Spanish researchers is much more efficient, giving **23** as a unique diastereomer, in 94% yield.

The adducts of enantiopure sulfoxide **18** with α,β-unsaturated esters in the presence of LDA were also converted into enantiomerically pure sulfinildienes **25** and **26** by carbonyl group enolization and quenching with *t*-butyldimethylsilyl triflate or trimethyloxonium tetrafluoborate (Scheme 9).[18c] Diene sulfoxides **25** were obtained as 9:1 mixtures of (1Z,3E) and (1E,3E), and the pure (1Z,3E) dienes were easily recovered by flash chromatography. Separation of the two isomeric dienes **26** (R^1=H, R^2=Me), which were obtained as a 84:16 mixture of (1Z,3E) and (1E,3E), was impossible.

Organometallic reagents, such as vinylstannanes, which are normally used in coupling reactions



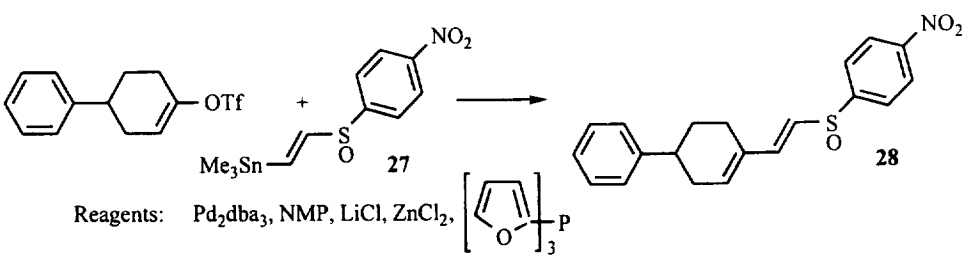
Scheme 8.



Scheme 9.

with carbonyl compounds according to the Stille methodology,[19] have been employed for the synthesis of sulfinyldienes.

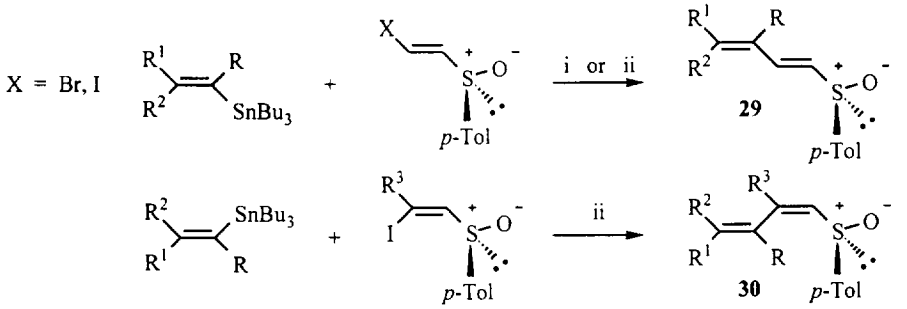
The coupling with vinyl triflate of sulfinylvinylstannane **27**, easily prepared from halovinylsulfoxide,[20] gave 1-sulfinyldiene **28** in good yield (Scheme 10) as mixture of epimers at sulfur.



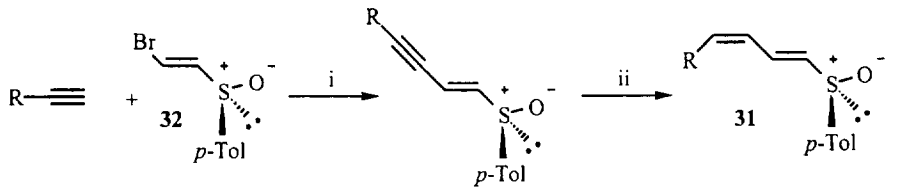
Scheme 10.

An interesting approach was recently developed for the synthesis of enantiomerically pure sulfinyldienes with controlled double bond geometries. Three class of stereoisomeric 1-sulfinyldienes **29–31** were prepared in good yields by utilizing Pd(0)-catalyzed coupling methodologies

(Scheme 11).[21] While dienes **29** and **30** were obtained by modified Stille coupling, the synthesis of (1E,3Z)-sulfinyldienes **31** involved the use of Sonogashira–Schreiber methodology[22] for coupling an alkyne with the enantiopure *trans*-2-bromovinylsulfoxide **32**.



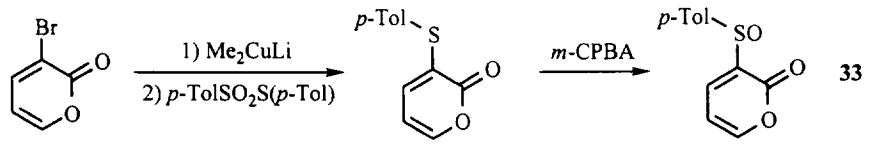
Reagents: i) $Pd_2dba_3.CHCl_3$, PPh_3; ii) $Pd(MeCN)_2Cl_2$



Reagents: i) $Pd(PPh_3)_3$, CuI, DBU; ii) H_2, $RhCl(PPh_3)_3$

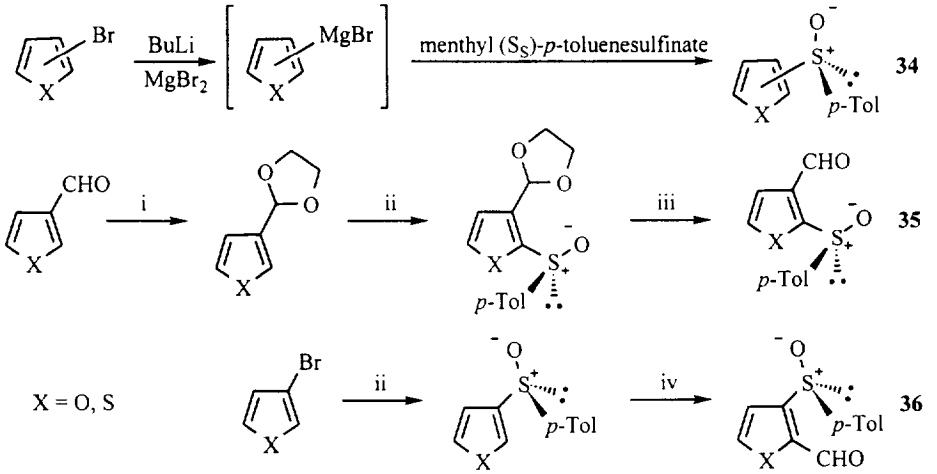
Scheme 11.

The nucleophilic character of organocopper compounds has been exploited in the synthesis of vinylsulfoxides, and easily extended to the preparation of 1-sulfinyldienes.[23,24] Posner et al. described a synthesis of 3-sulfur substituted 2-pyrones, based on the conversion of 3-bromo-2-pyrone into the corresponding 3-cuprio derivative (Scheme 12).[24a,25] The copper substituted pyrone couples with *p*-tolyl *p*-toluenethiosulfonate to form 3-*p*-tolylthio-2-pyrone in 65% yield, which is easily oxidized to the corresponding racemic sulfoxide **33**. A more difficult task was represented by the synthesis of **33** in enantiomerically pure form: Posner prepared (S_S)-**33** (e.e. >96%) by dehydrogenating (S_S)-dihydropyrone sulfoxide[24b] in the presence of MnO_2, but he could never obtain more than a few milligrams of this enantiopure heterocyclic non-aromatic 1-sulfinyl-1,3-diene.[24c]



Scheme 12.

The most widely used approach to enantiomerically pure sulfoxides, the Andersen methodology, has been applied to the synthesis of enantiopure furyl and thienyl *p*-tolylsulfoxides,[26] and their formyl substituted analogues.[27] (S)-Menthyl *p*-toluenesulfinate was reacted with Grignard derivatives of furan or thiophene, leading to aromatic (S_S)-sulfoxides **34** (Scheme 13).[26] More recently the synthesis of sulfinylaldehydes **35** and **36** by a similar strategy has been reported.[27] Yields and enantiomeric excesses were very high. Compounds **34–36** can be regarded as 1- or 2-sulfinyl-1,3-dienes; synthetic approaches to this last family of diene sulfoxides will be widely discussed in the next paragraph.

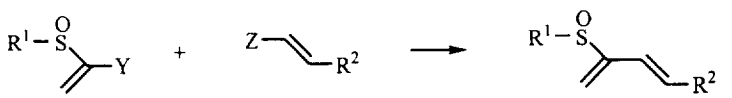


Reagents: i) $HOCH_2CH_2OH$, *p*-TSA; ii) BuLi, $MgBr_2$, menthyl (S_S)-*p*-toluenesulfinate; iii) acetone, PPTS; iv) LDA, DMF

Scheme 13.

