The synthesis of thiols, selenols, sulfides, selenides, sulfoxides, selenoxides, sulfones and selenones

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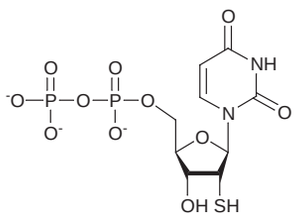
1 Introduction

This review is the latest in a series that began in 1994 and covers new approaches to the synthesis of thiols and selenols, disulfides and diselenides, sulfides and selenides, sulfoxides and selenoxides, and sulfones and selenones.[1–4] Unlike previous reviews in the series, cyclic systems have been covered and are considered alongside related acyclic systems. Each section deals first with general routes to simple systems, and then proceeds to discuss the synthesis of more heavily functionalised molecules. As with previous reviews in the series, emphasis has been placed on new stereo- and enantioselective reactions, and in addition, new areas of interest such as solid phase chemistry are also discussed.

2 Synthesis of thiols, sulfides and disulfides, and selenols, selenides and diselenides

2.1 Preparation of thiols, disulfides, selenols and diselenides

As thiols are readily obtained by the reduction of disulfides, the disulfide moiety is a convenient protecting group for use in the synthesis of more complex thiols. 2′-Thiouridine 5′-phosphate **1** has been conveniently prepared by deprotection of a mixed disulfide precursor, and has been shown to be a potent inhibitor of the *E. coli* ribonucleotide reductase.[5] 2,4-Dinitrophenyl 4-methoxybenzyl disulfide is a new reagent for the electrophilic



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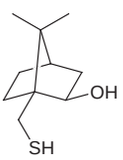
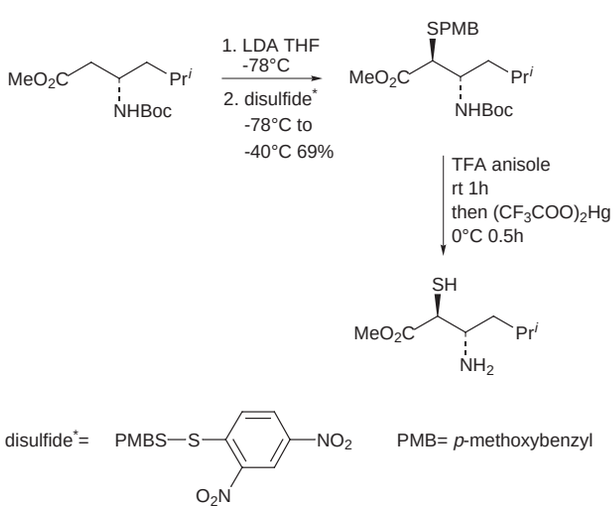
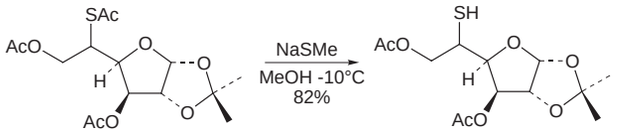


2

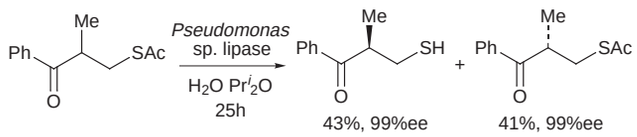
sulfenylation of enolates. Deprotection of the 4-methoxybenzyl group allows the corresponding thiol to be prepared (Scheme 1).[6] Similarly, thioacetates can be used for the protection of the thiol group. A mild method for the deprotection of primary, secondary, tertiary and aryl thioacetates has recently been used to chemoselectively deacetylate a thioacetate group in the presence of acetate groups (Scheme 2).[7] The synthesis of optically active γ-keto-thiols and the corresponding thioacetates has been achieved *via* the lipase catalysed hydrolysis of β-methyl-γ-keto thioacetates (Scheme 3).[8] Tertiary and allylic thiols have been prepared by treatment of the corresponding halides with zinc thiocyanate followed by hydrolysis and reduction of the intermediate thiocyanate.[9] An improved synthesis of the synthetically important ligand, (1*S*)-(+)-10-mercaptoisoborneol **2**, from (1*S*)-(+)-camphor-10-sulfonyl chloride has recently been reported.[10] A general route to the important, naturally occurring antioxidants, 4-mercaptoimidazoles, has recently been reported.[11] Novel heterocyclic thiols have been prepared in moderate yield by the reaction of bis-nucleophiles, such as hydrazines, with ketene dithioacetals (Scheme 4).[12] Thiols have also been prepared from the corresponding halides using a polymer-supported hydrosulfide reagent. Simple filtration and evaporation allows the product thiols to be isolated whilst the recovered resin can be conveniently regenerated and reused (Scheme 5).[13]



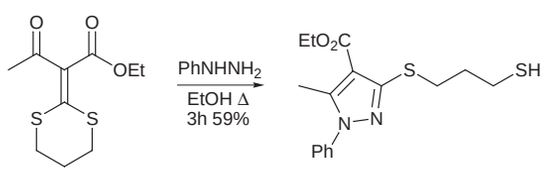
Scheme 1



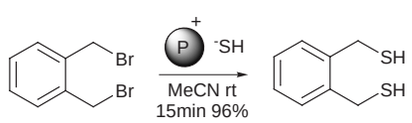
Scheme 2



Scheme 3

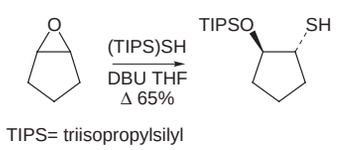


Scheme 4

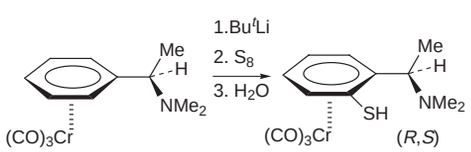


Scheme 5

The regioselective ring-opening of epoxides with triisopropylsilane thiol and DBU generates 2-triisopropylsilyloxyalkyl thiols after spontaneous migration of the silicon group from sulfur to oxygen (Scheme 6).[14] Optically active (*R*,*S*)- and (*S*,*R*)-tricarbonyl{2-[1-(dimethylamino)ethyl]benzenethiol} chromiums have been prepared in modest yield by regioselective *ortho*-lithiation of the parent chromium tricarbonyl complex and subsequent reaction with elemental sulfur (Scheme 7).[15] The ring-opening of *meso*-epoxides with these benzenethiol chromium reagents has been investigated.[15]



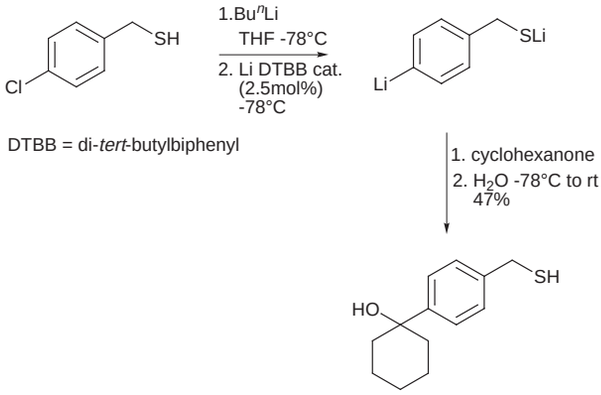
Scheme 6



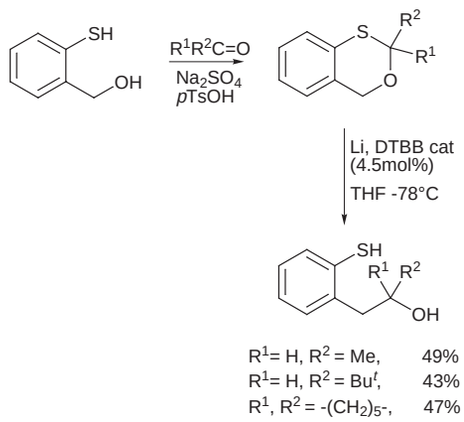
Scheme 7

The treatment of chlorinated benzyl thiols with butyllithium followed by lithiation with an excess of lithium powder and a catalytic amount of 4,4′-di-*tert*-butylbiphenyl (DTBB), gives the corresponding dianion which reacts with carbonyl compounds to give alkylated products in modest yield (Scheme 8).[16] In a related study, the treatment of readily prepared 1,3-oxathiines with lithium and a catalytic amount of DTBB, gives 2-(2-mercaptophenyl)ethyl alcohols in moderate yield (Scheme 9).[17] The use of selenocarbamates, selenoacetates and selenocarbonates as protecting groups for selenols has recently been reported.[18]

Symmetrical disulfides can be obtained by the oxidation of thiols. Several new reagent systems for this transformation have been reported and these include molecular oxygen and an

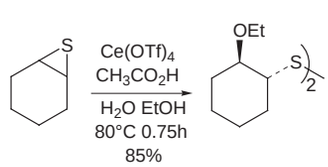


Scheme 8



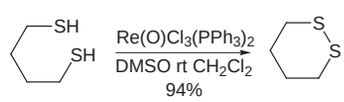
Scheme 9

iron(III) ethylenediaminetetraacetic acid complex as catalyst;[19] molecular oxygen and redox enzymes;[20] hydrated copper(II) nitrates;[21] copper(II) nitrate dinitrogen tetroxide;[22] 'chemical' manganese dioxide;[23] and aqueous sodium hypochlorite, or *tert*-butyl chloride and potassium carbonate.[24] Symmetrical disulfides have also been prepared by the kaolinitic clay catalysed one-pot reaction of sulfur monochloride with simple aromatics.[25] The reduction of arenesulfonyl chlorides with samarium metal, nickel(II) chloride and potassium iodide gives symmetrical aryl disulfides in good yield.[26] Symmetrical dialkyl disulfides have been prepared by the reduction of alkyl thiocyanates with samarium metal and titanium tetrachloride.[27] The cerium(IV) trifluoromethanesulfonate mediated ring-opening of thiiranes in acetic acid and alcoholic solvent gives disulfide products in good yield (Scheme 10).[28]



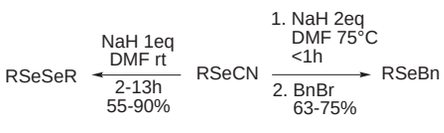
Scheme 10

Cyclic disulfides have been prepared by oxidation of dithiols with a catalytic rhenium–dimethyl sulfoxide oxidising system (Scheme 11),[29] and by the reaction of elemental sulfur with 1,3-dienes.[30] The first isolable dithiirane, a three-membered ring disulfide, has recently been prepared.[31]



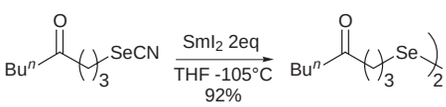
Scheme 11

Selenocyanates can be converted into either selenolates or diselenides selectively on treatment with sodium hydride simply by varying the amount of reducing agent and the temperature used (Scheme 12).[32] The reduction of selenocyanates, having ketone or aldehyde groups elsewhere in the molecule, with samarium(II) iodide at low temperature, gives the corresponding diselenides in excellent yield and with complete chemoselectivity (Scheme 13).[33] L-Selenocystine and L-[^{77}Se]selenocystine are useful nuclear magnetic resonance probes and have been prepared from a protected iodoalanine derivative (Scheme 14).[34] Finally, dialkenyl diselenides have been prepared by treatment of ketone toluene-*p*-sulfonyl hydrazones with base and elemental selenium (Scheme 15).[35]

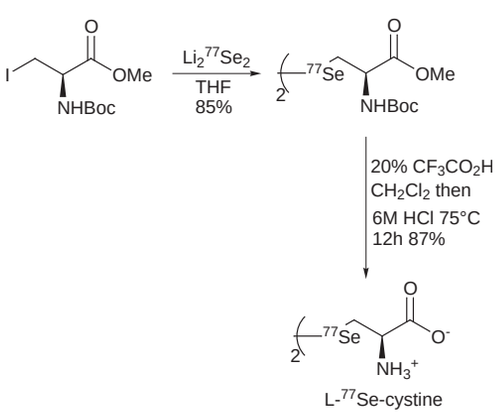


R = Ph, Bu^n, Dec^n, Pr^i

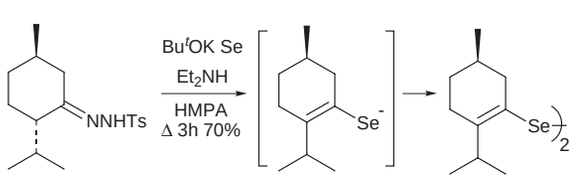
Scheme 12



Scheme 13



Scheme 14



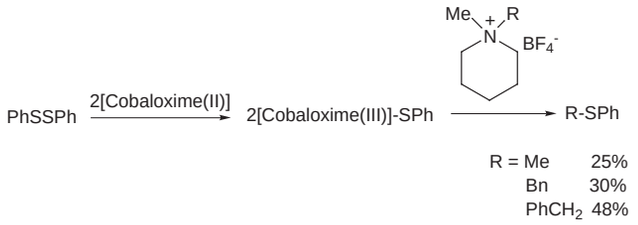
Scheme 15

2.2 Synthesis of sulfides and selenides

2.2.1 Simple sulfides and selenides

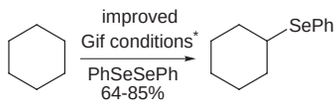
The deoxygenation of simple sulfoxides and selenoxides with nickel boride, formed *in situ* from nickel chloride and sodium borohydride, has been reported.[36] Titanium(II) porphyrin complexes have also been found to deoxygenate sulfoxides by a two electron process which results in overall oxygen transfer from sulfur to titanium.[37] Symmetrical dialkyl sulfides have been prepared by the treatment of alkane thiols with an alumina catalyst.[38] A biomimetic alkyl transfer process in which an alkyl ammonium salt reacts with phenylthiolatocobaloxime to give alkyl phenyl sulfides has been reported (Scheme 16).[39] Unsymmetrical sulfides can be prepared by the treatment of thiols with *n*-butyllithium followed by quenching with alkyl halides.[40]

Further studies on the selective phenylselenation of saturated hydrocarbons using Gif chemistry have been carried out and



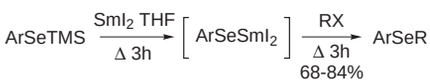
Scheme 16

have led to improved conditions for the process (Scheme 17).[41] Simple unsymmetrical selenides have been prepared by reduction of the Se–Si bond in arylselenotrimethylsilanes with samarium(II) iodide. The samarium areneselenolates formed react with alkyl halides to give the desired selenides in good yield (Scheme 18).[42] An otherwise analogous method for the preparation of unsymmetrical sulfides has also been reported.[43]



*Picolinic acid, $FeCl_2.4H_2O$, Bu_3P, 4-*tert*-butylpyridine
MeCN, H_2S, H_2O_2, 0°C, 3-4h