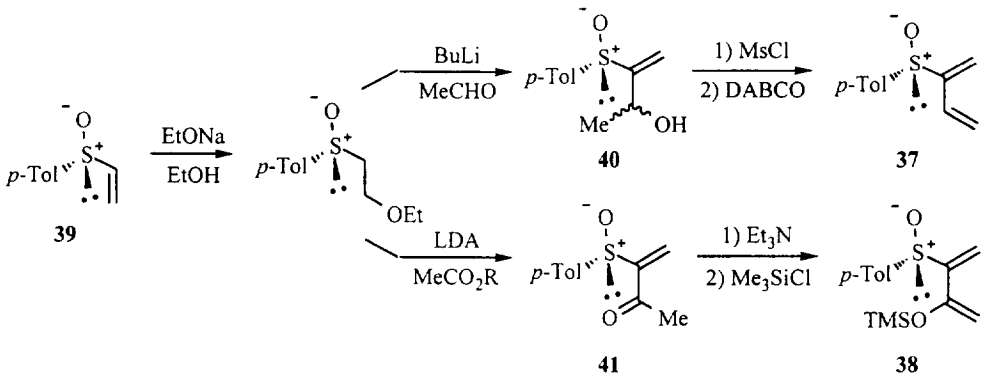
2.2 Synthesis of 2-sulfinyl-1,3-dienes

The most common approach to the synthesis of 2-sulfinyldienes involves the coupling of vinylsulfoxides with carbonyl or functionalized olefinic compounds for the formation of C_2–C_3 bond (Scheme 14). Enantiopure 2-sulfinyldienes are easily obtained by this strategy, if the enantiopure vinylsulfoxide is easily available. This is the case of both *p*-tolyl(vinyl)sulfoxide enantiomers which in turn can be prepared from vinylmagnesium chloride and the commercially available (−)-menthyl (S_S)- or (+)-menthyl (R_S)-*p*-toluenesulfinate.[28] Thus, a number of enantiopure 2-*p*-tolylsulfinyldienes have been recently reported in the literature, the first significant example of this approach being described by Maignan et al.[29] for the synthesis of enantiomerically pure 2-*p*-tolylsulfinyl-1,3-butadienes **37** and **38** (Scheme 15). (R_S)-(+)-*p*-tolyl(vinyl)sulfoxide **39** was the precursor of allylic alcohol **40** and unsaturated β-ketosulfoxide **41** which were used to produce 2-sulfinylbutadienes **37** and **38** respectively. Reaction of **40** with methanesulfonyl chloride afforded the mesylate which was treated with DABCO to provide **37** in 62% yield. β-Ketosulfoxide **41** was transformed into the silyloxysulfinylbutadiene **38** (51% yield) *via* treatment of its enolate with trimethylsilyl chloride. The sensitivity of **38** towards hydrolysis made its purification very difficult.



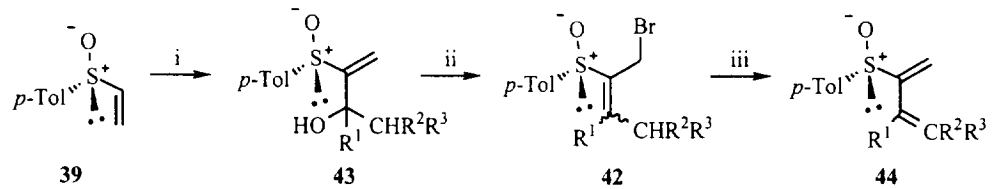
Scheme 14.

These synthetic procedures offer easy access to chiral 2-sulfinylbutadienes but their generalization proved to be unsuccessful, and the same Authors reported a more general procedure based on elimination from chiral sulfinylallylic bromides **42** (Scheme 16).[30] Alcohols **43** were directly obtained from (R)-(+)-*p*-tolyl(vinyl)sulfoxide **39**, and their subsequent treatment with N-bromosuccinimide led to the allylic bromides **42**. Various basic media and alcohols were used to finally reach dienes **44**, and KOH/*i*-PrOH appeared the more convenient combination. Recently, French authors[31] simplified the overall procedure, by reacting the lithiated anion of (+)-R-*p*-tolyl(vinyl)sulfoxide **39** with α-selenylcarbonyl compounds to give the corresponding β-hydroxy selenides; subsequent Krief–Reich



Scheme 15.

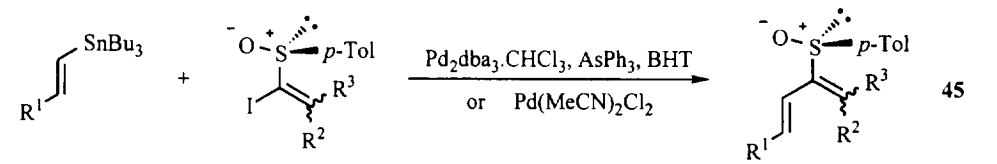
elimination[32] afforded enantiomerically pure mono-, di-, and trisubstituted 2-sulfinyl-1,3-butadienes in good yields.



Reagents: i) LDA, $R^1COCHR^2R^3$, aq. NH_4Cl; ii) NBS, Me_2S; iii) KOH, ROH

Scheme 16.

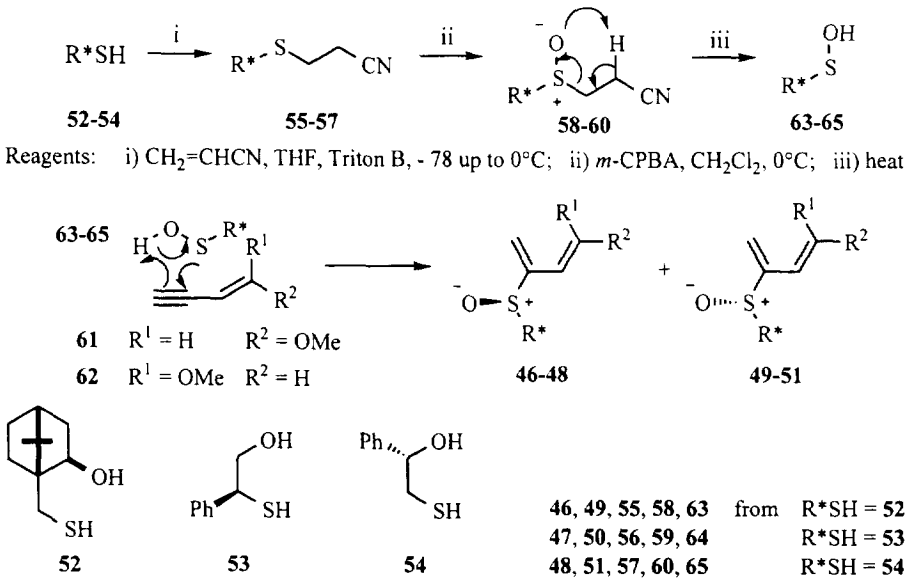
The same general approach to the synthesis of 2-sulfinyldienes, involving the formation of C_2–C_3 bond of the diene moiety, has been successfully employed by Paley et al.[33] Having developed a route to enantiopure 1-sulfinyldienes via Stille coupling of vinylstannanes with (E)- or (Z)-2-halovinylsulfoxides (see Scheme 11),[21] the authors extended this strategy to the preparation of enantiopure 2-sulfinyldienes **45** (Scheme 17). These compounds are easily accessible by coupling of 1-iodovinylsulfoxides with vinyltributylstannanes in the presence of $Pd(MeCN)_2Cl_2$ or $Pd_2(dba)_3.CHCl_3$ and the radical inhibitor BHT.



Scheme 17.

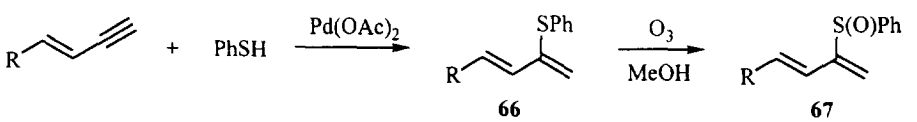
The general observation that sulfenic acids, conveniently generated by thermolysis of readily available sulfoxide precursors, add regiospecifically and in good yields to 1-alkynes[34] was applied to the synthesis of enantiopure 2-sulfinyldienes **46–51** (Scheme 18).[35] Base-catalyzed addition of hydroxythiols **52–54** to acrylonitrile afforded cyanohydroxysulfides **55–57** which were subjected to oxidation with *m*-CPBA to give sulfoxides **58–60** with very high diastereoselection in the case of sulfides **55** and **56**. Compounds **58–60** were thermolyzed in the presence of the appropriate enyne **61** or **62** to generate transiently the corresponding sulfenic acids **63–65** which were trapped by the enyne providing the required 2-sulfinylbutadienes **46–51** in acceptable to good yields. Each of these sulfinyldienes was formed as a mixture of sulfur epimers which were separated by chromatography

on silica gel. 10-Camphorsulfonic and mandelic acids, which are readily available members of the 'chiral pool', provided the precursors for hydroxythiols which were chosen because the contiguity and consequent intramolecular hydrogen bonding of hydroxy and sulfoxide functions in their derivatives facilitate the chromatographic separation of diastereoisomers and enhance diastereofacial selection in pericyclic processes. The high degree of stereochemical control, good yields and easy separation observed in the preparation of 2-sulfinyldienes derived from (1S)-10-mercaptoisoborneol **52** demonstrate the more general utility of camphor skeleton in designing of chiral auxiliaries based on sulfoxides.



Scheme 18.

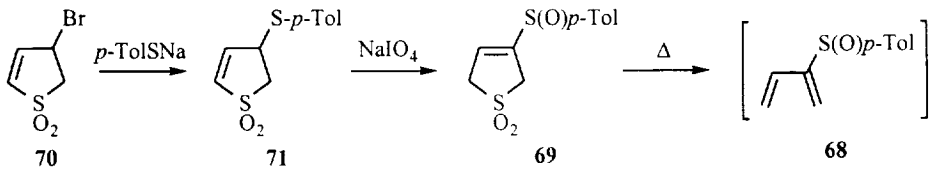
Recently, the regioselective Pd-catalyzed addition of thiophenol to conjugated enynes with a terminal triple bond has been reported (Scheme 19).[36] Oxidation of the 2-phenylthio-1,3-dienes **66** led to the corresponding 2-phenylsulfinyl-1,3-dienes **67** in racemic form. This approach, which shows many analogies with 2-sulfinyldiene formation by sulfenic acid-enyne regioselective addition (see Scheme 18), has been used by Aversa et al.[37] in an alternative attempt to obtain dienes **46–51**: this would avoid the disadvantageous step of the thermolytic generation of sulfenic acids and would reduce the steps of the already short synthesis of **46–51**. Failure of this attempt seems to confine to thiophenols the effectiveness of the approach shown in Scheme 19.