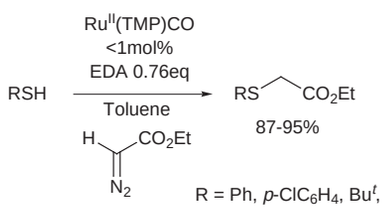
Scheme 17



Ar = Ph, *o*-MeC$_6$H$_4$
RX = BnCl, BnBr, C$_8$H$_{17}$Br, MeI, EtI,Pr^{i}I

Scheme 18

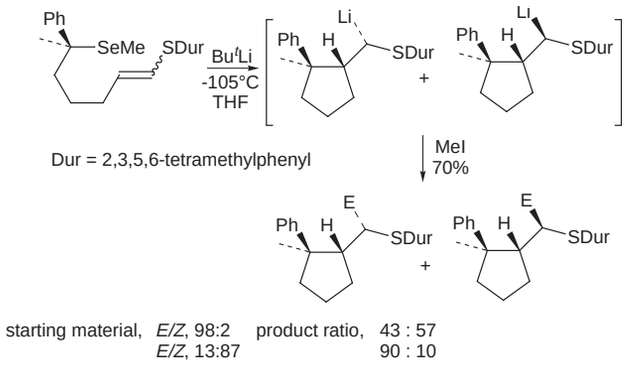
A general route to α-ethoxycarbonyl sulfides has been reported and involves the ruthenium porphyrin catalysed selective insertion of ethyl diazoacetate (EDA) into the S–H bond of thiols. Interestingly, and in contrast to alternative catalysts, competitive insertion into the O–H bond is not observed (Scheme 19).[44] Further studies on the intramolecular carbolithiation of vinyl sulfides have been carried out. Employing duryl vinyl sulfides leads to α-durylthioalkyllithiums which have increased configurational stability. The stereochemical outcome of the carbolithiation process has thus been investigated using these more stable intermediates and found to be dependent on the initial olefin geometry (Scheme 20).[45]



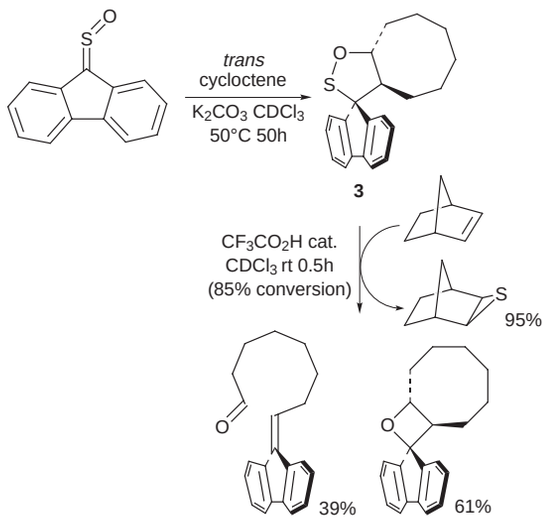
TMP = 5,10,15,20-tetramesityl porphyrin dianion

Scheme 19

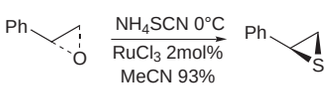
The development of sulfur-atom transfer reagents continues to be an area of great interest. The direct formation of thiiranes from olefins *via* photolytic sulfur-atom transfer from sulfines has been reported.[46] In a related system, treatment of the sultene cycloadduct **3** with acid triggers efficient sulfur-atom transfer to reactive alkenes (Scheme 21).[47] Thiiranes have also been prepared directly from epoxides in a process catalysed by ruthenium trichloride (Scheme 22).[48] The rhodium



Scheme 20

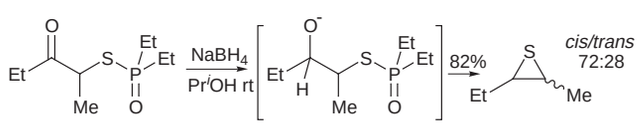


Scheme 21



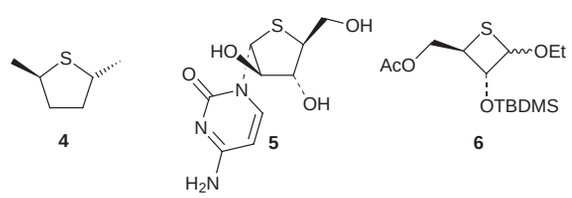
Scheme 22

acetate catalysed sulfur-atom transfer from propylene sulfide to norbornene has also been reported but requires more forcing conditions.[49] Thiiranes have also been prepared by the reduction of *S*-(β-oxoalkyl) thiophosphinates with sodium borohydride (Scheme 23),[50] and by the addition of diethoxy-(oxo)phosphoranesulfenyl chloride to alkenes followed by treatment with fluoride.[51]

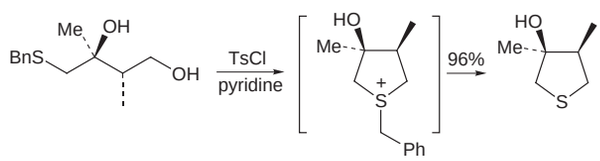


Scheme 23

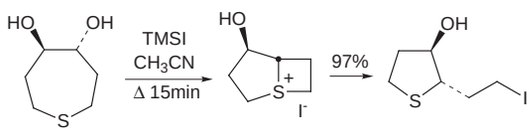
A number of new approaches to the preparation of cyclic sulfides have been reported. Enantiopure (2*R*,5*R*)-(+)-2,5-dimethylthiolane **4** has been prepared *via* a route involving the



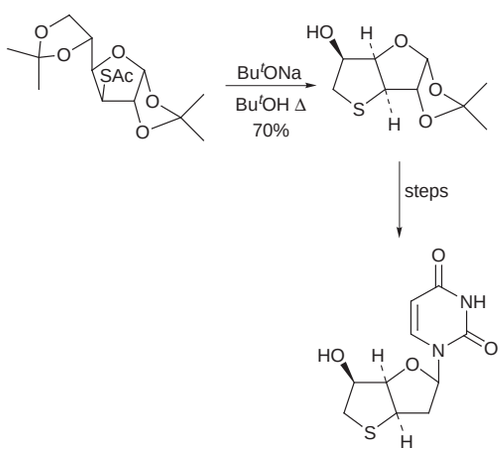
enzymatic reduction of acetonylacetone.[52] Thiolanes have also been prepared in a stereocontrolled manner by treatment of enantiomerically pure 4-benzylsulfanyl-1,3-diols with toluene-*p*-sulfonyl chloride. The process occurs *via* 1,4-participation of the benzylsulfanyl group and debenzylation of the key sulfonium salt intermediate (Scheme 24).[53] Various hydroxylated thiepanes prepared from D-mannitol, undergo ring contraction *via* Lewis acid induced transannular cyclisations to give hydroxylated cyclic sulfides in good yield (Scheme 25).[54] Substitution of sulfur for oxygen in the carbohydrate moiety of nucleosides has provided compounds that have extremely useful biological activity. L-4′-Thioarabinofuranosyl pyrimidine nucleosides have recently been prepared from xylose, and the α-anomer **5** has been shown to have significant anti-viral activity.[55] The replacement of oxygen with sulfur in a bicyclic carbohydrate analogue has recently been achieved by intramolecular thiolate addition to an acetal protected 5′,6′-diol (Scheme 26).[56] Thietanose **6**, a little studied four-membered sugar analogue, has also been prepared.[57] The anti-viral agent Lamivudine has been prepared by an approach involving enzymatic resolution of appropriately substituted α-acetoxy sulfides. Hydrolysis of the enantiomerically enriched α-acetoxy sulfides, and *in situ* cyclisation gives cyclic *S*,*O*-acetals with almost complete retention of stereochemical integrity (Scheme 27).[58] The direct α-functionalisation of 1,3-oxathiolanes using benzoyl peroxide has been employed in the synthesis of 1,3-oxathiolane cytosine nucleosides.[59] The stereoselective synthesis of *syn*- and *anti*-thiepane-4,5-diols from the heterocyclic precursor **7** has been achieved by reduction using chelating and non-chelating reducing agents (Scheme 28).[60]



Scheme 24

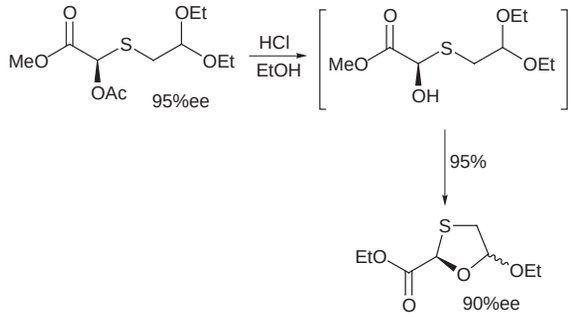


Scheme 25

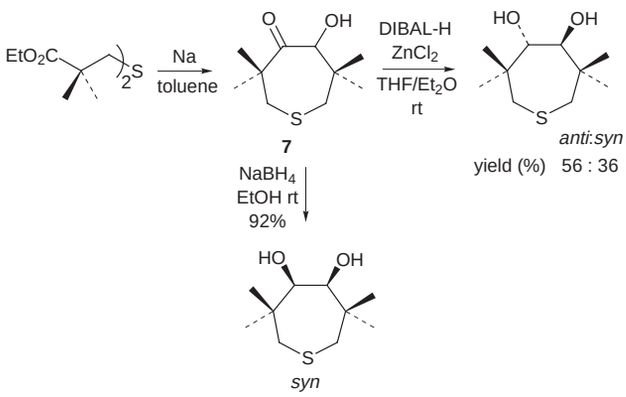


Scheme 26

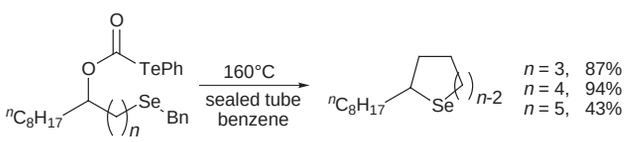
Cyclic selenides have been prepared by thermolysis of benzylseleno (phenyltelluro)formates in an unexpectedly facile nucleophilic displacement of the telluroformate group by the selenium atom (Scheme 29).[61] The treatment of 2-(3-hydroxyalkylseleno)benzoxazoles with potassium hydride gives selenetanes in good yield. The reaction is thought to occur *via* a spiro-intermediate which then breaks down to generate a selenolate ion (Scheme 30).[62]



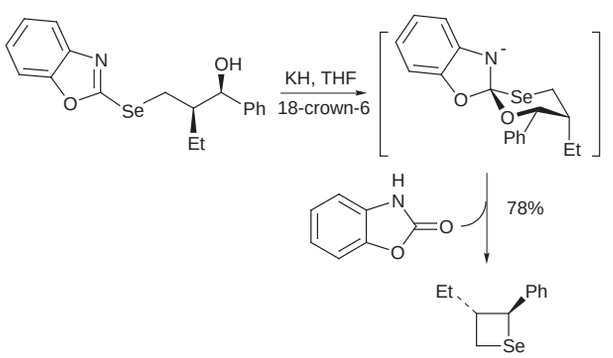
Scheme 27



Scheme 28



Scheme 29

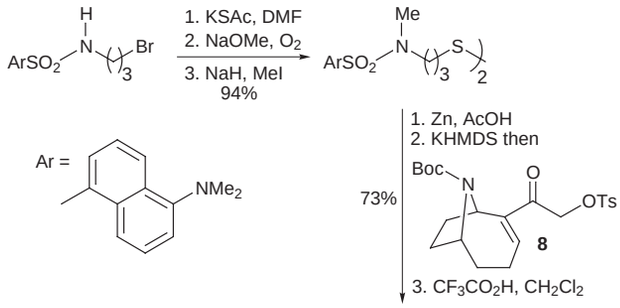


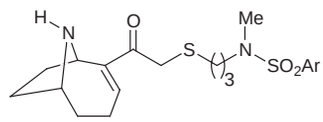
Scheme 30

The nucleophilic displacement of leaving groups with thiolate anions is a convenient method for the synthesis of sulfides. The preparation of fluorescent structural probes *via* functionalisation of Anatoxin A, a potent nicotinic agonist, is conveniently achieved by treatment of α-tosyloxy ketone **8** with thiolates (Scheme 31).[63] The reaction of α-halo ketones with sodium alkyl thiosulfates in the presence of indium metal in aqueous media gives phenacyl sulfides in good yield (Scheme 32).[64] The insertion of selenium into the zinc–carbon bond in alkyl and aryl zinc halides gives zinc alkyl and aryl selenolates which react with α-bromo carbonyl compounds to afford α-selenocarbonyl compounds (Scheme 33).[65] Finally, the nucleophilic ring-opening of enantiomerically pure oxazolidin-2-ones with thiolates provides a convenient route to optically pure β-amino sulfides.[66]

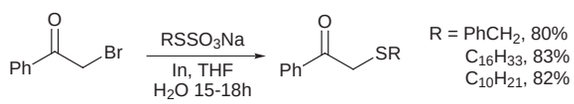
2.2.2 Functionalised sulfides and selenides

α-Metalated sulfides are useful intermediates for the elaboration of sulfides. The direct deprotonation of acyclic and cyclic aliphatic sulfides with Schlosser's base provides a convenient route to these intermediates, and their reaction with electrophiles gives the expected sulfide adducts in good yield (Scheme 34).[67] Reaction of α-metalated sulfides formed by this method with carbon electrophiles has not been fully studied but appears to be inefficient in all but the simplest cases. The deprotonation and subsequent alkylation of (phenylseleno)acetonitrile has been studied and under optimised conditions has been shown to be synthetically useful.[68] Similarly, the deprotonation of methoxy(methylseleno)methylbenzene and reaction with electrophiles gives substituted α-methoxy benzyl selenides in good yield (Scheme 35).[69] The regioselective ring-opening of epoxides with tributylstannyl phenylselenolate under Lewis acid conditions has been employed in the synthesis of β-hydroxy selenides (Scheme 36).[70] Samarium(III) thiolates, generated by the reduction of aryl thiocyanates with samarium(II) iodide, also react with epoxides to give β-hydroxy sulfides.[71] The regiospecific ring-opening of potassium glycidate with *tert*-butyl thiol and lithium hydroxide has also been reported.[72]

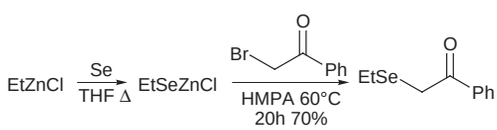




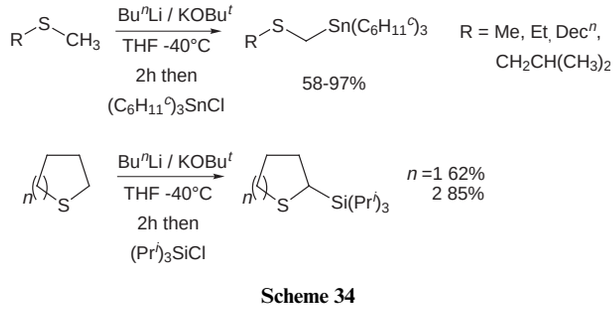
Scheme 31



Scheme 32

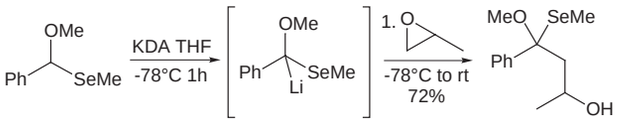


Scheme 33

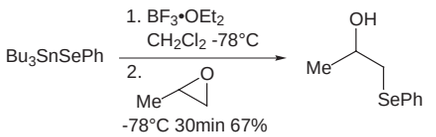


Scheme 34

A series of recent studies on the diastereoselectivity of addition to carbonyl groups in systems having an α-oxathiolane ketal has appeared in the literature.[73] In simpler spirocyclic sulfides the nucleophile favours approach from the face *anti*

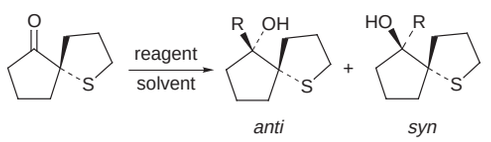


Scheme 35



Scheme 36

to the sulfur atom thus avoiding the electron density on the heteroatom (Scheme 37).[73]