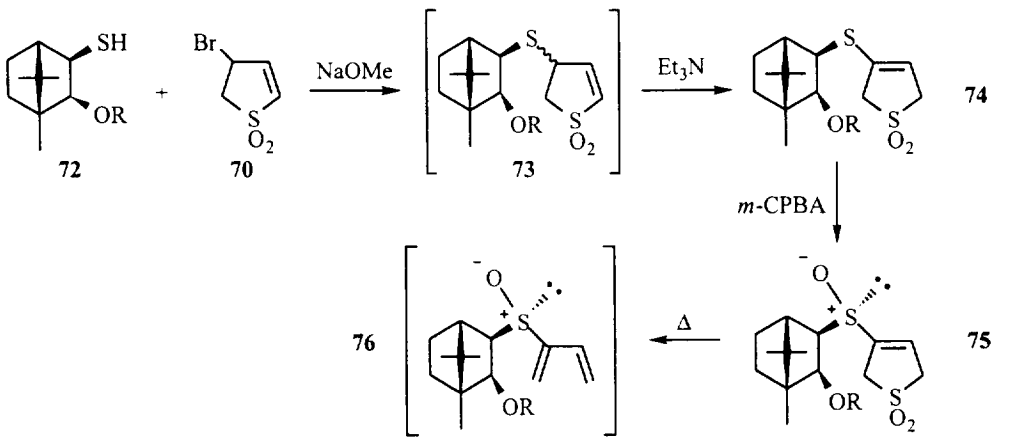
Scheme 19.

Readily available 3-sulfolenes lose SO_2, giving pure 1,3-butadienes, on heating at 110–130°C. The in situ preparation of racemic sulfinyldiene **68**, from 3-(*p*-tolylsulfinyl)-3-sulfolene **69** (Scheme 20), and its DA reactions have been firstly reported in 1978.[38] Sulfolene **69** was obtained in three steps by reacting 4-bromo-2-sulfolene (**70**) with sodium *p*-toluenethiolate to give 4-(*p*-tolylthio)-2-sulfolene **71**; $NaIO_4$ oxidation of **71**, accompanied by double bond shifting, gave the desired sulfoxide sulfone **69**.[39] The cheletropic process shown in Scheme 20 has been recently extended to the synthesis of

enantiomerically pure 2-sulfinyldienes by attaching the chiral auxiliary to stable 3-sulfolenes which would then generate chiral dienes by thermal extrusion.[40] The synthetic strategy starts with coupling of thiol **72** with 4-bromo-2-sulfolene **70** in the presence of sodium methoxide (Scheme 21). Triethylamine induces rearrangement of the diastereomeric 4-mercapto-2-sulfolenes **73** to 3-mercapto-3-sulfolenes **74**. Oxidation of **74** with *m*-CPBA gives essentially the single isomers **75** in high yield as precursors of dienes **76** which are generated in situ to be reacted as will be later discussed.



Scheme 20.



Scheme 21.

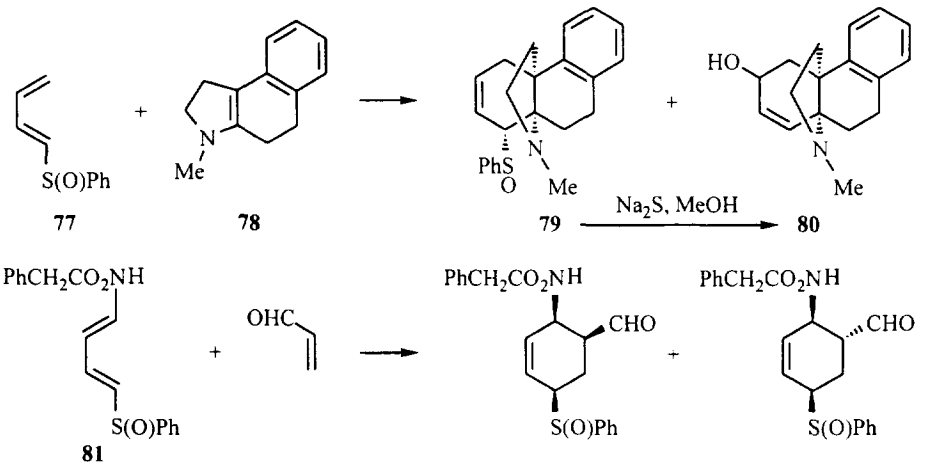
3. Asymmetric Diels–Alder cycloadditions of chiral sulfinyl-1,3-dienes

An evaluation of the potential of chiral sulfinyldienes in asymmetric synthesis is inevitably centred in their DA reactions. The role of the sulfinyl group, in controlling π-facial diastereoselectivity of cycloadditions where sulfinylvinyl derivatives are involved as dienophiles, is well recognized,[41] but the behaviour of enantiomerically pure sulfinyldienes in DA reactions have received hitherto little attention, presumably owing to difficulties in their preparation, even if the incorporation of the sulfoxide function into the diene component provides a wide scope for synthetic transformations of the initial adducts. To the best of our knowledge, only nine papers [15,18d,e,35b,40,42a,43–45] are concerned at present with DA reactions of enantiopure diene sulfoxides.

3.1 1-Sulfinyl-1,3-dienes in Diels–Alder reactions

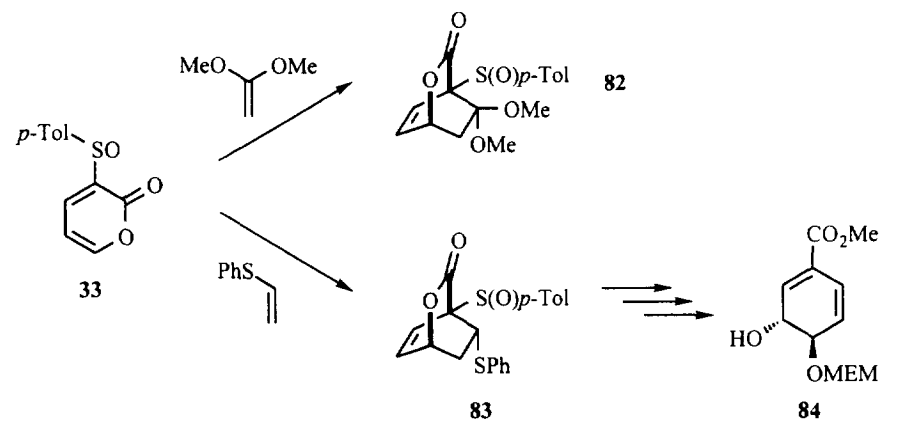
Thiophene sulfoxides, and their methyl and phenyl substituted analogues, are very unstable and reactive intermediates which are formed, together with the corresponding sulfones, during *m*-CPBA oxidation of thiophenes: sulfoxides and sulfones react each other in DA fashion having both ene and diene properties, to give polycyclic 'sesquioxides'. These results were described by a Dutch paper in 1953,[46] which can be regarded as the first report concerning the formation of 1-sulfinyldienes and their DA cycloadditions. Later on, Torssell[47] proposed the oxidation of substituted thiophenes in the presence of benzo- or naphtho-quinones as trapping dienophiles, to lead to DA adducts which

in turn underwent further transformations. However Evans letter[4] can be regarded as the first paper pointing out the potentiality of 1-sulfinyldienes as chiral counterparts in asymmetric DA reactions.[48] (E)-1-(Phenylsulfinyl)-1,3-butadiene **77** was easily cycloadded to the tetrahydrobenzindole **78** to give a diastereoisomeric mixture of sulfoxides **79** (with a *syn*-relationship between sulfur and amino functions) as well as some rearranged amino alcohol **80** (Scheme 22). The orientating effect of PhSO group on *endo/exo* stereoselection was again observed by Overman et al.[5] when sulfinyl diene carbamate **81** was subjected to thermal cycloaddition with acrolein. The measured *endo/exo* ratio was 10:1 (Scheme 22). The complete regioselectivity of the cycloaddition was instead attributed to the stronger influence of the $NHCO_2CH_2Ph$ group which influences also the reaction rate.



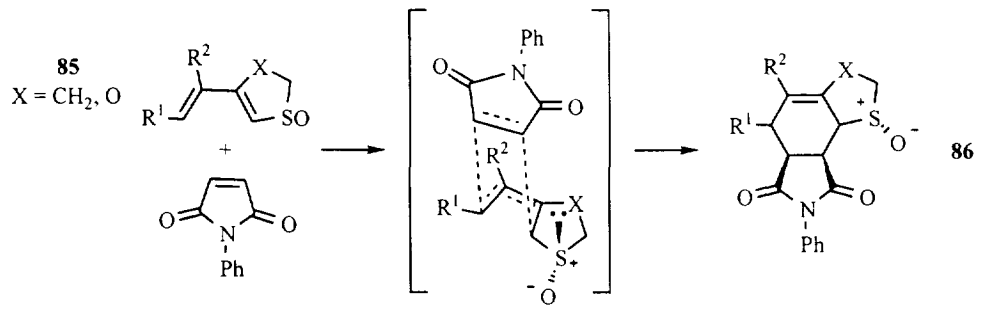
Scheme 22.

It was Posner in 1985[49] who first claimed the influence of sulfinyl group on the face selectivity in DA reactions. The racemic pyrone sulfoxide **33** underwent an inverse electron demand DA cycloaddition with 1,1-dimethoxyethylene (Scheme 23) to yield bicyclic adduct **82** as a mixture where one facial diastereoisomer was decidedly prevalent (88:12). Pyrone sulfoxide **33** also underwent highly *endo* and facial diastereoselective cycloaddition with phenyl(vinyl)sulfide giving mainly the adduct **83** which was further transformed into the chorismic acid intermediate **84** (Scheme 23).[24c]



Scheme 23.

Dienes **85** were reacted with the electron-deficient N-phenylmaleimide (NPM) under thermal conditions giving in each case a single cycloadduct in good yield (Scheme 24).[6] Adducts **86** resulted from the *endo* attack of NPM to the *anti*-face to the sulfoxide oxygen. This high *anti*-face selectivity was attributed to the destabilizing electronic interactions between the sulfur oxygen and the dienophile in the *syn*-transition state.



Scheme 24

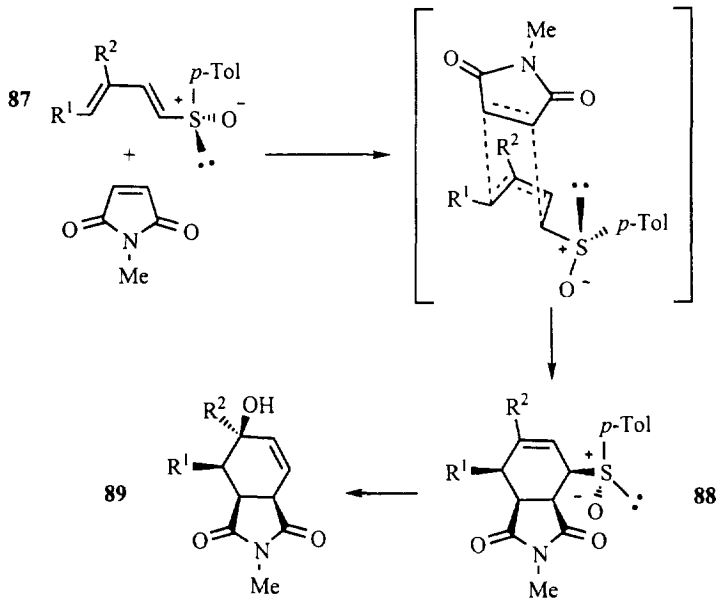
[4+2]-Cycloadditions described to date have been performed on racemic 1-sulfinyldienes, though the interest of utilizing enantiopure sulfinyl compounds was perceived by Posner who tried, with no success, the synthesis of sulfinylpyrone (S_S)-**33** (section 2.1).[24c] The first DA reaction of enantiomerically pure 1-sulfinyldienes was described by Carreño et al. in 1994.[18e] (R_S,1E)-1-*p*-Tolylsulfinyl-1,3-butadienes **87** were reacted with N-methylmaleimide (NMM) in both thermal and catalytic conditions (Scheme 25). *endo*-Cycloadducts **88** were obtained as unique compounds which easily rearrange to allylic alcohols **89** depending on the selected reaction conditions: long reaction times and NMM excess favoured the formation of alcohols **89** whereas the presence of Lewis acid increased the reactivity of sulfinyldienes **87** and allowed the clean isolation of adducts **88**. The high enantiomeric excess (>98%) of compounds **88** is strictly related to the high π-facial diastereoselectivity exerted by the sulfoxide function. The stereochemical course of these cycloadditions was explained by considering the transition state resulting from the *endo* approach of the dienophile to the less hindered face of the diene adopting s-*trans* conformation of S=O and C_1=C_2 bonds. In the indicated approach the NMM carbonyl oxygen and sulfinyl oxygen suffer minimum steric and electrostatic repulsions.

Polycondensed bicyclo[2.2.2]octenes **90** were obtained in highly stereocontrolled manner from the *endo*-diastereoselective cycloaddition of enantiopure cyclic dienes **91** to NMM, followed by [2,3]-sigmatropic rearrangement of the allylic sulfoxides **92** to compounds **93**, which underwent easy dehydration to conjugated dienes **94** (Scheme 26).[18d] Further DA reaction of **94** to NMM explains the formation of compounds **90** through the more favourable *endo*-approach on the less hindered diene face opposite to the five-membered ring. Similar cyclic substrates, used by Pindur[15] in cycloadditions with NMM, afforded similar results.

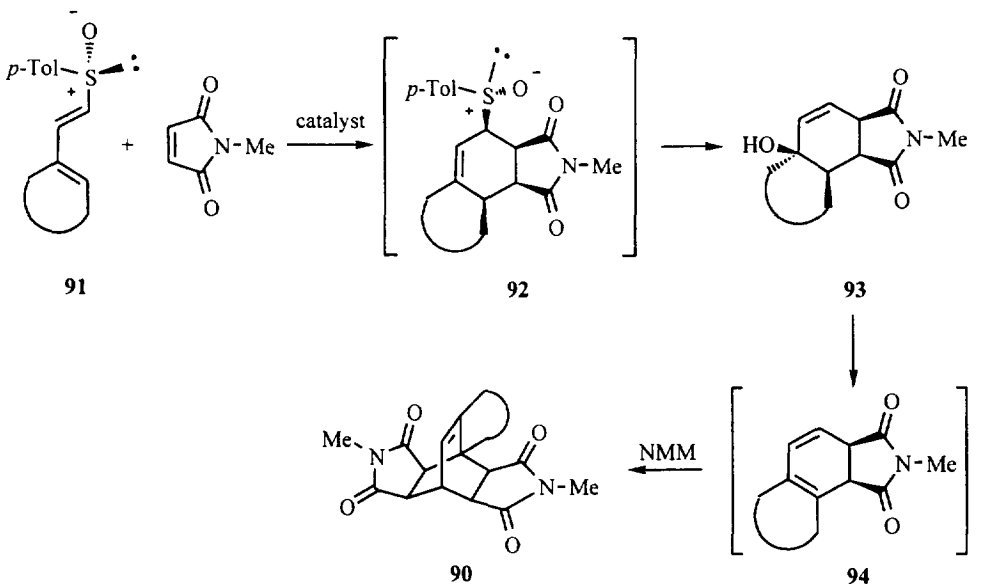
Going on with their investigations on DA reactions of enantiomerically pure 1-*p*-tolylsulfinyl-1,3-dienes, Cantoblanco researchers studied the cycloaddition between (R_S,E,E)-1-*p*-tolylsulfinyl-1,3-pentadiene **95** and maleic anhydride (MA) (Scheme 27): adducts **96** evolved stereoselectively in situ to lactones **97** and **98** through several intramolecular *tandem* reactions involving [2,3]-sigmatropic sulfoxide-sulfenate rearrangement, intramolecular acylation of the sulfinyl oxygen and elimination of the sulfur function.[44] Some cogent arguments are used by the authors to explain the low π-facial diastereoselection observed in the initial DA reaction.

3.2 2-Sulfinyl-1,3-dienes in Diels–Alder reactions

The first example of DA reaction in which 2-sulfinyldienes are involved involves cycloaddition of diene **68** generated in situ from racemic 3-*p*-tolylsulfinyl-3-sulfolene **69** (see Scheme 20) and reacted



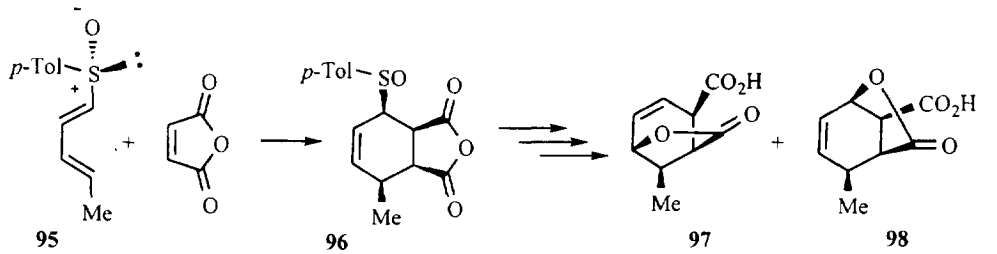
Scheme 25.



Scheme 26.

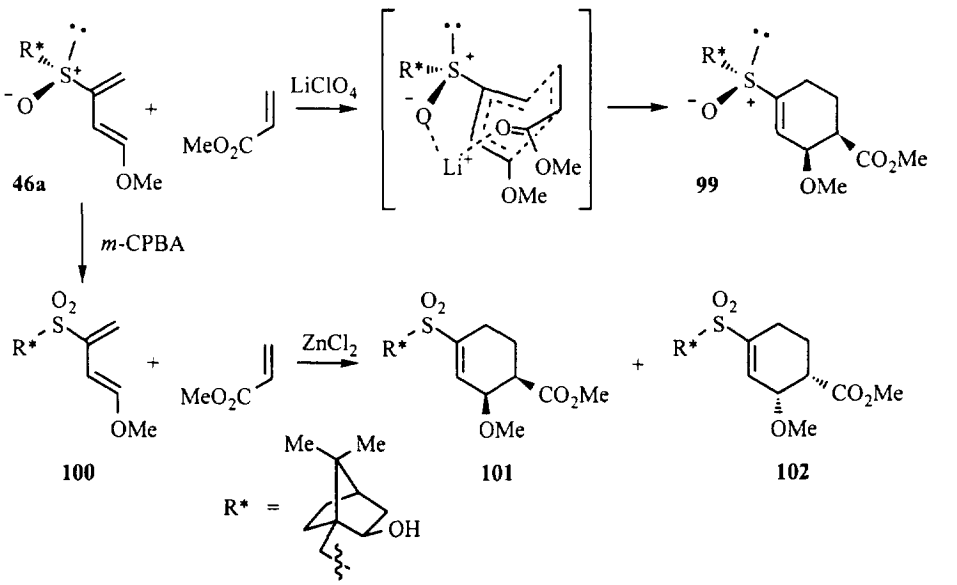
with various dienophiles.[38] This is also the only example of a DA reaction performed with racemic 2-sulfinyldienes, most of which were more recently synthesized and used in enantiomerically pure form.