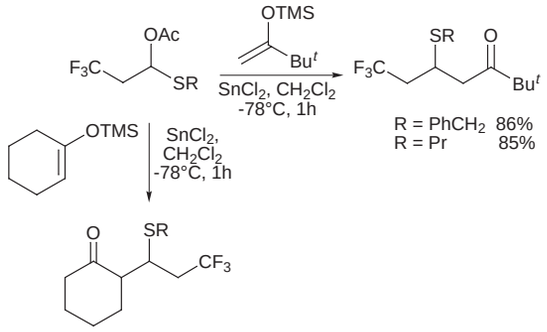
R = Me, H
solvent = Et_2O, THF, CH_2Cl_2, MeOH
reagent = MeLi, MeMgBr, $NaBH_4$, $LiBH_4$, $LiAlH_4$, DIBAL-H

anti/syn, typically 90:10

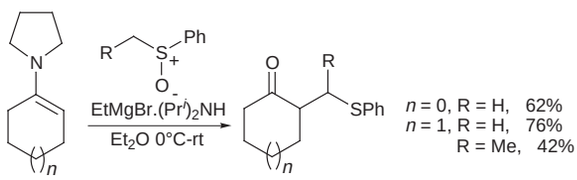
Scheme 37

The regioselective anodic α-difluorination of simple sulfides having an electron-withdrawing group in the α-position has been reported and employs a novel fluorine source to achieve the difficult transformation.[74] The synthesis of partially fluorinated sulfides has also been achieved by treatment of fluorine-containing α-acetoxy sulfides with Lewis acid in the presence of silyl enol ethers (Scheme 38).[75] In a related procedure, the reaction of cyclic and acyclic enamines with sulfoxides in the presence of magnesium diisopropylamide, gives α-alkylated sulfides in moderate yield (Scheme 39).[76] Enantiomerically pure fluoropyruvaldehyde *N*,*S*-ketals have been prepared *via* a tandem process involving a sulfurane mediated, stereospecific Pummerer rearrangement and a 1,2-migration of a *p*-tolylsulfanyl group (Scheme 40).[77,78] The Sommelet [2,3]-sigmatropic dearomatisation of cyclic sulfonium salts gives product sulfides with good diastereoselectivity (Scheme 41).[79] Unfortunately, analogous acyclic systems show little diastereoselectivity.[79] In a related reaction involving the [2,3]-sigmatropic rearrangement of sulfur ylides, novel sulfur-containing heterocycles are formed from thienyl substituted cyclic sulfonium salts (Scheme 42).[80] The asymmetric [2,3]-sigmatropic rearrangement of chiral allylic selenonium ylides has been used in the preparation of diastereoisomerically pure substituted homoallylic selenides (Scheme 43).[81] Methylthiomethyl esters of α,β-unsaturated acids are readily converted into the corresponding ketene acetals by *O*-silylation. Subsequent thermal rearrangement gives a sulfur ylide which undergoes [2,3]-sigmatropic rearrangement to give, after methanolysis, δ-alkylthio-α,β-unsaturated methyl esters in moderate yield. The overall transformation corresponds to the introduction of an alkylthiomethyl group at the γ-carbon of an α,β-unsaturated ester (Scheme 44).[82]

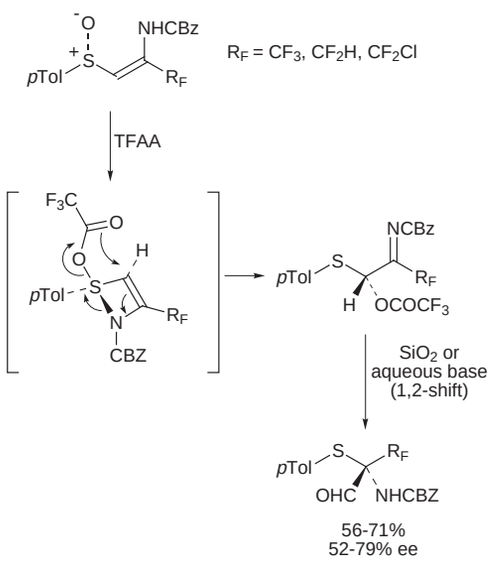
The sulfenylation of olefins remains a common approach to the preparation of sulfides and the development of several new sulfenylating systems has been reported. The treatment of trimethylsilyl enol ethers derived from ketones and esters with quinone mono-*S*,*O*-acetals gives α-sulfenylated products in excellent yield (Scheme 45).[83] The system is also effective for the sulfenylation of electron-rich aromatic and heteroaromatic



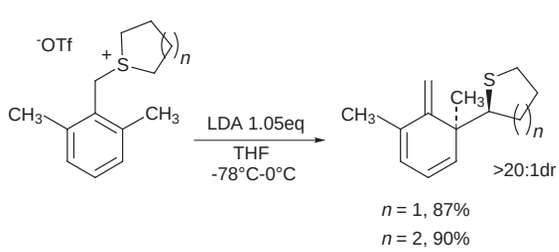
Scheme 38



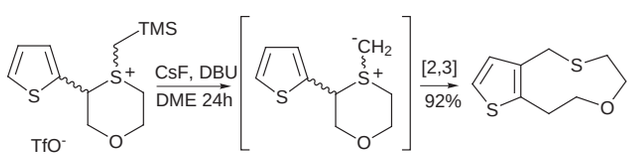
Scheme 39



Scheme 40

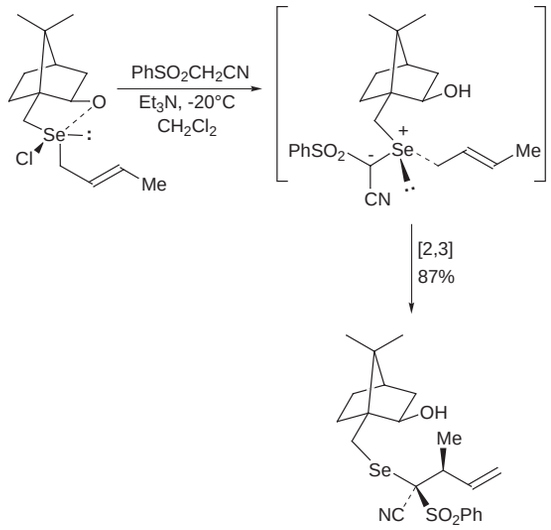


Scheme 41

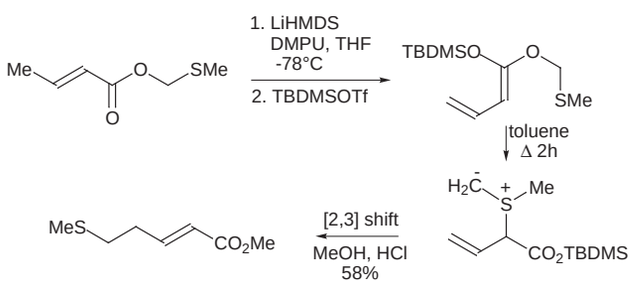


Scheme 42

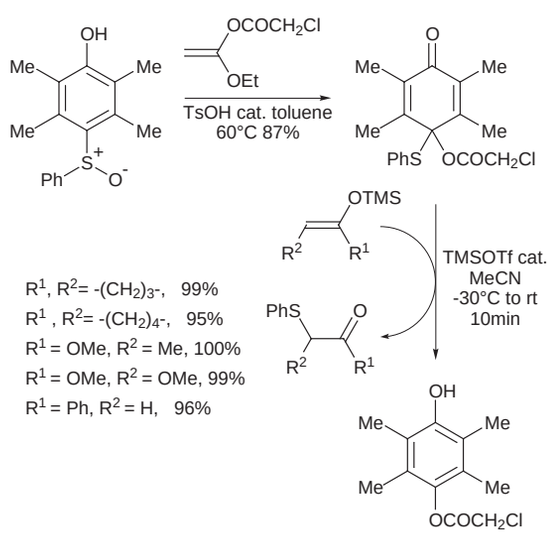
compounds and, in addition to thioaryl groups, thioalkyl groups can be transferred with equal efficiency. 2,2,2-Trifluoroethyl *tert*-butyl sulfoxide has been reported to be an effective



Scheme 43



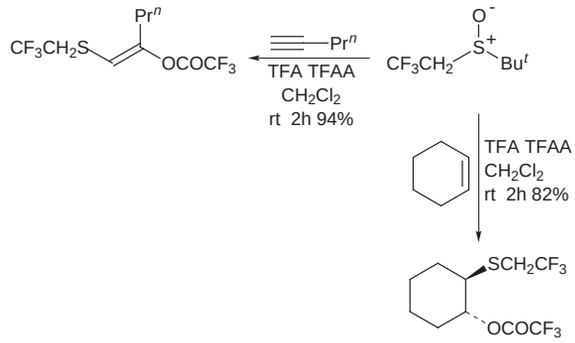
Scheme 44



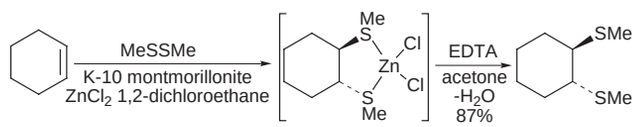
Scheme 45

trifluoroethyl sulfenylating agent for alkenes and alkynes (Scheme 46).[84] The 1,2-addition of simple alkyl disulfides to alkenes using K-10 montmorillonite impregnated with $ZnCl_2$ has been reported. Decomplexation of the intermediate zinc chloride complex gives the desired *trans*-1,2-bis(methylthio) addition products in good yield (Scheme 47).[85] Finally, the conversion of Michael acceptors into α-phenylthio carbonyl compounds *via* cobalt-catalysed hydrosulfenylation has recently been reported. The process, however, is still far from general and is effective only for acceptors unsubstituted in the β-position (Scheme 48).[86] Trapping experiments indicate that the reaction proceeds *via* radical intermediates.

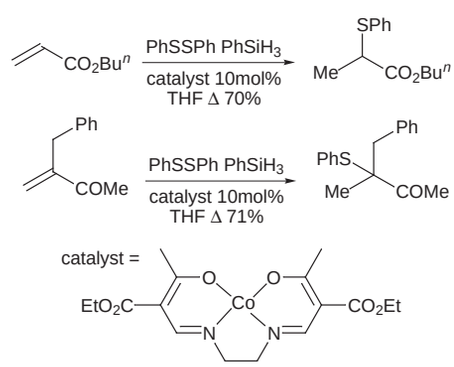
The radical addition of thiophenol to methacrylamide **9**, bearing the (*R*,*R*)-2,5-diphenylpyrrolidine chiral auxiliary, pro-



Scheme 46

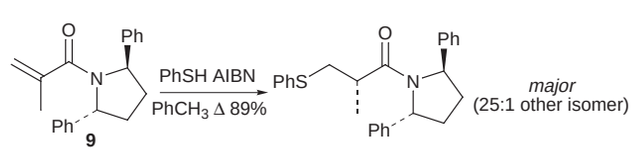


Scheme 47

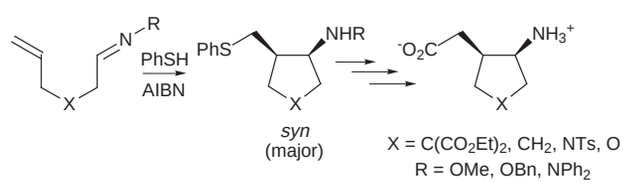


Scheme 48

ceeds to give sulfide adducts in good yield and with excellent diastereoselectivity (Scheme 49).[87] A new route to conformationally restricted cyclic β-amino acids has been developed which involves a sequential thiophenol radical addition–cyclisation strategy (Scheme 50).[88] Treatment of sulfides with triisopropylsilyl substituted acetylenic trifluoromethane sulfones (triflones) under radical conditions leads to α-alkynylated products in good yield (Scheme 51).[89] A novel and direct α-azidation of cyclic sulfides with a hypervalent iodine(III) reagent and trimethylsilyl azide has also been reported.[90]

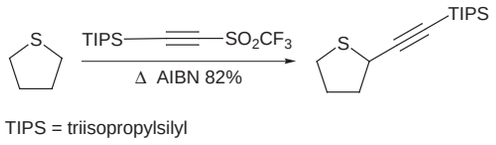


Scheme 49

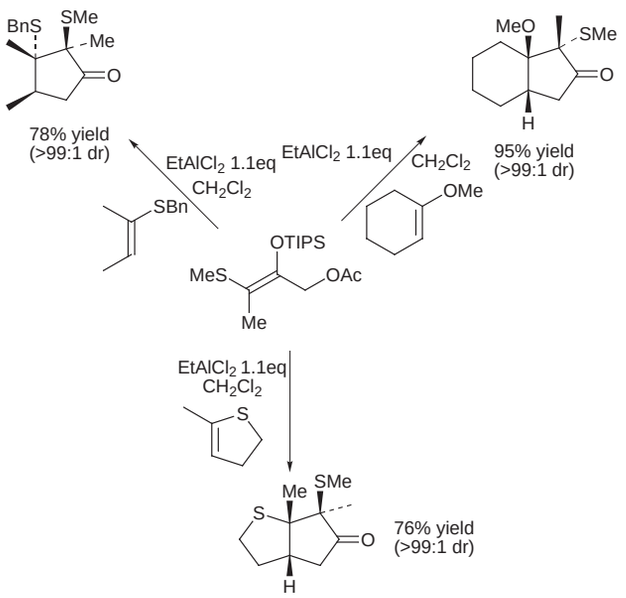


Scheme 50

A novel [3 + 2] cycloaddition approach to α-(methylthio) cyclopentanones has been reported. The intermediate allyl cationic species can react with vinyl ethers and thioethers generating substituted cyclopentanones in good yield, and with excellent selectivity for the more sterically hindered regioisomer (Scheme 52).[91] The cycloaddition reactions of vinyl selenides

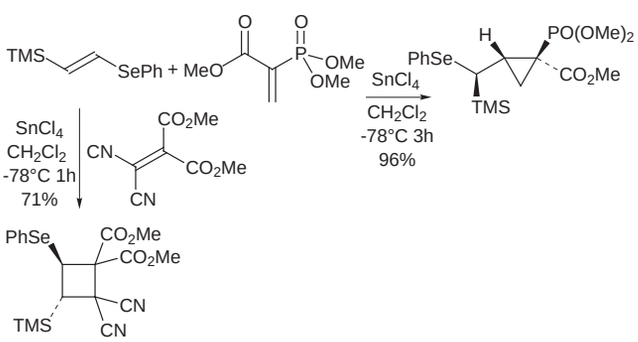


Scheme 51



Scheme 52

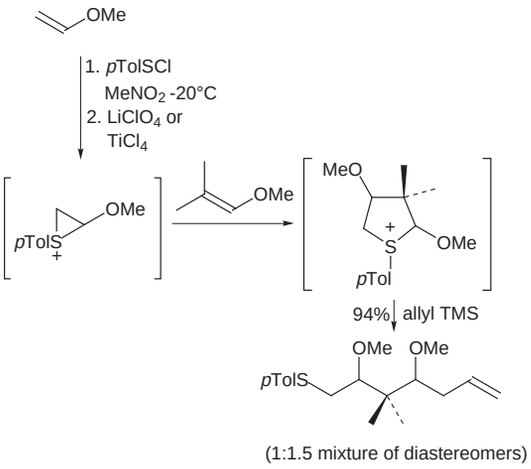
have also been studied. (*E*)-1-Phenylseleno-2-(trimethylsilyl)-ethene undergoes stereoselective Lewis acid promoted [2+1] cycloadditions to give highly functionalised cyclopropyl selenide adducts (Scheme 53).[92] The same substrate reacts with dimethyl 1,1-dicyanoethene-2,2-dicarboxylate under Lewis acid conditions to give [2 + 2] cycloadducts. Variation of the Lewis acid was found to change the regiochemistry of the cycloaddition.[93]



Scheme 53

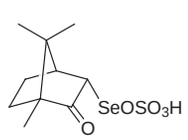
Thiiranium and seleniranium ions are useful intermediates in the synthesis of sulfides and selenides. The chemistry of these species has been the subject of a recent review.[94] The treatment of alkyl vinyl ethers with toluene-*p*-sulfenyl chloride and a Lewis acid, generates the corresponding thiiranium ions. Subsequent treatment of these intermediates with another alkyl vinyl ether unit followed by a carbon nucleophile, allows the formation of polyfunctional sulfides in good yield (Scheme 54).[95] An intramolecular cyclisation involving a 'sterically protected' seleniranium ion has been reported.[96] A bulky aryl substituent on selenium prevents nucleophilic attack on the selenium centre in the seleniranium ion, and thus promotes the selective formation of carbocycles.