No reports about promotion of asymmetric induction in DA reactions by enantiopure sulfinyl groups linked to the diene moiety had been published when we faced this matter,[35b,42] although a great number of enantiocontrolled syntheses of both 1- and 2-sulfinyldienes was already known (section 2). Cycloadditions of methyl acrylate to (R_S,E)- and (S_S,E)-3-alkylsulfinyl-1-methoxybutadienes **46–51** (R^1=H, R^2=OMe) (see Scheme 18), catalyzed by $LiClO_4$ or $ZnCl_2$, proceeded under very mild



Scheme 27.

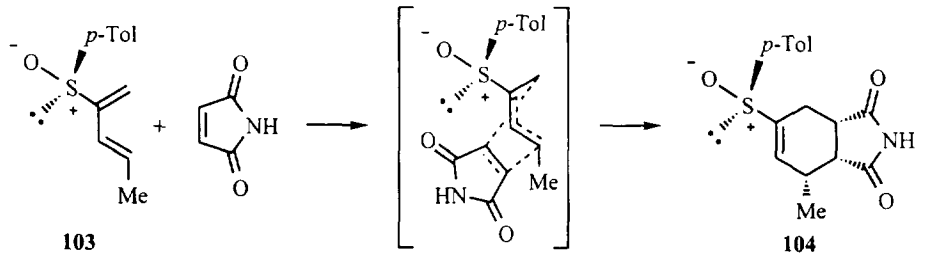
conditions with complete regioselectivity and very high stereoselectivity. A suspension of $LiClO_4$ in CH_2Cl_2 was used by us for the first time to catalyse DA reactions and gave the best results among various Lewis acids. For instance (Scheme 28) the enantiopure diene **46a** reacts with methyl acrylate in the presence of $LiClO_4$ to give the *endo*-adduct **99** with very good facial diastereoselection (92% d.e., 70% total yield). Good stereochemical results were obtained even with the less reactive (R_S,Z)-3-[(1S)-isoborneol-10-sulfinyl]-1-methoxy-1,3-butadiene **46b**. $ZnCl_2$ catalyzed DA reaction of methyl acrylate with sulfonyldiene **100** (readily obtained by oxidation of **46a** with *m*-CPBA) provided a 10:1 mixture of *endo*- and *exo*-adducts. The 1:1 ratio of facial diastereoisomers **101** and **102** shows that the chiral alkyl group linked to the sulfur function does not significantly influence the stereoselectivity of the cycloaddition, so confirming the fundamental role that sulfoxide plays in determining diastereoselectivity of 2-sulfinyldiene cycloadditions. The stereochemical control of the catalyzed DA reactions exerted by sulfur configuration may be rationalized in terms of mutual coordination of the metal cation with sulfinyl oxygen of the diene and carbonyl oxygen of the dienophile. These results showed a promising potentiality of chiral sulfoxide group, linked to the diene moiety, in promoting high *endo* and facial diastereoselectivities in [4+2] cycloadditions, and subsequent papers confirmed these expectations.



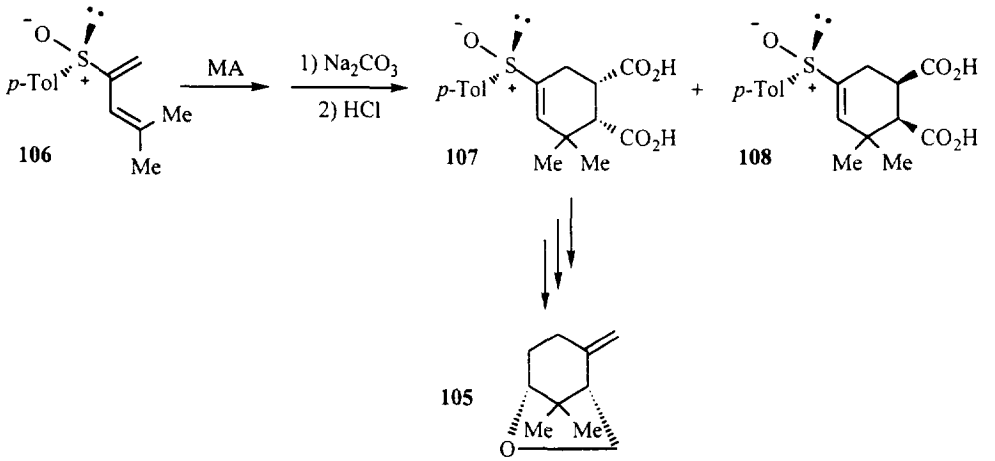
Scheme 28.

Reaction of (R_S,E)-2-*p*-tolylsulfinyl-1,3-pentadiene **103** with maleimide afforded compound **104**

as a single, enantiomerically pure adduct (Scheme 29), coming from *endo*-approach of dienophile to the less hindered and most nucleophilic side of the diene, opposite to *p*-tolyl group.[43] Recently, the same authors[45] described the synthesis of a natural product, the Karahana ether **105**, starting with the stereoselective DA reaction of (R$_S$)-4-methyl-2-(*p*-tolylsulfinyl)-1,3-pentadiene **106** with maleic anhydride (MA). After basic hydrolysis and acidification of the adducts, dicarboxylic acids **107** and **108** were easily isolated in 4:1 ratio (Scheme 30) being **107** the precursor of Karahana ether **105**.

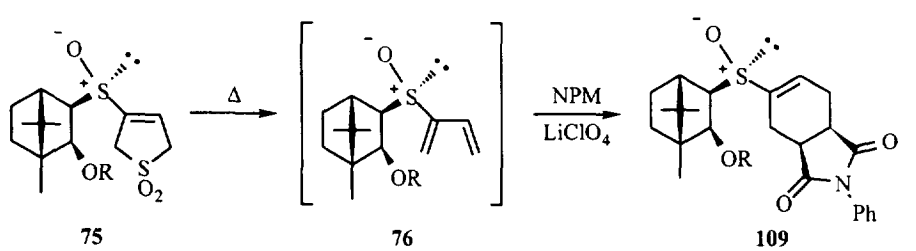


Scheme 29.



Scheme 30.

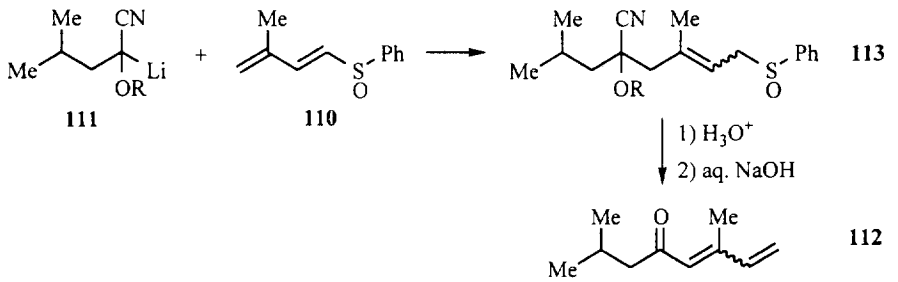
Enantiopure 2-sulfinyldienes **76**, generated in situ from 3-sulfinyl-3-sulfolenes **75** (see Scheme 21), were involved in cycloadditions with NPM (Scheme 31).[40] Among the various Lewis acids used as catalysts, $LiClO_4$ appeared the more efficient, giving almost exclusively the *endo*-cycloadduct **109**. The authors observed a significant steric effect on stereoselectivity, related to the size of the Lewis acid: the diastereoselectivity would be increased along with the size increment of the catalyst.



Scheme 31.

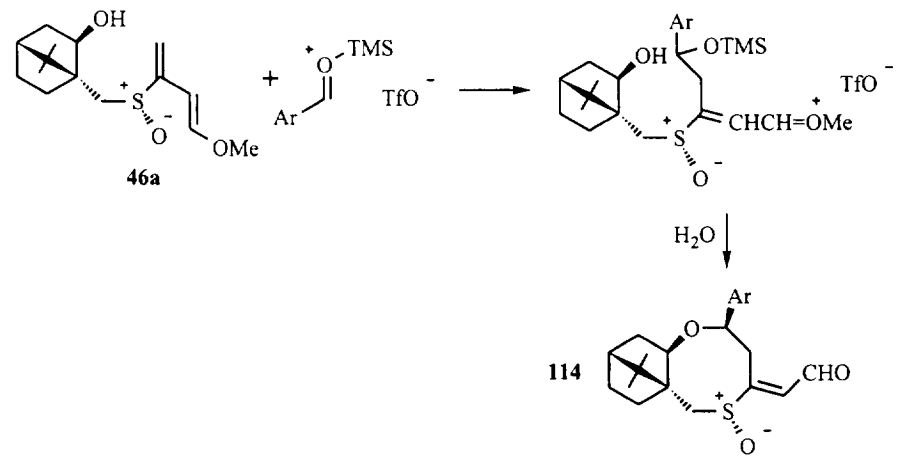
4. Other asymmetric reactions of chiral sulfinyl-1,3-dienes

Michael addition can be performed on 1-sulfinyl-1,3-dienes as described by Julia et al. for the synthesis of some terpenoid dienones.[8a,b,50] (E)-3-Methyl-1-phenylsulfinyl-1,3-butadiene **110** was reacted with the lithiated protected cyanohydrines **111** to give a mixture of (E) and (Z) terpenoid dienones **112**, after acidic hydrolysis of the sulfoxides **113** and basic removal of the sulfinyl group (Scheme 32).