The introduction of selenium into unsaturated molecules in a stereocontrolled fashion *via* the asymmetric selenenylation of

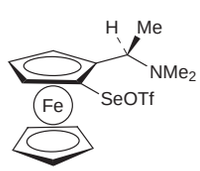


Scheme 54

olefins remains an active area of research. Recent advances in the asymmetric oxyselenenylation of olefins have been reviewed.[97,98] The subject is also discussed in a recent review on thiiranium and seleniranium ions.[94] In essentially all the systems developed to date, the chiral selenenylating reagent, for example the selenenyl triflate, sulfate or halide, is formed from the corresponding diselenide. In a recent study, camphor derived selenenyl sulfate **10**, prepared *in situ* by reaction of the



10

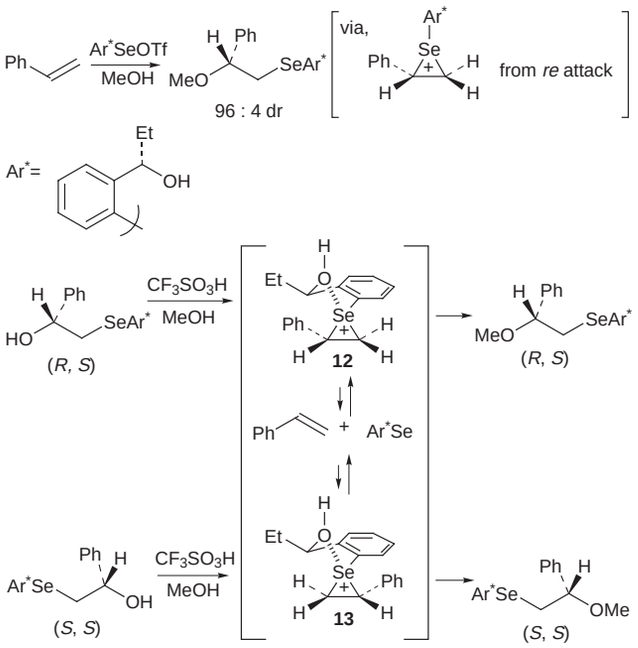


11

corresponding diselenide with ammonium persulfate, was shown to be highly effective in the asymmetric methoxyselenenylation of mono- and disubstituted olefins.[99] Interestingly, the counterion appears to have a marked effect on the selectivity and yield of the reaction. The otherwise analogous camphor selenenyl chloride, bromide, and triflate were all found to be much less effective in the reaction.[99] Chiral ferrocenyl selenenyl triflate **11** has also been used in the highly diastereoselective methoxyselenenylation of a variety of olefins.[100]

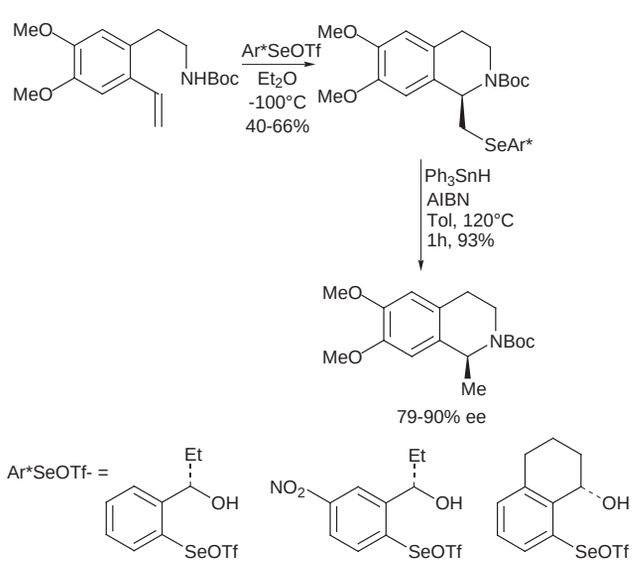
The mechanistic course of the asymmetric methoxyselenenylation reaction has recently been studied in some detail.[101] In the reaction, the use of chiral selenium electrophiles results in the preferential formation of one seleniranium ion intermediate. Using competition experiments, it has been shown that seleniranium ion formation is reversible and hence, any preference for one seleniranium ion over the others must arise from a difference in stability between them. This has been elegantly illustrated by independently preparing both *syn*-seleniranium ions that would arise in a typical methoxyselenenylation reaction and studying their reaction with methanol. In the case of seleniranium ion **12**, corresponding to the intermediate formed by *re* attack in the methoxyselenenylation of styrene and which is assumed to be the more stable seleniranium ion, quenching with methanol gives the expected (*R*,*S*)-product with no loss of stereochemical information at the benzylic position. In the case of seleniranium ion **13**, corresponding to the product of *si* attack on styrene and presumably the least stable seleniranium ion, a mixture of (*S*,*S*) and (*R*,*S*) products was obtained, clearly showing that some dissociation–reassociation to form the most stable seleniranium ion had occurred (Scheme 55).[101] In the same study, calculations have been carried out which support the experimental observations.

In reactions with olefin substrates having a pendent nucleo-



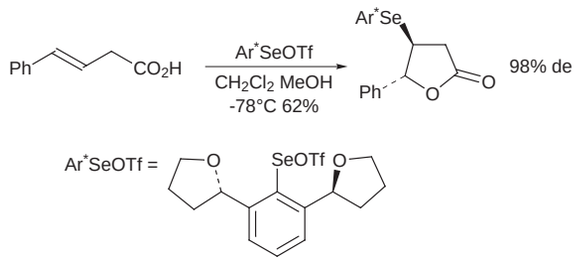
Scheme 55

phile, the intermediate seleniranium ion reacts in an intramolecular fashion to give non-racemic cyclic products. A family of new asymmetric selenenylating agents has been prepared and these have been used in a short route to tetrahydroisoquinoline alkaloids (Scheme 56).[102] A detailed study into the structural and electronic optimisation of these selenium electrophiles has been carried out.[103] An asymmetric selenenylation approach to enantiomerically enriched butyrolactones has recently been reported using an enantiomerically pure selenenyl triflate reagent (Scheme 57).[104] Finally, the development of a catalytic system for oxyselenenylation–elimination has been reported. In this system, the active selenenylating agent is a chiral selenenyl sulfate generated from the diselenide by electron-transfer in the presence of peroxodisulfates and a metal salt. Oxidation of the intermediate selenide with peroxodisulfate induces elimination and regeneration of the key selenenyl sulfate. Although turnover is still inefficient the system shows considerable promise (Scheme 58).[105]

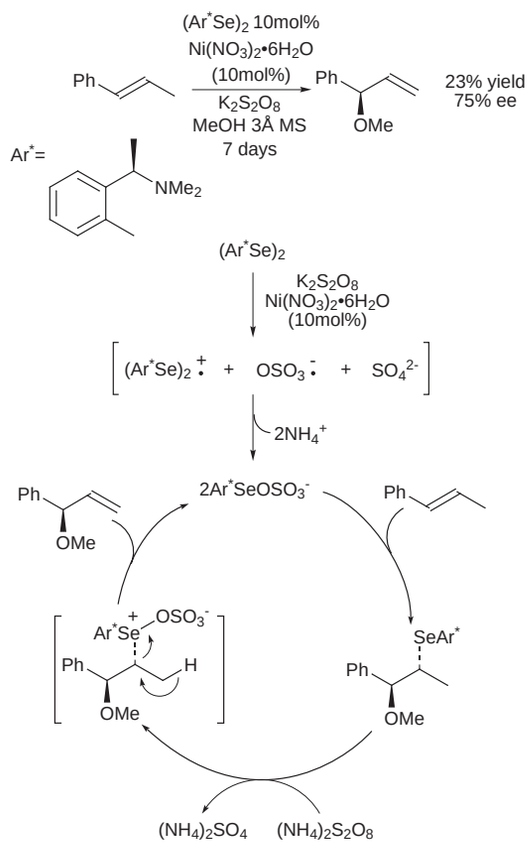


Scheme 56

The regio- and relative stereochemistry of the non-asymmetric selenenylation of allylic alcohols has been the subject of a recent study.[106] The azidoselenenylation of phenyl

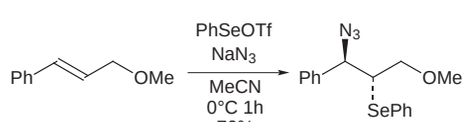


Scheme 57

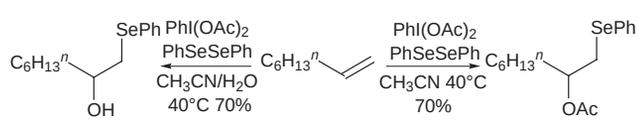


Scheme 58

substituted alkenes has been reported and proceeds with complete regio- and stereocontrol (Scheme 59).[107] Iodosobenzene diacetate–diphenyl diselenide has recently been developed as an electrophilic selenenylating system (Scheme 60).[108] Finally, the mechanism of phenylselenoetherification of unsaturated alcohols, involving seleniranium ion intermediates, has been investigated in a recent molecular orbital study.[109]



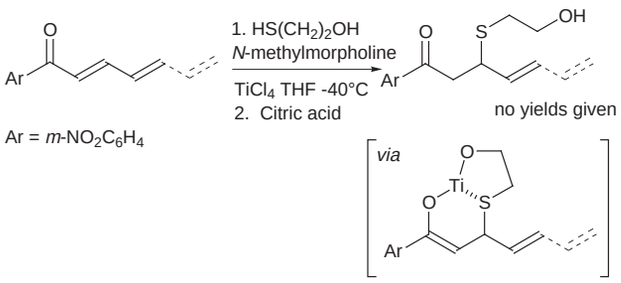
Scheme 59



Scheme 60

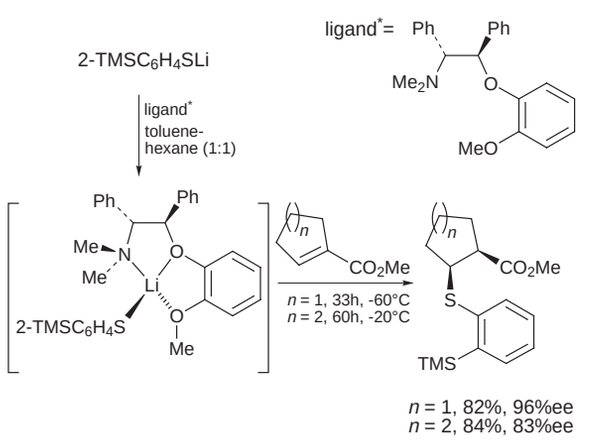
The Michael addition of thiols or thiolates to α,β-unsaturated carbonyl compounds remains a convenient method for the introduction of a thioalkyl or aryl group into a molecule. The Michael addition of thiols to unsubstituted dien- and

trienones usually occurs at the terminal position of the conjugated system. Carrying out the addition in the presence of titanium tetrachloride allows the β-addition product to be obtained selectively (Scheme 61).[110] Zeolites have been found to catalyse the addition of aliphatic thiols to various α,β-unsaturated carbonyl compounds giving sulfide adducts in good yield.[111]



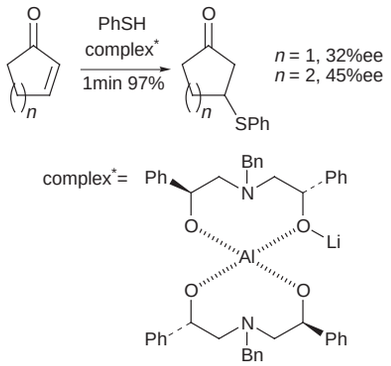
Scheme 61

Further work has been carried out on the catalytic asymmetric addition of thiolates to α,β-unsaturated carbonyl compounds. Recent studies have concentrated on the design of the chiral ligand employed in the process and have highlighted the importance of the *trans*-arrangement of groups on the ethylene bridge of the ligand and also the need for the ligand to bind in a tridentate fashion.[112] It has also been found that a bulky substituent in the 2-position of the aryl ring of the thiolate was essential for high reactivity and enantioselectivity in the addition reactions. Addition to cyclic and acyclic α,β-unsaturated esters gives the sulfide adducts in good yield and high enantiomeric excess (Scheme 62).[113] A heterobimetallic catalyst conveniently prepared from an amino diol and $LiAlH_4$ catalyses the asymmetric Michael addition of thiols to cyclic and acyclic α,β-unsaturated ketones (Scheme 63).[114] Perhaps the most general catalytic asymmetric system to date has recently been reported and employs a chiral lanthanum–sodium heterobimetallic catalyst (Scheme 64).[115] In an interesting extension of the chemistry, asymmetric protonation of a chiral samarium(III) enolate intermediate formed upon the addition of thiols to acyclic α,β-unsaturated thioesters, gives chiral sulfide adducts, substituted in the β-position, in high enantiomeric excess. The hydroxy group of a proximal part-coordinated binaphthol moiety appears to act as the proton source in the asymmetric protonation step (Scheme 65).[115]

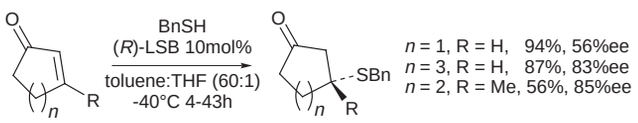


Scheme 62

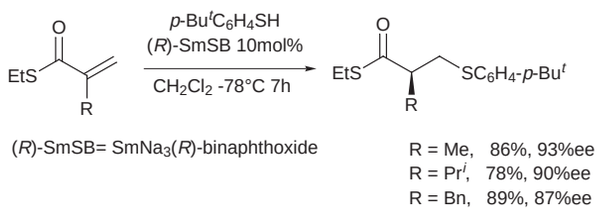
A thiolate or selenolate triggered tandem Michael–aldol reaction has been used in the synthesis of α-phenylthiomethyl and α-phenylselenomethyl-β-hydroxy esters (Scheme 66).[116] A similar tandem process involving Michael addition of methyllithium to dimethyl 2-phenylselenofumarate has been employed



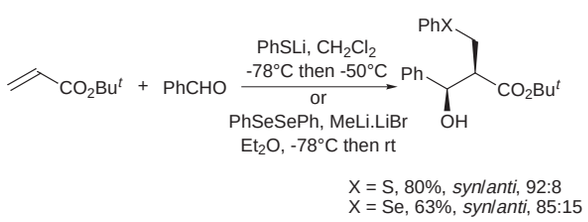
Scheme 63



Scheme 64

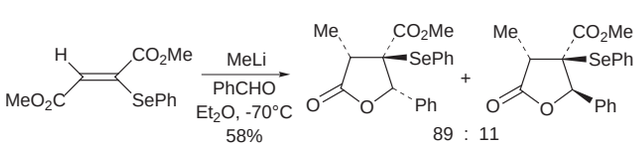


Scheme 65



Scheme 66

in the synthesis of highly substituted 4-phenylselenobutyrolactones (Scheme 67).[117] In addition, the conjugate addition of primary and secondary amines to the same Michael acceptor gives 2-phenylseleno-3-aminosuccinates in good yield and with moderate diastereoselectivity.[118]

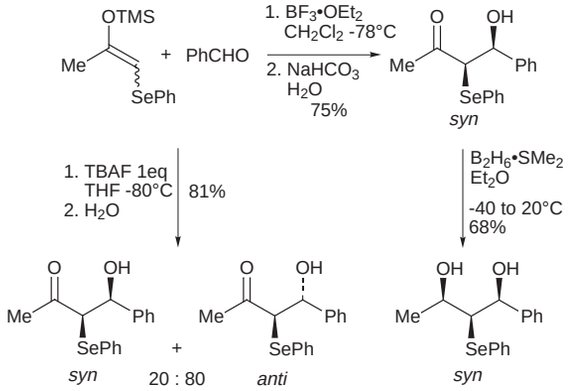


Scheme 67

Finally, the aldol reaction of β-phenylselanyl trimethylsilyl enol ethers with benzaldehyde has been studied. Under Lewis acid conditions, the *syn* aldol product predominates regardless of the stereochemistry of the starting silyl enol ether. The fluoride mediated aldol reaction, however, gives predominantly the *anti* aldol product at low temperatures (Scheme 68). [119]

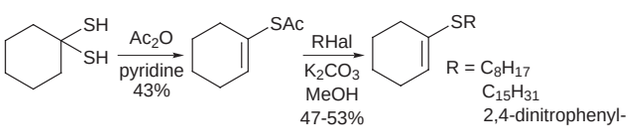
2.2.3 Vinylic and acetylenic sulfides and selenides

Many new approaches to the preparation of vinyl selenides and sulfides have been developed. The desilylation of (*Z*)-α-dimethylphenylsilyl vinyl sulfides with fluoride ion gives the expected vinyl sulfides in most cases.[120] A convenient procedure

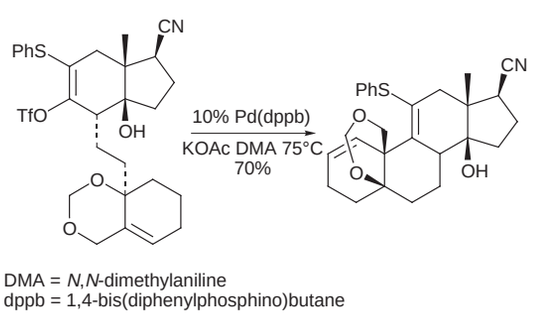


Scheme 68

to convert cyclohexanone, *via* the *gem*-dithiol, into cyclohexenyl sulfide has been reported (Scheme 69).[121] The intramolecular Heck reaction of an α-sulfenyl enol triflate has been used in the synthesis of a vinyl sulfide precursor to the cardenolides (Scheme 70).[122]

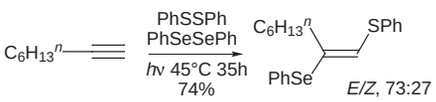


Scheme 69

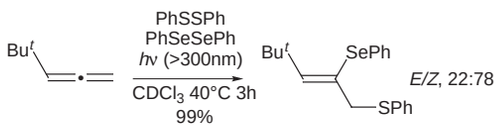


Scheme 70

The regioselective thioselenation of acetylenes and allenes has been reported. Treatment of acetylenes with diphenyl disulfide and diphenyl diselenide under photochemical conditions gives the mixed addition product in moderate yield (Scheme 71).[123] Thioselenation of allenes under similar conditions gives β-selenoallylic sulfides in excellent yield and with moderate selectivity for the *Z*-isomers (Scheme 72).[124] In a related reaction, dithiolation of allenes has been achieved using diphenyl disulfide and a catalytic amount of diphenyl ditelluride (Scheme 73).[124] A similar system has also been employed in the 1,4-dithiolation of 1,3-dienes.[125]

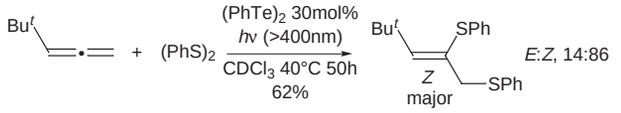


Scheme 71



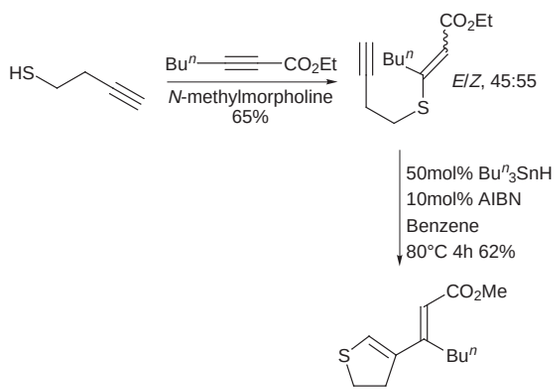
Scheme 72

A double radical cyclisation–β-fragmentation protocol has been reported which allows the regio- and stereoselective preparation of 3-vinyldihydrothiophenes from acyclic γ-yne vinyl



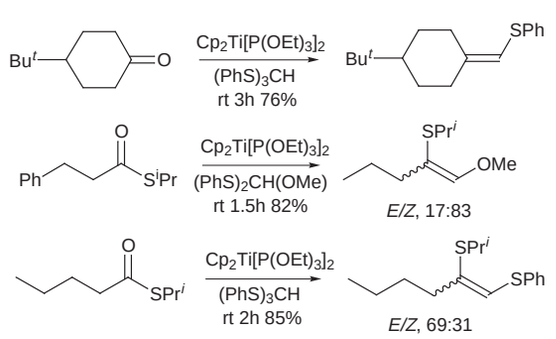
Scheme 73

sulfides. The reaction is of particular interest as it proceeds *via* a 5-*exo*-*trig*, β-fragmentation, and 5-*endo*-*trig* cyclisation sequence (Scheme 74).[126]

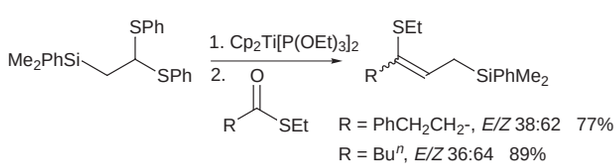


Scheme 74

A series of recent studies has led to a versatile approach to the synthesis of vinyl sulfides which is based on the reaction of titanocene alkylidenes with carbonyl compounds. The treatment of aldehydes, ketones, esters and thioesters with organotitanium species formed from either methoxybis(phenylthio)methane or tris(phenylthio)methane and a low valent titanium species, gives substituted vinyl sulfides in good yield (Scheme 75).[127,128] A similar titanocene-promoted olefination reaction of thioesters using 1,1-bis(phenylthio)-2-(dimethylphenylsilyl)ethanes gave γ-alkylthio allylsilanes in moderate to good yield (Scheme 76).[129]

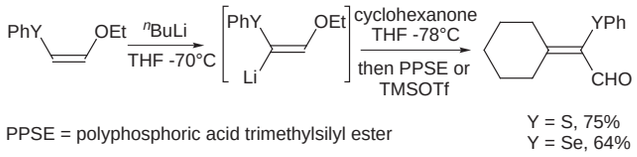


Scheme 75



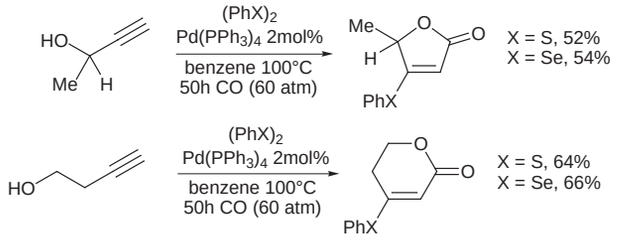
Scheme 76

The 1-chalcogenoformylolefination of ketones and aldehydes has been achieved by initial treatment of a carbonyl substrate with 1-lithio-2-ethoxyvinyl phenyl sulfide or selenide followed by dehydration to give substituted vinyl sulfide or selenide products (Scheme 77).[130] The reaction of but-3-ynylic 1-ols and 2-ols with diaryl disulfides or diselenides and carbon monoxide in the presence of tetrakis(triphenylphosphine)-palladium, results in an interesting thio/seleno lactonisation to afford β-(arylthio) and β-(arylseleno) α,β-unsaturated γ- and

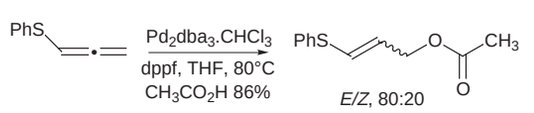


Scheme 77

δ-lactones in moderate yield (Scheme 78).[131] The palladium-catalysed hydrocarboxylation of phenylthioallene has recently been reported and gives phenyl 3-acetoxypropenyl sulfide products in good yield (Scheme 79).[132] In addition, the palladium-catalysed coupling of bis(triisopropylsilyl) disulfide with acetylenes gives 1,2-thioalkyl substituted olefins after *in situ* removal of the silyl groups and quenching with a suitable electrophile (Scheme 80).[133]

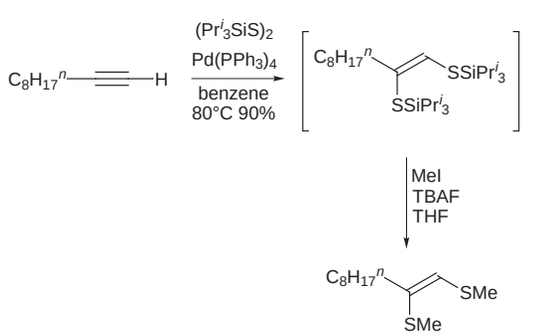


Scheme 78



dppf = 1,1'-bis(diphenylphosphino)ferrocene

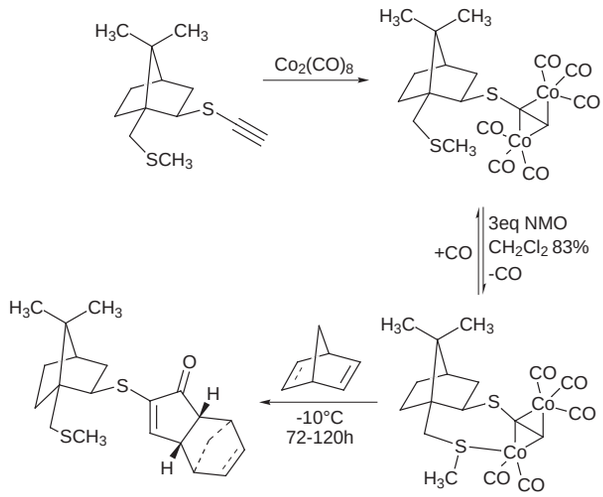
Scheme 79



Scheme 80

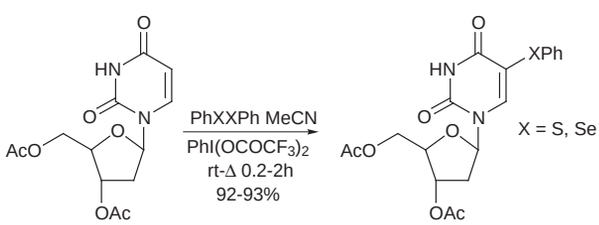
Vinyl sulfides have been prepared *via* a highly diastereoselective Pauson–Khand reaction between a stable, internally chelated, dicobalt pentacarbonyl complex of a camphor-derived acetylenic sulfide and strained olefins (Scheme 81).[134] A series of uracil nucleosides have been found to react with diphenyl disulfide, or diphenyl diselenide, in the presence of bis(trifluoroacetoxy)iodobenzene to give the corresponding C-5 phenylsulfenylated or phenylselenenylated products in good yield (Scheme 82).[135]

Vinyl sulfides undergo facile carbonyl ene reactions with aldehydes under Lewis acid conditions to give vinyl sulfide products in good yield and with excellent diastereoselectivity (Scheme 83).[136] The Pummerer reaction of vinyl spiro sulfoxide **14** proceeds *via* a butadienylthionium ion to give acyclic 1,3-diene sulfides in good yield (Scheme 84).[137] In recent years the utility of vinylogous and additive Pummerer reactions in the synthesis of carbo- and heterocyclic ring systems has been studied. The vinylogous Pummerer reaction of amido sulfoxides has been used to great effect in the formation of nitrogen containing heterocycles (Scheme 85).[138] The additive Pummerer

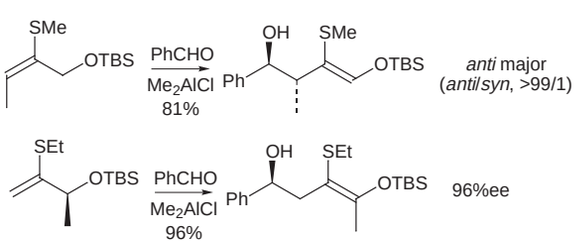


for norbornadiene, 65%, dr 95:5
for norbornene, 66%, dr 86:14

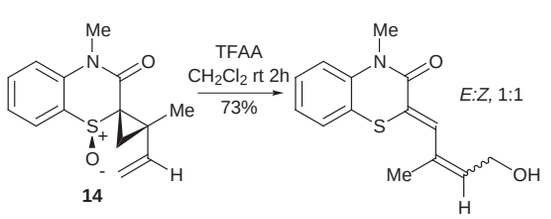
Scheme 81



Scheme 82



Scheme 83

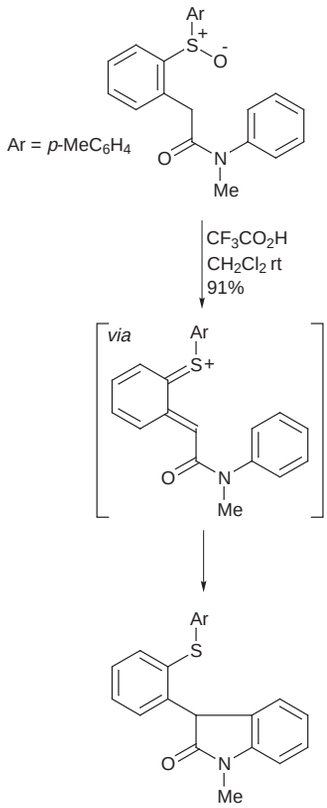


Scheme 84

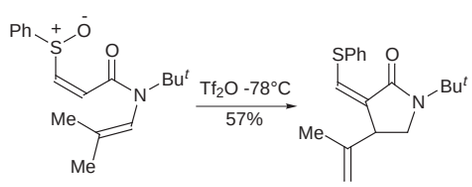
reaction of simple alkenes has been used for the preparation of γ-lactams (Scheme 86).[138]

Finally, *ortho*-substituted aryl alkyl sulfides have been prepared by treatment of chloro-substituted fused thiophenes with organolithiums. The ring-opening reaction appears to proceed *via* attack at sulfur and the anion generated from the ring-opening can be quenched with various electrophiles (Scheme 87).[139]

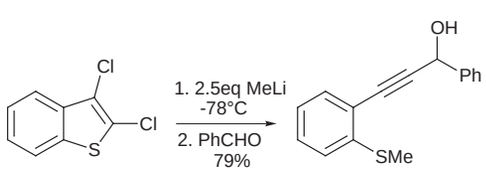
The hydroboration of bis(alkylseleno)acetylenes with dicyclopentyl- or dicyclohexylborane followed by iodination under basic conditions gives (*Z*)-1,2-bis(alkylseleno)-1-cycloalkylethenes in good yield (Scheme 88).[140] In a more general approach, (*Z*)-1,2-bis(alkylseleno)ethenes are conveniently prepared by the hydrozirconation of bis(alkylseleno)acetylenes. Further reaction of the (*Z*)-1,2-bis(alkylseleno)ethenes with organozinc halides in the presence of a nickel catalyst gives