Scheme 32.

More recently we described the unexpected results[51] of the reaction of the enantiopure isoborneolsulfinyldiene **46a** with benzaldehyde or *p*-nitrobenzaldehyde, performed in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf). The reaction path begins with nucleophilic addition of **46a** onto the aldehyde C=O group, activated by trimethylsilyl cation attack on the carbonyl oxygen, and leads to the formation of 2-aryl-4-formylmethylidene-1,5-oxathiocane-S-oxides **114**, *via* acid catalyzed ring closure and subsequent hydrolytic loss of the methoxy moiety (Scheme 33). The recovery of only one C–Ar epimer of the fused oxathiocane-S-oxides **114** is a consequence of the conformational control on cyclization, which gives rise to the formation of the thermodynamically favoured isomer.



Scheme 33.

Few other examples involving sulfinyldienes in Michael additions have been reported,[36,52] some of which[52b] involve more generally vinyl sulfoxides.

Furyl- and thienyl-aldehydes containing an enantiopure *p*-tolylsulfoxide group (see section 2.1) have been involved in the stereoselective reduction of the carbonyl group for the preparation of optically active furyl- and thienyl-alcohols which in turn represent versatile intermediates in the synthesis of biologically active or natural compounds.[53] The same substrates have been employed in hetero-

Diels–Alder (HDA) cycloadditions where the carbonyl group acts as heterodienophile.[54,55] These and few more reactions,[56] however, do not involve the sulfinyldiene moiety as a whole, and for this reason they are beyond the scope of the present report.

5. Concluding remarks

Stimulating conclusions can be taken on the reactivity of chiral sulfinyl-1,3-dienes, some of which are more evident such as the fundamental role exerted by sulfur chirality on the asymmetric induction in DA reactions, and some not yet understood such as the increased DA reactivity of 2-sulfinyl- in comparison with 1-sulfinyl-1,3-dienes. High *endo–exo* and/or π-facial diastereoselectivities are observed in most of the cases. Lewis acid catalysis plays an important role in increasing both rate and stereoselection of these reactions and, peculiarly, Li^+ coordination to both diene and dienophile has been proposed to explain some very good stereochemical results.[35b,42] The camphor skeleton linked to the sulfoxide moiety generally guarantees crystalline DA adducts so demonstrating its usefulness in the design of chiral auxiliaries based on sulfoxides, even if the *p*-tolyl group involves two orders of advantages: the easy availability of enantiomerically pure starting material for the synthesis of *p*-tolylsulfinyldienes and the easy removal of the sulfur auxiliary. For instance, in the case of 1-sulfinyldienes used in DA reactions, the allylic *p*-tolylsulfoxide group can be removed from the cycloadducts by sulfoxide-sulfenate [2,3]-sigmatropic rearrangement to allylic alcohols which in turn can be easily involved in further synthetic transformations.

Sulfinyldienes have not yet subjected to DA cycloadditions with heterodienophiles, the scope of this extension being the building of substituted heterocycles of biological interest. However, our preliminary experiments of cycloadding ethyl glyoxalate to (R_S,E)-3-[(1S)-isoborneol-10-sulfinyl]-1-methoxy-1,3-butadiene **46a** have been very encouraging, and will be reported in due course.

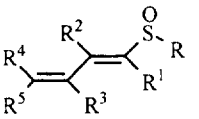
Acknowledgements

Financial support by MURST 40% is gratefully acknowledged.

Appendix A

Tables 1–3 and Schemes 34–39 follow:

Table .1. Open-chain *trans*-1-sulfinyl-1,3-dienes



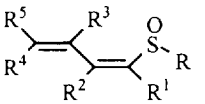
R	R^1	R^2	R^3	R^4	R^5	S*	Registry No.	Ref.
Cyclohex-anon-2-yl	H	H	H	H	H		79774-01-9 (R,R_S)[a] 79774-02-0 (S,R_S)[a]	57
Et	H	Me	Me	H	H		66464-00-4	39
Me	H	H	H	H	H		79773-93-6	57
Me	H	H	Me	H	H		66463-94-3	39
Me	H	Me	H	H	H		55833-46-0	23,39
Me	H	Me	Me	H	H		66463-98-7	39
Me	Cl	H	H	H	Et		161957-12-6	12e,43
Ph	H	H	H	H	H		40110-69-8	4,5,12b,17 39
Ph	H	H	H	H	*t*-BuOCONH		86802-63-3	5
Ph	H	H	H	H	Me		155091-42-2	12b-d,58
Ph	H	H	H	H	Ph		40110-72-3	12a,b,17,5
Ph	H	H	H	H	$PhCH_2OCONH$		86784-95-4	5,59
Ph	H	H	H	H	$PhSO_2$		150587-28-3	60
Ph	H	H	H	$C(=CH_2)(CH_2)_3CMe_2$			103149-80-0	8d-f,61
Ph	H	H	H	Me	$Me_2C=CH(CH_2)_2$		55816-11-1	12a,62
Ph	H	H	H	$Me_2C=CH(CH_2)_2$	Me		66967-57-5	12a
Ph	H	H	H	$PhSO_2$	H		145950-04-5	63
Ph	H	H	Me	H	H		66463-96-5	8a,b,12b, 39,50
Ph	H	H	Me	H	$PhSO_2$		145950-07-8	60,63
Ph	H	H	Me	$PhSO_2$	H		145950-06-7	63
Ph	H	Me	H	H	H		66464-10-6	12b,39
Ph	H	Me	H	H	Me		66464-03-7[b]	39
Ph	H	Me	H	H	(L)-Menthoxy		142351-18-6 (R_S) 142434-99-9 (S_S)	9b
Ph	H	Me	H	H	(-)-8-Phenyl-menthoxy		142351-19-7 (R_S) 142435-01-6 (S_S)	9b
Ph	H	Me	Me	H	H		66464-02-6	39,64
Ph	*t*-Bu	H	H	$C(=CH_2)(CH_2)_3CMe_2$				8d,f
Ph	Et	H	H	$C(=CH_2)(CH_2)_3CMe_2$			103149-84-4	8d,f
Ph	Me	H	H	$C(=CH_2)(CH_2)_3CMe_2$			103149-82-2	8d-f,61,65
Ph	*i*-Pr	H	H	$C(=CH_2)(CH_2)_3CMe_2$			103149-86-6	8d,f
Ph	HOCO	H	Me	H	H		80352-69-8	8b
Ph	Me	H	Me	H	H		80352-68-7	8b
Ph	$TBDMSO(CH_2)_2$	H	H	Cyclohepten-1-yl	H		127914-66-3	61
p-Tol	H	H	H	H	H	R_S	73766-36-6	14,21a
p-Tol	H	H	H	H	3-(1,3-Dithiolane-2-yl)propyl	R_S	148873-22-7	21a

R	R^1	R^2	R^3	R^4	R^5	S*	Registry No.	Ref.
p-Tol	H	H	H	H	Et	R_S	139024-88-7	18b
p-Tol	H	H	H	H	$(EtO)_2CH$	R_S	148873-20-5	21a,66b
p-Tol	H	H	H	H	$(EtO)_2PO$	R_S	170956-56-6	16
p-Tol	H	H	H	H	EtS	R_S	170956-58-8	16
p-Tol	H	H	H	H	Me	R_S	139024-87-6	18b,e,44
p-Tol	H	H	H	H	$2\text{-}MeOC_6H_4$	R_S	139024-90-1	18b
p-Tol	H	H	H	H	MeOCO	R_S	170956-54-4	16
p-Tol	H	H	H	H	CN	R_S	170956-55-5	16
p-Tol	H	H	H	H	Ph	R_S	139024-89-8	18b,e,21a
p-Tol	H	H	H	H	$PhSO_2$	R_S	170956-57-7	16
p-Tol	H	H	H	Bu	H	R_S	150764-27-5	21b
p-Tol	H	H	H	$HOCH_2$	H	R_S	150764-26-4	21b
p-Tol	H	H	H	Me	Me	R_S	139048-05-8	18b,21a
p-Tol	H	H	EtO	H	H	R_S	148873-18-1	21a
p-Tol	H	H	Me	H	H	R_S	148873-17-0	21a
p-Tol	H	H	Me	H	EtO	R_S	155409-79-3	18e
p-Tol	H	MeO	H	H	Me	R_S	143919-70-4	18c
p-Tol	H	TBDMSO	H	H	Me	R_S	143919-66-8	18c
p-Tol	H	TBDMSO	H	H	Ph	R_S	143919-68-0	18c
p-Tol	H	TBDMSO	H	Me	Me	R_S	143919-67-9	18c
p-Tol	(S_S)-*p*-TolSO	H	H	H	Et	S_S	135510-12-2	18a
p-Tol	(S_S)-*p*-TolSO	H	H	H	Me	S_S	135510-11-1	18a
p-Tol	(S_S)-*p*-TolSO	H	H	H	$2\text{-}MeOC_6H_4$	S_S	135510-14-4	18a
p-Tol	(S_S)-*p*-TolSO	H	H	H	Ph	S_S	135510-13-3	18a

[a]Relative stereochemistry.

[b]Double bond geometry not assigned.