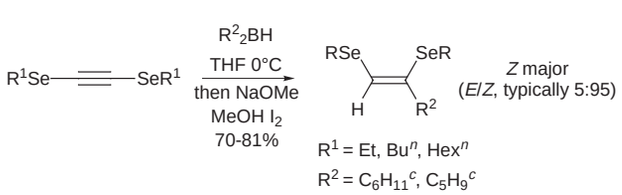
Scheme 85



Scheme 86

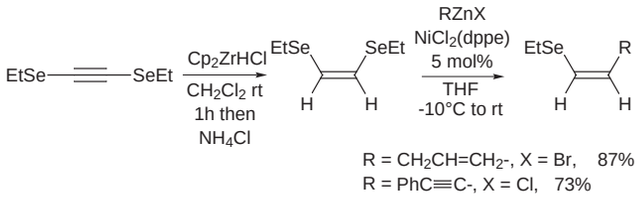


Scheme 87



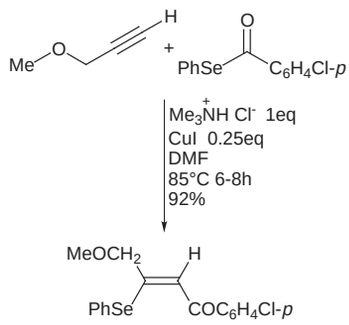
Scheme 88

(*Z*)-1-alkylselenoalk-1-enes in good yield and with retention of the alkene stereochemistry (Scheme 89).[141] Another approach to vinyl selenides also involves the hydrozirconation of acetylenic selenides and subsequent protonolysis.[142] The selenocarbonylation of terminal alkynes using selenoesters with copper(I) catalysis has been reported and gives (*Z*)-β-arylseleno-α,β-unsaturated ketones in good yield (Scheme 90).[143] Treatment of α-bromovinyl selenides and sulfides with butyl lithium gives α-chalcogeno vinyllithiums *via* bromine–lithium exchange. Subsequent quenching with a variety of electrophiles gave functionalised vinyl selenides and sulfides (Scheme 91).[144] The stereoselective synthesis of 1,4-dienyl selenides has been

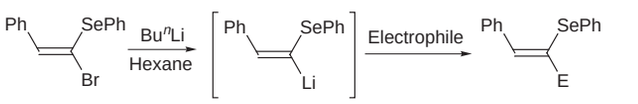


dppe = 1,2-bis(diphenylphospino)ethane

Scheme 89



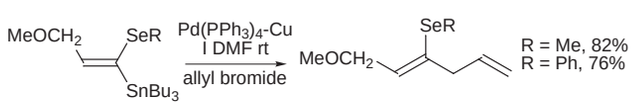
Scheme 90



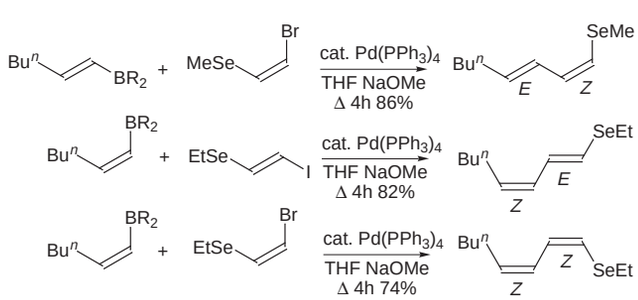
Electrophile = $(MeS)_2$, E = SMe, 76%
PhCOBr, E = COPh, 30%
CH_3CHO, E = CH(OH)CH_3, 75%

Scheme 91

achieved *via* the palladium catalysed cross-coupling of (*E*)-α-selanylvinylstannanes with allylic bromides (Scheme 92).[145] The analogous coupling of α-selanylvinylstannanes with vinyl bromides has been employed as a route to 1,3-dienyl selenides.[146] The stereoselective synthesis of stereochemically defined 1,3-dienes *via* the palladium-catalysed coupling of (*Z*)- or (*E*)-alkenylboranes with (*Z*)- or (*E*)-2-halo-1-(alkylseleno)ethenes has been reported (Scheme 93).[147] A similar approach to related systems involves the treatment of bis(alkylseleno)ethenylboranes with sodium methoxide and copper bromide–dimethyl sulfide complex. The resultant vinyl copper species were then coupled with allyl bromide [148] The preparation of enynyl selenides and sulfides has been achieved *via* the direct palladium catalysed coupling of α-bromovinylic selenides and sulfides with terminal alkynes (Scheme 94).[149] Similar systems have also been prepared by the palladium catalysed cross-coupling of (*E*)-selanylvinylstannanes with haloalkynes.[146]

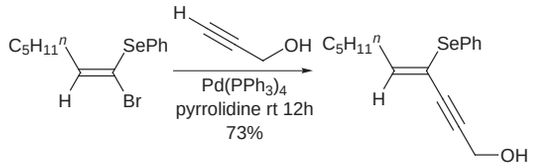


Scheme 92



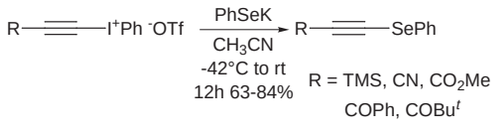
R = cyclohexyl

Scheme 93

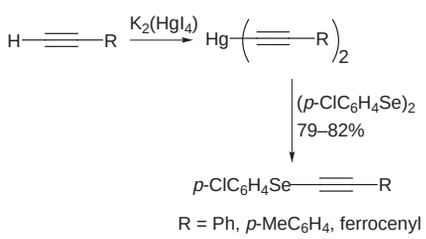


Scheme 94

Two reports of the preparation of acetylenic selenides *via* the reaction of alkynyliodonium sulfonates with aryl selenolates have been made.[150,151] In one example, a series of functionalised alkynyl phenyl selenides were efficiently prepared from alkynyliodonium triflates (Scheme 95).[150] Finally, alkynyl aryl selenides have been prepared in good yield by the reaction of bis(alkynyl)mercury compounds with diaryl diselenides (Scheme 96).[152]



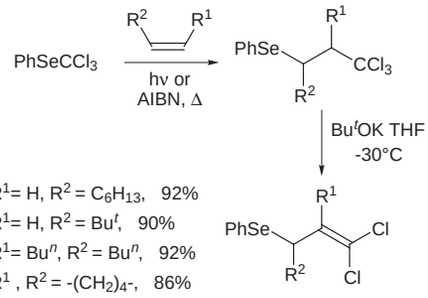
Scheme 95



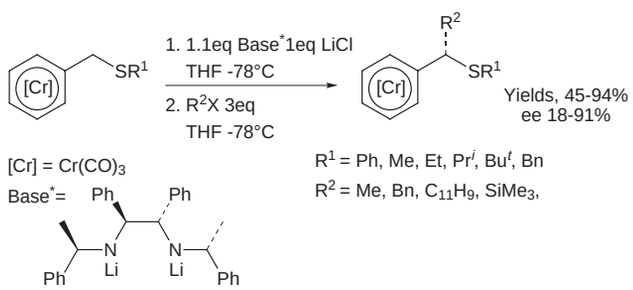
Scheme 96

2.2.4 Allylic and benzylic sulfides and selenides

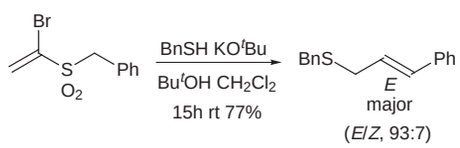
The free radical addition of phenyl trichloromethyl selenide to alkenes and subsequent dehydrochlorination gives 3,3-dichloroallylic selenides in excellent yields (Scheme 97).[153] Chiral functionalised benzylic sulfides have been prepared in good yield and in moderate to high enantiomeric excess by chiral base-mediated asymmetric alkylation of tricarbonylchromium(0) benzyl sulfide complexes (Scheme 98).[154] Interestingly, the asymmetric deprotonation of tricarbonylchromium(0) benzyl sulfide complexes under these conditions proceeds in the opposite stereochemical sense to the deprotonation of the corresponding benzyl ethers. The novel Michael-induced Ramberg–Backlund reaction of α-bromovinyl sulfones has been reported. Nucleophilic thiol addition to the vinyl sulfone, proton transfer, and subsequent rearrangement gives allylic sulfides in good yield and with good selectivity for the (*E*)-allyl sulfide isomer (Scheme 99).[155] An allylsamarium reagent, prepared by the reduction of allyl bromide with samarium metal, reacts with sodium alkyl thiosulfates,[156] or dialkyl and diaryl disulfides to give allyl sulfides in good yield (Scheme 100).[157] Similarly, allyl sulfides have been prepared by the reaction of allyl bromide with sodium alkyl thiosulfates promoted by indium in aqueous media.[158] Tin in aqueous media has also been used to prepare allylic and propargylic selenides from the corresponding bromides and dialkyl or diaryl diselenides.[159] The insertion of selenium into the zinc–carbon bond of allylzinc bromide and reaction of the resulting zinc allyl selenolates with diaryliodonium salts gives allyl aryl selenides.[65] Finally, a single example of the enantioselective synthesis of allylic sulfides has been reported, and is achieved *via* the palladium catalysed reaction of an allylic carbonate with *tert*-butyl trimethylsilyl sulfide in the presence of a chiral ligand (Scheme 101).[160]



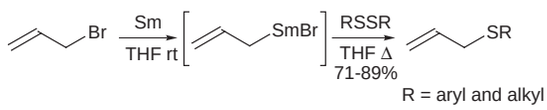
Scheme 97



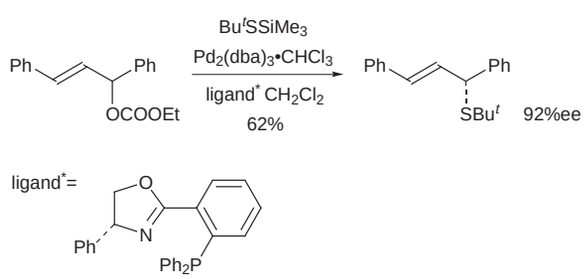
Scheme 98



Scheme 99



Scheme 100



Scheme 101

3 Synthesis of sulfoxides and selenoxides

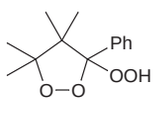
3.1 Oxidation of sulfides and selenides

The oxidation of sulfides and selenides to the corresponding sulfoxides and selenoxides remains a popular subject for research. This section will deal first with new achiral oxidising systems before discussing new methods for enantioselective oxidation. All the examples deal specifically with the oxidation of sulfides although it is likely that the majority of these oxidising systems would be equally applicable to the oxidation of selenides. The synthesis of optically active selenium compounds is the subject of a recent review which contains a section on the preparation of non-racemic selenoxides by asymmetric oxidation.[161]

3.1.1 Non-stereoselective oxidising systems

New methods for the oxidation of dialkyl, aryl alkyl, and diaryl

sulfides have been reported. These include hydrogen peroxide with a molybdenum-silicate catalyst;[162] silica gel supported magnesium monoperoxyphthalate;[163] calcium hypochlorite and moist alumina;[164] sodium periodate supported on wet silica with microwave thermolysis;[165] molecular oxygen oxidation catalysed by either an aminopolycarboxylate complex of ruthenium(III),[166] or a $BiBr_3$–$Bi(NO_3)_3$ binary catalyst;[167] molecular oxygen and aldehydes;[168] hydrated $Bi(NO_3)_3$ in acetic acid;[169] hydrated iron(III) and copper(II) nitrates under solvent free conditions;[21] hydrogen peroxide with either 2-phenylselenobenzoic acid or 2-iodosobenzoic acid as catalyst;[170] hydrogen peroxide in hexafluoropropan-2-ol;[171] hydrogen peroxide and imine derivatives as mediators;[172] 3-hydroperoxy-1,2-dioxolane **15**;[173] alumina-supported iodobenzene diacetate with



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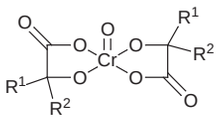

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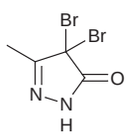

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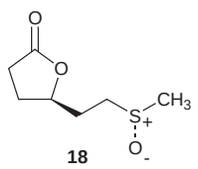
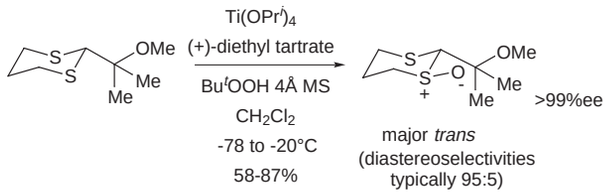


18

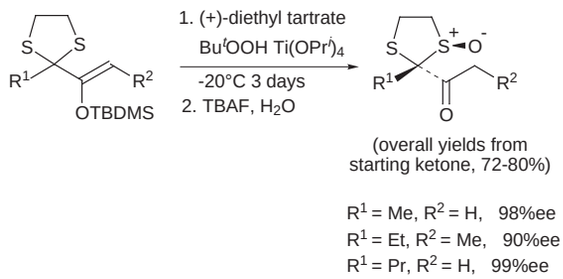
microwave irradiation under solvent-free conditions;[174] and iodosobenzene activated by a catalytic amount of a quaternary ammonium salt.[175] New methods for the oxidation of aryl alkyl sulfides have also been reported. These include an oxochromium(V) complex **16**;[176] 3-aryl-2-*tert*-butyloxaziridines under high pressure;[177] manganese dioxide and hydrochloric acid;[178] Oxone® and aluminium trichloride in the solid state;[179] iron(III) and copper(II) nitrate dinitrogen tetroxide complexes in solution or solid phase;[180] and 4,4-dibromo-5-methylpyrazol-3-one **17** with acetic acid.[181] In an example of a diastereoselective oxidation using an achiral oxidant, enantiomerically pure *N*-protected β-amino sulfides were treated with sodium hypochlorite, 2,2,6,6-tetramethylpiperidin-1-yloxyl and potassium bromide to give, after deprotection at nitrogen, *syn*-β-amino sulfoxides.[182]

3.1.2 Stereoselective oxidising systems

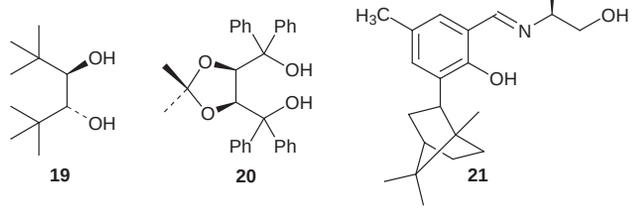
A discussion of the area of asymmetric sulfoxidation can be found in a chapter of a recent monograph.[183] Many of the more popular methods for the asymmetric oxidation of sulfides and selenides involve the use of modified Sharpless conditions. The non-linear effects (NLEs) of several reagent systems derived from the original Sharpless formulation have been measured. Each variant shows very different NLEs indicating that different active complexes are present in each case.[184] Further examples of the use of modified Sharpless conditions in the asymmetric oxidation of sulfides have been reported. The potential anti-cancer agent erylsulfoxide **18** has been prepared by asymmetric sulfoxidation with *tert*-butyl hydroperoxide (TBHP)–$Ti(OPr^i)_4$ and (−)-diethyl tartrate, the absolute configuration of the natural product thus being confirmed.[185] Oxidation of 2-substituted 1,3-dithianes with TBHP–$Ti(OPr^i)_4$ and (+)-diethyl tartrate give the product 1,3-dithiane 1-oxides with high *trans*-selectivity and enantioselectivities which depend markedly on the substituent at the 2-position of the dithiane (Scheme 102).[186] Under identical conditions, acyldithiolane sulfoxides have been prepared in high enantiomeric excess *via* the Sharpless asymmetric oxidation of silyl enol ethers derived from the starting ketones (Scheme 103).[187] The new chiral ligand, 2,2,5,5-tetramethylhexane-3,4-diol **19**, has been used with $Ti(OPr^i)_4$ and cumene hydroperoxide in the oxidation of



Scheme 102



Scheme 103

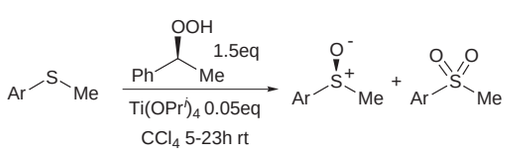


19

20

21

sulfides. Good enantioselectivities are observed but yields of sulfoxide are low, with significant quantities of sulfone being isolated. Kinetic studies have shown that a combination of enantioselective oxidation and kinetic resolution in the over-oxidation step is responsible for the high enantioselectivities observed.[188] The use of enantiomerically pure TADDOL† ligand **20** in the modified Sharpless oxidation of sulfides has also been reported, however enantioselectivities were generally lower than those obtained with more conventional ligands.[189] The use of other hydroperoxides in the Sharpless oxidation has been disclosed. Furyl hydroperoxides have been employed as stoichiometric oxidants and appear to shorten reaction times, and in some cases, lead to an improvement in enantioselectivity.[190–192] The use of enantiomerically pure (*S*)-1-phenylethyl hydroperoxide as the stoichiometric oxidant in the $Ti(OPr^i)_4$ mediated oxidation of aryl alkyl sulfides, leads to poor asymmetric induction in the oxidation step followed by efficient kinetic resolution in the subsequent oxidation to the sulfone (Scheme 104).[193] Further studies into the nature of oxygen transfer from enantiomerically pure titanium(IV)-alkylperoxo complexes to sulfides have also been made.[194]



Ar = *p*-MeC_6H_4,	71%ee	20	:	80
Ph,	79%ee	19	:	81
p-$MeOC_6H_4$,	31%ee	56	:	44
p-$NO_2C_6H_4$,	15%ee	41	:	59

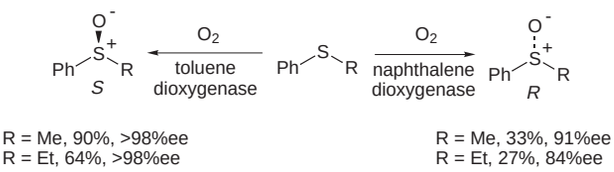
Scheme 104

The vanadium catalysed asymmetric oxidation of substituted thioanisoles using hydrogen peroxide and a chiral Schiff-base

† TADDOL = α,α,α′,α′-tetraaryl-1,3-dioxolane-4,5-dimethanol.

ligand **21** has been reported.[195] A similar ligand has been used in the vanadium catalysed oxidation of di(*tert*-butyl) disulfide in a catalytic asymmetric approach to enantiomerically pure amines.[196]

The use of biocatalysts for asymmetric oxidation of sulfides remains a viable alternative to chemical methods. The fungus *Beauveria bassiana* has been used in the preparation of two diastereoisomers of methionine sulfoxide,[197] whilst toluene dioxygenase and naphthalene dioxygenase have been shown to give complementary selectivities in the sulfoxidation of a limited number of aryl alkyl sulfides (Scheme 105).[198] Similarly, two enantiocomplementary Baeyer–Villiger monooxygenases have been used to catalyse the biooxidation of a variety of prochiral sulfides.[199] A vanadium containing bromoperoxidase was found to be effective specifically in the asymmetric oxidation of cyclic sulfides.[200] Finally, the active site of myoglobin has been engineered to mimic the action of a peroxidase. Replacement of key residues in the active site gives rise to a mutant which oxidises sulfide substrates more efficiently than horseradish peroxidase.[201]

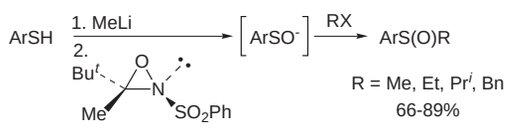


Scheme 105

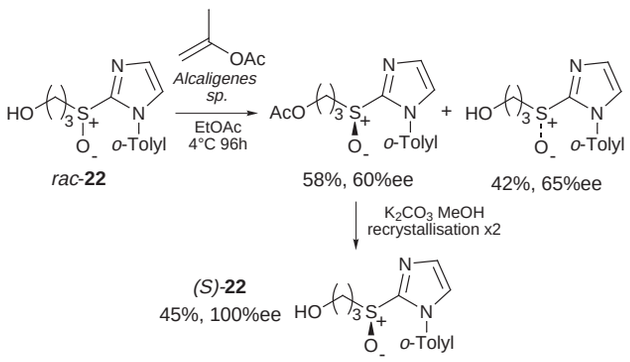
3.2 Non-oxidative routes to sulfoxides and selenoxides

3.2.1 Unfunctionalised sulfoxides and selenoxides

The synthesis of chiral sulfoxides *via* nucleophilic displacement at sulfur is the subject of a chapter in a recent monograph.[202] The preparation of optically active selenoxides *via* optical resolution and other miscellaneous methods has recently been reviewed.[161] A new general one-pot synthesis of aryl alkyl sulfoxides involves the oxaziridine mediated oxidation of thiolates, the intermediate sulfenates then being alkylated *in situ* to give sulfoxides in good yield (Scheme 106).[203] Alkyl pyridyl sulfoxides have been prepared in high enantiomeric excess by resolution through inclusion complexation with a tartaric acid derived chiral host.[204] Lipase-catalysed kinetic resolution of racemic sulfoxide **22**, where the sulfoxide group is remote from the reacting site, has been used to obtain both enantiomers of the sulfoxide, a key intermediate in the synthesis of a platelet aggregation inhibitor (Scheme 107).[205] A sulfoxide reagent bound to a soluble PEG polymer support has been prepared for use in a modified Swern oxidation procedure.[206] The use of a polymer bound reagent allows the odourless, bound sulfide by-product to be conveniently recovered, reoxidised, and reused with no loss of activity (Scheme 108). The nickel catalysed



Scheme 106

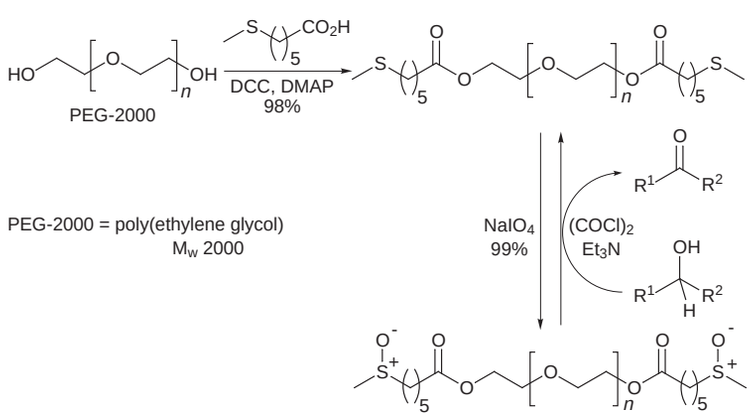


Scheme 107

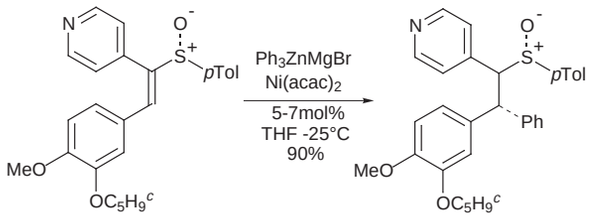
addition of aryl and alkyl zincate reagents to enantiomerically pure vinyl sulfoxides proceeds with good diastereoselectivity, the product sulfoxides being key intermediates in a synthesis of a phosphodiesterase IV inhibitor (Scheme 109).[207] Lithiation of *tert*-butylsulfinylferrocene and reaction with a variety of electrophiles provides a convenient route to enantiopure 1,2-disubstituted sulfinylferrocenes.[208] Complexation of 1-*tert*-butylsulfinyl-2-formylferrocene, prepared by this approach, with $Ti(OPr^i)_4$ followed by the addition of Grignard reagents, gave the product alcohols with complete diastereocontrol (Scheme 110).[208]

The addition of alkyl radicals to vinyl sulfoxides has been the focus of a series of recent studies.[209] The diastereoselectivity of the β-addition of alkyl radicals to 2-arylsulfinylcyclopent-2-enones depends largely on the aryl group and also upon the presence of Lewis acid additives. In all cases addition occurs to give *trans*-products but introduction of a bidentate Lewis acid reverses the enantioselectivity of the addition by chelating to both the ketone carbonyl group and the sulfoxide oxygen (Scheme 111).[210] The addition of alkyl radicals to a diastereoisomeric mixture of (4*R*)- and (4*S*)-4-methyl-2-arylsulfinylcyclopent-2-enones gave the diastereoisomerically pure (4*R*)-addition product while the (4*S*)-isomer of the starting material remained unreacted (Scheme 112).[211] Similarly, radical addition to the corresponding 5-methyl substrates shows an analogous kinetic separation.[211]

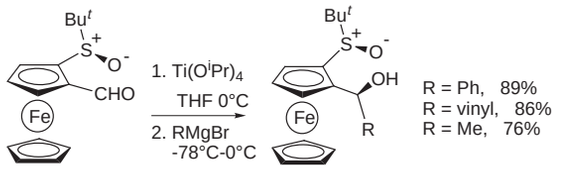
An interesting approach to the preparation of cyclic sulfoxides involves the development of SO transfer agents. The thiirane 1-oxide, or episulfoxide, of hindered olefin **23**, undergoes thermal decomposition and concomitant SO transfer to a



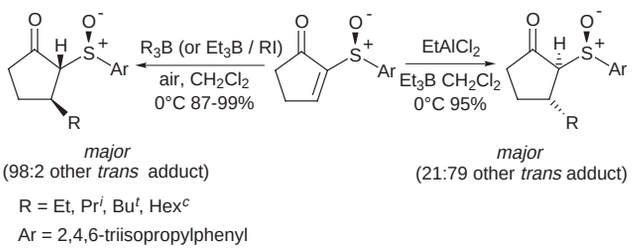
Scheme 108



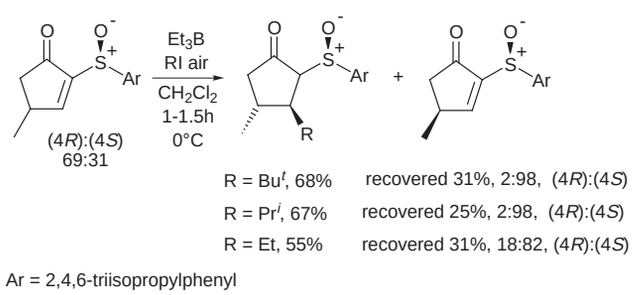
Scheme 109



Scheme 110

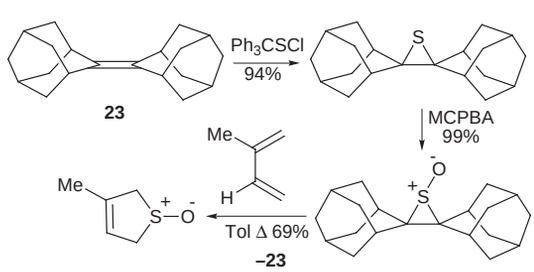


Scheme 111



Scheme 112

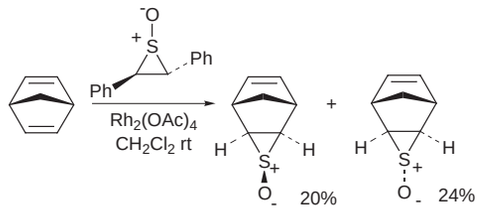
variety of 1,3-dienes giving cyclic sulfoxides in good yields (Scheme 113).[212] Similarly, rhodium catalysed SO transfer from *trans*-stilbene episulfoxide to norbornadiene gives the two *exo*-orientated episulfoxides in moderate yield (Scheme 114).[49]



Scheme 113

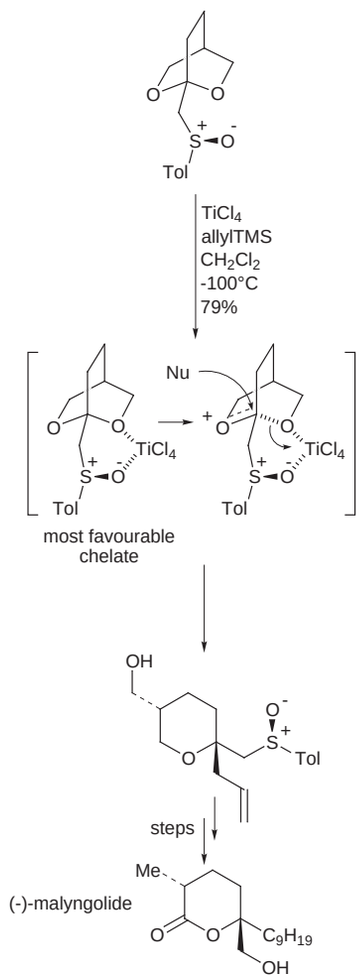
3.2.2 Functionalised sulfoxides and selenoxides

The application of chiral sulfoxides as stereocontrol elements in organic synthesis is the subject of a chapter in a recent monograph.[213] The sulfoxide moiety has been successfully employed to mediate the asymmetric desymmetrisation of substituted bicyclic acetals.[214] 2,2,5-Trisubstituted tetrahydropyrans were prepared with high diastereoselectivity by the Lewis acid induced nucleophilic cleavage of bicyclic acetals.[215,216] The reaction displays simultaneous 1,3- and 1,6-asymmetric induction as a result of the chiral sulfoxide group. In one example,



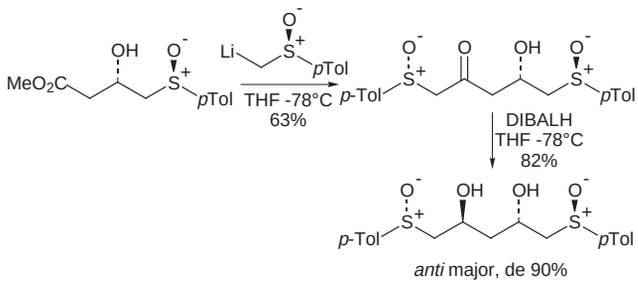
Scheme 114

the product sulfoxide was used in the total synthesis of (−)-malyngolide (Scheme 115).[215] Using a similar approach a C_2-symmetrical bis-sulfoxide has been employed in the asymmetric desymmetrisation of *meso*-cyclopentitol.[217]