Table .2. Open-chain *cis*-1-sulfinyl-1,3-dienes

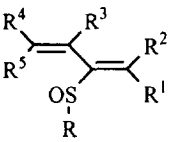


R	R^1	R^2	R^3	R^4	R^5	S*	Registry No.	Ref.
$AcCH_2$	H	H	H	H	H		79773-95-8	57
p-$BrC_6H_4COCH_2$	H	H	H	H	H		79773-98-1	57
p-ClC_6H_4	$Br(CH_2)_5$	H	H		$C(=CH_2)(CH_2)_3CMe_2$		124267-06-7	61
Cyclohexanon-2-yl	H	H	H	H	H		79773-99-2 (R,R_S)[a] 79774-00-8 (S,R_S)[a]	57
Et	H	H	H	H	H		79773-94-7	57
Et	H	Me	Me	H	H		66463-99-8	39
$EtOCOCH_2$	H	H	H	H	H		79773-96-9	57
Me	H	H	H	H	H		79773-92-5	57
Me	H	H	Me	H	H		66463-93-2	39
Me	H	Me	H	H	H		66464-08-2	39
Me	H	Me	Me	H	H		66463-97-6	39
Ph	H	H	H	H	H		40110-70-1	12b,1 39,64
Ph	H	H	H	H	Me		155091-43-3	12b-c 58
Ph	H	H	H	H	Ph		40110-71-2	12b,1 39,58 64
Ph	H	H	H		$C(=CH_2)(CH_2)_3CMe_2$		103149-79-7	8d-f, 61,65
Ph	H	H	Me	H	H		66463-95-4	12b,3
Ph	H	H	Me	H	$PhSO_2$		150587-48-7	60
Ph	H	Me	H	H	H		66464-09-3	12b,3
Ph	H	Me	H	H	Me		66464-03-7[b]	39
Ph	H	Me	H	H	(L)-Menthoxy		142434-96-6 (R_S) 142434-98-8 (S_S)	9b
Ph	H	Me	H	H	(-)-8-Phenylmenthoxy		142434-97-7 (R_S) 142435-00-5 (S_S)	9b
Ph	H	Me	Me	H	H		66464-01-5	39,64 67
Ph	t-Bu	H	H		$C(=CH_2)(CH_2)_3CMe_2$		103149-87-7	8d,f,6
Ph	Et	H	H		$C(=CH_2)(CH_2)_3CMe_2$		103149-83-3	8d,f
Ph	Me	H	H		$C(=CH_2)(CH_2)_3CMe_2$		103149-81-1	8d-f,61,6
Ph	i-Pr	H	H		$C(=CH_2)(CH_2)_3CMe_2$		103149-85-5	8d,f,6
Ph	$TBDMSO(CH_2)_2$	H	H	Cyclohepten-1-yl	H		127943-58-2	61
$PhCH_2$	H	H	H	H	H		79773-91-4	57
$PhCOCH_2$	H	H	H	H	H		79773-97-0	57
p-Tol	H	H	H	H	H	R_S	73766-38-8	14,21
p-Tol	H	H	H	H	(R)-CH_2=$CHCH_2CHOH$	R_S	183134-27-2	66b
p-Tol	H	H	H	H	$(EtO)_2CH$	R_S	148873-21-6	21a, 66b
p-Tol	H	H	H	Me	Me	R_S	148873-15-8	21a
p-Tol	H	H	EtO	H	H	R_S	151263-81-9	21a
p-Tol	H	H	Me	H	H	R_S	148873-19-2	21a
p-Tol	H	Bu	H	H	Ph	R_S		21a
p-Tol	H	MeO	H	H	Me	R_S	143919-69-1	18c
p-Tol	(S_S)-p-TolSO	H	H	H	Et	S_S	135510-12-2	18a
p-Tol	(S_S)-p-TolSO	H	H	H	Me	S_S	135510-11-1	18a
p-Tol	(S_S)-p-TolSO	H	H	H	2-$MeOC_6H_4$	S_S	135510-14-4	18a
p-Tol	(S_S)-p-TolSO	H	H	H	Ph	S_S	135510-13-3	18a

[a]Relative stereochemistry.

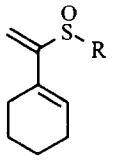
[b]Double bond geometry not assigned.

Table .3. Open-chain 2-sulfinyl-1,3-dienes

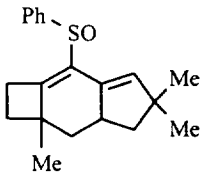


R	R^1	R^2	R^3	R^4	R^5	S*	Registry No.	Ref.
(1R,2S,3R)-Camphan-2-ol-3-yl	H	H	H	H	H	R_S	179938-62-6[a]	40
(S)-$HOCH_2CH(Ph)$	H	H	H	H	MeO	R_S	160833-96-5	35b
(S)-$HOCH_2CH(Ph)$	H	H	H	H	MeO	S_S	160833-95-4	35b
(S)-$HOCH_2CH(Ph)$	H	H	H	MeO	H	R_S	160833-94-3	35b
(S)-$HOCH_2CH(Ph)$	H	H	H	MeO	H	S_S	160833-93-2	35b
(1S)-Isoborneol-10-yl	H	H	H	H	MeO	R_S	143771-13-5	35a
(1S)-Isoborneol-10-yl	H	H	H	H	MeO	S_S	143838-66-8	35a
(1S)-Isoborneol-10-yl	H	H	H	MeO	H	R_S	143838-67-9	35a,42a,b,51
(1S)-Isoborneol-10-yl	H	H	H	MeO	H	S_S	143838-68-0	35a,42a
(1R,2S,3R)-2-Neopentoxycamphan-3-yl	H	H	H	H	H	R_S	179938-68-2[a]	40
Ph	H	H	Me	H	H		158750-17-5	36
Ph	H	H	Me	$HOCH_2$	H		158750-18-6	36
(S)-$PhCH(OH)CH_2$	H	H	H	H	MeO	R_S	160834-00-4	35b
(S)-$PhCH(OH)CH_2$	H	H	H	H	MeO	S_S	160833-99-8	35b
(S)-$PhCH(OH)CH_2$	H	H	H	MeO	H	R_S	160833-98-7	35b
(S)-$PhCH(OH)CH_2$	H	H	H	MeO	H	S_S	160833-97-6	35b
p-Tol	H	H	H	H	H		159533-17-2	38
p-Tol	H	H	H	H	H	R_S	142048-19-9	29,30,33
p-Tol	H	H	H	Et	H	S_S	154658-17-0	52a
p-Tol	H	H	H	Me	H	R_S	152836-39-0	30,31,43,68d
p-Tol	H	H	H	Me	H	S_S	154799-18-5	52a
p-Tol	H	H	H	Me	Me	R_S	152836-40-3	30,31,45
p-Tol	H	H	Me	H	H	S_S	153516-11-1	30
p-Tol	H	H	Me	Me	Me	S_S	181871-07-8	31
p-Tol	H	H	*i*-Pr	H	H	S_S	152836-41-4	30
p-Tol	H	H	TMSO	H	H	S_S	142048-20-2	29
p-Tol	H	Bu	H	H	H	R_S	167690-84-8	33,56b
p-Tol	H	Bu	H	Ph	H	S_S		33
p-Tol	Bu	H	H	H	H	R_S	167690-82-6	33,56b
p-Tol	Bu	Me	H	H	H	S_S		33
p-Tol	$PMBO(CH_2)_4$	H	H	H	H	R_S		33

[a]Generated in situ from the corresponding 3-sulfolenes.

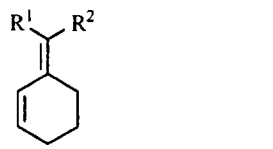


R	Registry No.	Ref.
(1S)-Isoborneol-10-yl	143771-14-6 (R_S)	35a
(1S)-Isoborneol-10-yl	143838-69-1 (S_S)	35a
Ph	74338-89-9	34,36
p-Tol	152836-42-5 (S_S)	30

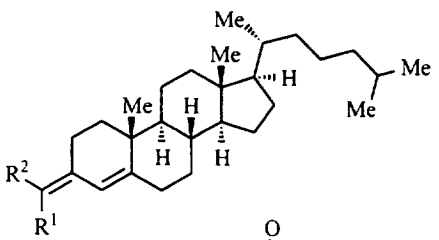


Registry No.	Ref.
114715-41-2 (S,S,R_S)	8g,66a
114636-41-8 (S,S,S_S)	
119904-14-2 (S,S,R_S-racemate)	
119904-15-3 (R,R,R_S-racemate)	

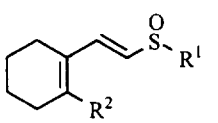
Scheme 34. Carbocyclic 2-sulfinyl-1,3-dienes.



R^1	R^2	Registry No.	Ref.
H	PhSO	80283-72-3	12b,17
PhSO	H	80283-73-4	12b,17

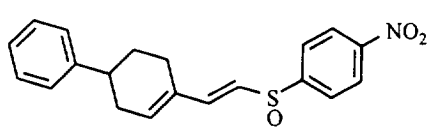


R^1	R^2	Registry No.	Ref.
H	PhSO	66967-54-2	12a
PhSO	H	66967-46-2	12a



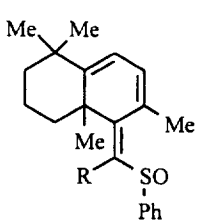
R^1	R^2	Registry No.	Ref.
Ph	$PhSO_2$	150587-51-2	60
p-Tol	H	158437-53-7 (R_S)	18d

24



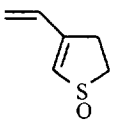
	Ref.
	20

28



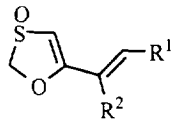
R	Registry No.	Ref.
H	94370-05-5 (R,S_S)	8c,66a,68a
	94370-06-6 (R,R_S)	
	94480-20-3 (S,R_S-racemate)	
	94480-21-4 (R,R_S-racemate)	
Et	114582-56-8 (E and Z)	68b
Me	114582-55-7 (E and Z)	61,68b
i-Pr	114582-57-9 (E and Z)	68b

Scheme 35. Carbocyclic 1-sulfinyl-1,3-dienes.



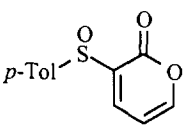
1

Registry No.	Ref.
114614-98-1	6a



2

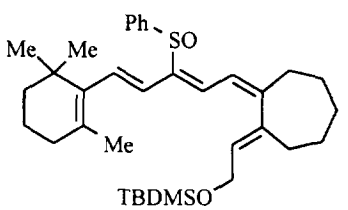
R^1	R^2	Registry No.	Ref.
H	H	114274-81-6	6a,b
H	Me	114274-84-9	6a,b
H	MeO	114299-62-6	6b
EtO	H	114274-85-0	6b
Me	H	114274-83-8	6b
MeO	Me	114274-86-1	6b
Ph	H	114274-82-7	6b
$(CH_2)_3$		114274-87-2	6b
$O(CH_2)_2CH_2$			6b



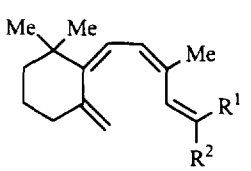
33

Registry No.	Ref.
99268-86-7	24a,c,25,49,68c
98061-55-3 (racemate)	

Scheme 36. Heterocyclic non-aromatic 1-sulfinyl-1,3-dienes.

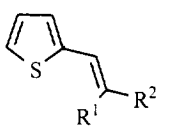


Ref.
61

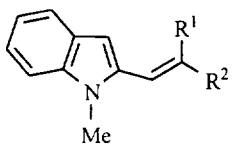


R^1	R^2	Registry No.	Ref.
t-Bu	PhSO	114582-60-4	68b
i-Pr	PhSO	114613-31-9	68b
PhSO	*t*-Bu	114582-59-1	68b
PhSO	*i*-Pr	114582-58-0	68b

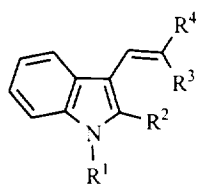
Scheme 37.



R^1	R^2	Registry No.	Ref.
Cl	MeSO	161957-11-5	12e
Cl	(S_S)-*p*-TolSO	185257-01-6	68e
(S_S)-*p*-TolSO	Cl	185257-02-7	68e



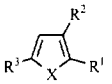
R^1	R^2	Registry No.	Ref.
H	(R_S)-*p*-TolSO	164164-80-1	15
(S_S)-*p*-TolSO	H	164164-83-4	15



	R^1	R^2	R^3	R^4	Registry No.	Ref.
	H	Me	H	(R_S)-*p*-TolSO	164164-76-5	15
23	Me	H	H	(R_S)-*p*-TolSO	158437-54-8	18d
	Me	H	H	(S_S)-*p*-TolSO	164164-74-3	15
	Me	H	(S_S)-*p*-TolSO	H	164164-73-2	15
	Me	Me	H	(R_S)-*p*-TolSO	164164-75-4	15
	$PhSO_2$	H	H	(S_S)-*p*-TolSO	164164-72-1	15
	$PhSO_2$	H	(S_S)-*p*-TolSO	H	164164-71-0	15
	$PhSO_2$	Me	H	(R_S)-*p*-TolSO	164164-77-6	15
	$PhSO_2$	Me	(R_S)-*p*-TolSO	H	164164-78-7	15

Scheme 38. Heterocyclic aromatic 1-sulfinyl-1,3-dienes with only one endocyclic double bond.

R^1	R^2	Ref.
H	Me	46,47
H	Ph	46
Me	H	46,47



X	R^1	R^2	R^3	Registry No.	Ref.
O	H	(S_S)-*p*-TolSO	H	143810-75-7	26,27,53a,55
O	(S_S)-*p*-TolSO	H	H	143810-74-6	26,27,53a,
				159169-40-1[a]	56a
O	*p*-TolSO	H	$Me(CH_2)_2CHOH$		56a
O	*p*-TolSO	H	CHO	159049-31-7	56a
O	(S_S)-*p*-TolSO	H	Me	143810-76-8	26
O	(R)-AcO(Ph)CH	(S_S)-*p*-TolSO	H		53a
O	(S)-AcO(Ph)CH	(S_S)-*p*-TolSO	H		53a
O	(R)-*t*-BuCHOH	(S_S)-*p*-TolSO	H	159698-50-7	53a
O	(S)-*t*-BuCHOH	(S_S)-*p*-TolSO	H	159698-51-8	53a
O	(R)-CH_2=$CHCH_2CHOH$	(S_S)-*p*-TolSO	H	159049-29-3[a]	56a
O	(S)-CH_2=$CHCH_2CHOH$	(S_S)-*p*-TolSO	H	160169-56-2	56a
O	CHO	(S_S)-*p*-TolSO	H	159812-85-8[b]	27,53a,54,
					55,56a,69
O	1,3-Dithiolane-2-yl	(S_S)-*p*-TolSO	H		27
O	(R)-EtCHOH	(S_S)-*p*-TolSO	H	159698-48-3	53a
O	(S)-EtCHOH	(S_S)-*p*-TolSO	H	159698-49-4	53a
O	(E)-MeCH=CHCO	(S_S)-*p*-TolSO	H	177547-57-8[c]	55
O	(E)-PhCH=CHCO	(S_S)-*p*-TolSO	H	177547-56-7[c]	55
O	(R)-PhCHOH	(S_S)-*p*-TolSO	H	159698-46-1	53a,69
O	(S)-PhCHOH	(S_S)-*p*-TolSO	H	159698-47-2	53a,69
O	(S_S)-*p*-TolSO	Br	H	171617-77-9	27
O	(S_S)-*p*-TolSO	(R)-*t*-BuCHOH	H		53a
O	(S_S)-*p*-TolSO	(S)-*t*-BuCHOH	H		53a
O	*p*-TolSO	$Me(CH_2)_2CHOH$	H		56a
O	(S_S)-*p*-TolSO	CHO	H	159812-86-9	27,53a,56a,
				159049-30-6[a]	70
O	(S_S)-*p*-TolSO	1,3-Dithiolane-2-yl	H		27
O	(S_S)-*p*-TolSO	(R)-EtCHOH	H		53a
O	(S_S)-*p*-TolSO	(S)-EtCHOH	H		53a
O	(S_S)-*p*-TolSO	(R)-PhCHOH	H	159698-52-9	53a
O	(S_S)-*p*-TolSO	(S)-PhCHOH	H	159698-53-0	53a,70
S	H	(S_S)-*p*-TolSO	H	143810-78-0	26,27,53b,69
S	(S_S)-*p*-TolSO	H	H	143810-77-9	26,27,69
S	(R)-CH_2=$CHCH_2CHOH$	H	(S_S)-*p*-TolSO		69
S	(S)-CH_2=$CHCH_2CHOH$	H	(S_S)-*p*-TolSO		69
S	CHO	H	(S_S)-*p*-TolSO	173381-53-8	69
S	(R)-CH_2=$CHCH_2CHOH$	(S_S)-*p*-TolSO	H	173522-19-5	69
S	(S)-CH_2=$CHCH_2CHOH$	(S_S)-*p*-TolSO	H	173381-56-1	69
S	(R)-$Me(CH_2)_4CHOH$	(S_S)-*p*-TolSO	H	182230-22-4	53b
S	(S)-$Me(CH_2)_4CHOH$	(S_S)-*p*-TolSO	H	182230-21-3	53b
S	$Me(CH_2)_4CO$	(S_S)-*p*-TolSO	H	182230-26-8	53b
S	CHO	(S_S)-*p*-TolSO	H	171617-79-1	27,53b,69
S	(R)-MeCHOH	(S_S)-*p*-TolSO	H	182230-16-6	53b
S	(S)-MeCHOH	(S_S)-*p*-TolSO	H	182230-15-5	53b
S	MeCO	(S_S)-*p*-TolSO	H	182230-23-5	53b
S	(R)-PhCHOH	(S_S)-*p*-TolSO	H	182230-18-8	53b
S	(S)-PhCHOH	(S_S)-*p*-TolSO	H	182230-17-7	53b
S	PhCO	(S_S)-*p*-TolSO	H	182230-24-6	53b
S	(R)-*i*-PrCHOH	(S_S)-*p*-TolSO	H	182230-20-2	53b
S	(S)-*i*-PrCHOH	(S_S)-*p*-TolSO	H	182230-19-9	53b
S	*i*-PrCO	(S_S)-*p*-TolSO	H	182230-25-7	53b
S	(S_S)-*p*-TolSO	(R)-CH_2=$CHCH_2CHOH$	H	173522-20-8	69
S	(S_S)-*p*-TolSO	(S)-CH_2=$CHCH_2CHOH$	H	173381-57-2	69
S	(S_S)-*p*-TolSO	CHO	H	171617-78-0	27,69
S	(S_S)-*p*-TolSO	1,3-Dithiolane-2-yl	H		27
S	(S_S)-*p*-TolSO	$HOCH_2$	H	173381-54-9	69

Scheme 39. Heterocyclic aromatic sulfinyl-1,3-dienes with both endocyclic double bonds (Refs [26,27,53–56,69,70]). [a]Racemate. [b]HDA adducts of this product with Danishefsky's diene are not shown in this Scheme. See ref. [54] [c]DA adducts of these dienophiles with cyclopentadiene are not shown in this Scheme. See ref. [55]

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