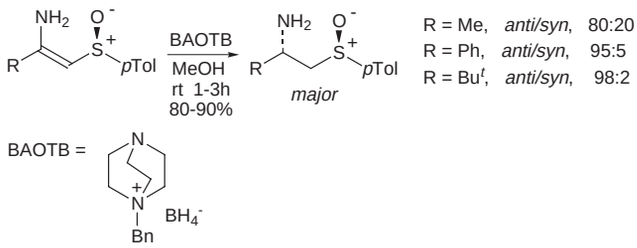


Scheme 115

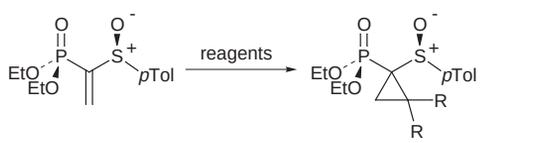
Many new examples of sulfoxide directed reactions have been reported. These include the directed reduction of β,γ-diketo sulfoxides;[218] the stereoselective reduction of β-keto sulfoxides having a stereogenic hydroxylic centre at the δ-position (Scheme 116);[219] the hydrocyanation of enantiomerically pure β-(*p*-tolylsulfinyl) aldehyde which gives the corresponding β-sulfinyl cyanohydrin in high diastereoisomeric excess;[220] the highly diastereoselective reduction of chiral β-imino sulfoxides with 1-benzyl-1,4-diazabicyclo[2.2.2]octane tetrahydroborate (BAOTB), giving *anti* β-amino sulfoxides in excellent yield (Scheme 117);[179] the conversion of β-keto sulfoxides to the corresponding epoxides;[221] and the cyclopropanation, under various conditions, of (*S*)-(+)-α-(diethoxyphosphoryl)vinyl *p*-tolyl sulfoxide (Scheme 118).[222] Finally, the Michael triggered, intramolecular Michael addition of ester enolates to enantiomerically pure vinyl sulfoxides gives product sulfoxides with high diastereoselectivity (Scheme 119).[223]



Scheme 116

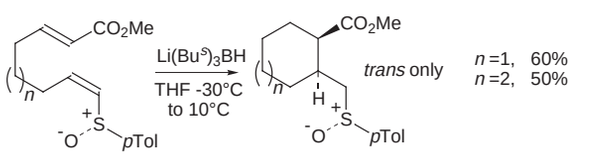


Scheme 117



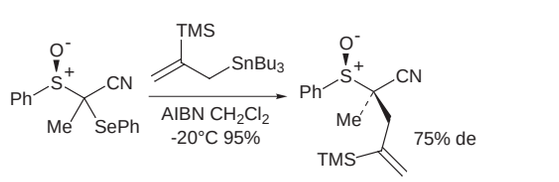
$(CD_3)_2S^+(O)CD_2^-$, $[^2H_6]$DMSO R = D, 92%
$Ph_2S^+C(Me)_2^-$, THF R = Me, 65%
Ph_2CN_2, Et_2O R = Ph, 86%

Scheme 118

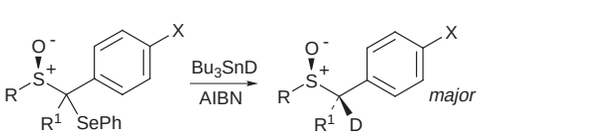


Scheme 119

Sulfoxides are very effective in controlling the stereochemistry of radical reactions at the α-carbon and this is particularly so when the radical is further stabilised by an electron-withdrawing group (Scheme 120).[224] Studies to probe the influence of dipole-dipole interactions and allylic strain on the diastereoselectivities of reactions involving substituted sulfinyl arylmethyl radicals have been carried out (Scheme 121).[224]



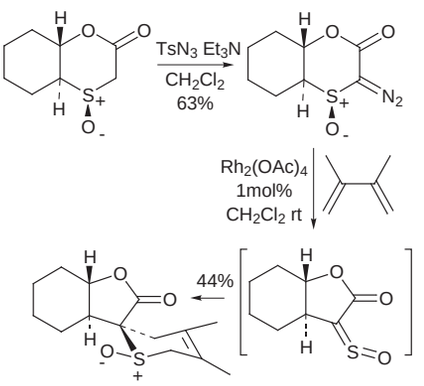
Scheme 120



R = Ph, R^1 = H, X = H, 87%, 66% de
R = Me, R^1 = H, X = H, 59%, 50% de
R = Ph, R^1 = H, X = CF_3, 94%, 71% de
R = Ph, R^1 = Me, X = H, 59%, 80% de

Scheme 121

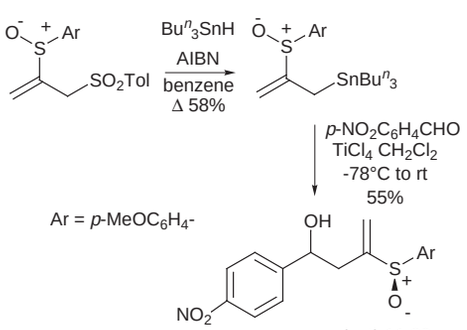
A chiral sulfoxide moiety has been incorporated into a tether for the intramolecular [5C + 2C] pyrone–alkene cycloaddition giving modest diastereoselectivity in the formation of the product cyclic sulfoxides.[225] α-Diazo-β-oxo sulfoxides have been prepared by diazo transfer adjacent to the sulfoxide group.[226] The rhodium catalysed decomposition of these compounds in the presence of a suitable diene allows the thione *S*-oxide intermediate to be trapped (Scheme 122).[227] The diene–dienophile dual reactivity of conjugated sulfines has been studied. Diels–Alder reaction of these species with a range of dienes and dienophiles allows access to a variety of cyclic sulfoxides.[228]



Scheme 122

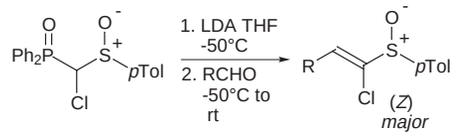
3.2.3 Unsaturated sulfoxides and selenoxides

New approaches to the synthesis of unsaturated sulfoxides have been reported. Tributyl[2-(*p*-methoxyphenylsulfinyl)prop-2-enyl]stannane reacts with aldehydes in the presence of titanium chloride with useful levels of 1,4-induction to give product vinyl sulfoxides in moderate yield (Scheme 123).[229] A general route to (*Z*)-1-chlorovinyl sulfoxides has been reported and involves the reaction of (α-lithiated-α-*p*-tolylsulfinylmethyl)diphenylphosphine oxide with a variety of aldehydes in a Horner–Wittig reaction. Selectivity for the (*Z*)-vinyl sulfoxides was found to decrease dramatically as the steric demand of the aldehyde increased (Scheme 124).[230] The Michael addition of β-keto sulfoxides to highly stabilised acceptors occurs to give functionalised 2-amino-4*H*-pyrans in good yield and with high diastereoselectivity (Scheme 125).[231]



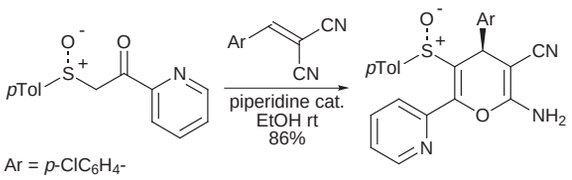
Scheme 123

Enantiomerically pure sulfinyl dienes have been prepared *via* Stille coupling of halovinyl sulfoxides and vinylstannanes. Using a range of iron tricarbonyl transfer agents, the corresponding sulfinyl diene iron(0) tricarbonyl complexes were formed in good yield and with high diastereoselectivity (Scheme 126).[232] The diastereoselectivity of allylations on enantiomerically pure sulfinyl dienal iron(0) tricarbonyl complexes has also been studied.[233] Sulfinyl chlorohydrins have been converted *via* the corresponding epoxyvinyl sulfoxides into enantiomerically pure hydroxy 2-sulfinyl dienes for use in the

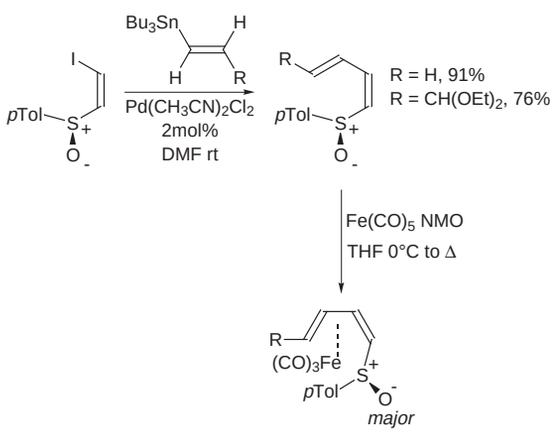


R = Ph, 60% yield, *Z*:*E*, >98:2
R = prop-1-enyl, 71% yield, *Z*:*E*, 96:4
R = Bu^n, 74% yield, *Z*:*E*, 96:4
R = Hex^c, 69% yield, *Z*:*E*, 3.3:1

Scheme 124



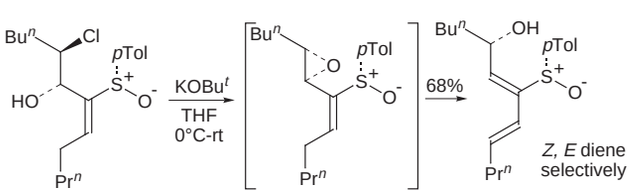
Scheme 125



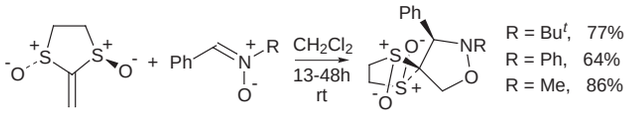
R = H, 59% α/β, 16:1
R = CH(OEt)$_2$, 80% α/β, 16:1

Scheme 126

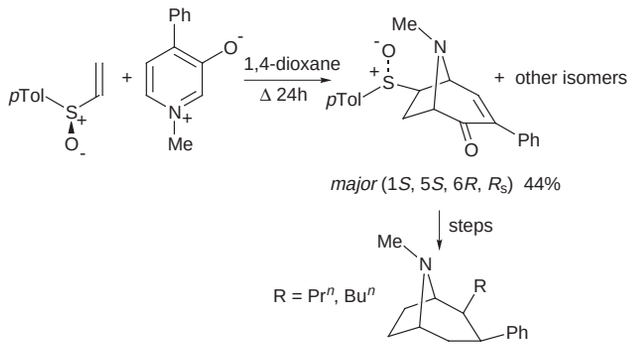
Diels–Alder reaction (Scheme 127).[234,235] The use of unsaturated sulfoxides as dienes, dienophiles and dipolarophiles in cycloaddition reactions remains an important area of research. *trans*-2-Methylene-1,3-dithiolane 1,3-dioxide, a chiral ketene equivalent, readily undergoes 1,3-dipolar cycloaddition with cyclic and acyclic nitrones (Scheme 128).[236] Similarly, chiral vinyl sulfoxides have been employed as dipolarophiles in asymmetric 1,3-dipolar cycloadditions with oxidopyridinium betaines allowing rapid access to the tropane skeleton (Scheme 129).[237] The dienophilic behaviour of enantiomerically pure (*Z*)-3-*p*-tolylsulfinylacrylonitriles **24** has also been studied.[238] The synthesis of sulfinyl-1,3-dienes and their use in asymmetric synthesis has recently been reviewed.[239] In addition, other enantiomerically pure sulfoxide-containing dienes have recently been reported. These include (*S*)-2-(*p*-tolylsulfinyl)-1,4-benzoquinones **25**;[240] (*R*)-4-(*p*-tolylsulfinylmethyl)quinols **26**;[241] and enantiomerically pure 2-sulfinylbuta-1,3-dienes **27**, employed for the first time in a hetero Diels–Alder reaction.[242,243] The diastereoselectivity of the 1,4-conjugate addition of organoaluminium reagents to substituted quinols such as **26** has also been studied.[244]



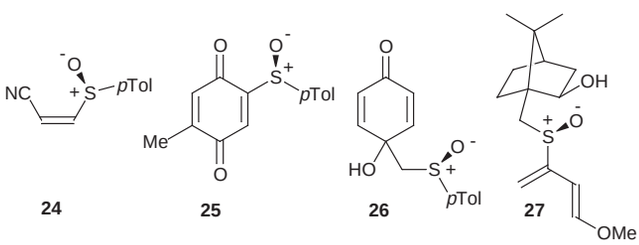
Scheme 127



Scheme 128



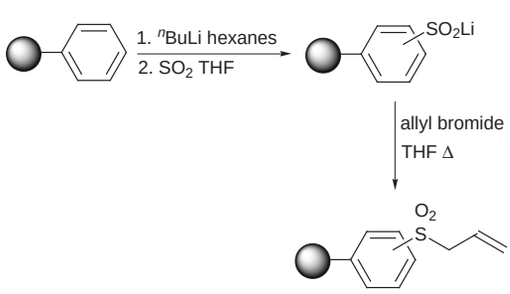
Scheme 129



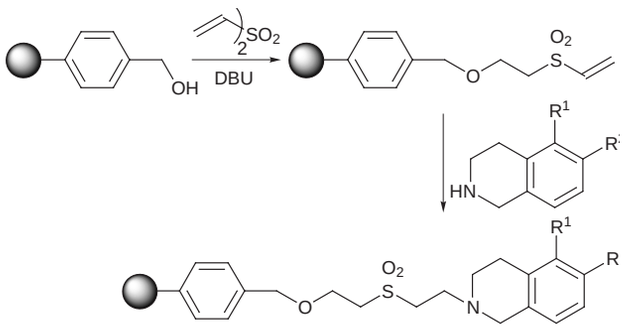
4 Synthesis of sulfones and selenones

Selenones have yet to be exploited to any significant degree in organic synthesis and hence this section will deal solely with the preparation of sulfones.

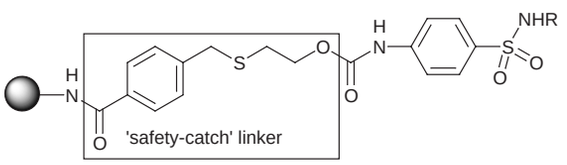
The present interest in solid phase synthesis has led to the development of a number of new sulfone-based linkers. Most of these rely, for their cleavage, on the propensity of sulfones to undergo β-elimination under basic conditions or S_N2' displacements with organometallic reagents. Polymer-bound allylic sulfones have been prepared by lithiation of polystyrene beads and subsequent quenching with sulfur dioxide then allyl bromide (Scheme 130). A similar tether has been utilised in the solid phase synthesis of tertiary amines.[245] A closely related linker has been prepared by treating a hydroxylated polystyrene resin with divinyl sulfone. Attachment of the starting material to the solid support can be achieved by a second Michael addition and cleavage can be achieved on treatment with base. This new sulfone linker has been used in the synthesis of tetrahydroisoquinolines (Scheme 131).[246] Finally, a 'safety-catch' linker, sulfide **28**, has been developed and used in the solid phase synthesis of aryl sulfonamides. Only after oxidation of the sulfide to the sulfone does the linker become base labile, hence, premature cleavage of the substrate from the support is prevented.[247]



Scheme 130

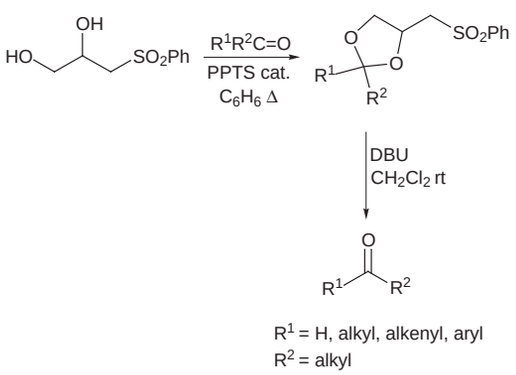


Scheme 131



28

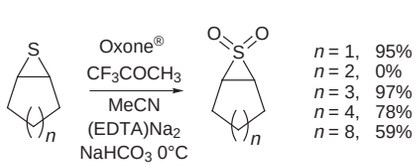
Sulfones have also found application recently in a new class of carbonyl protecting group cleavable by treatment with base (Scheme 132).[248]



Scheme 132

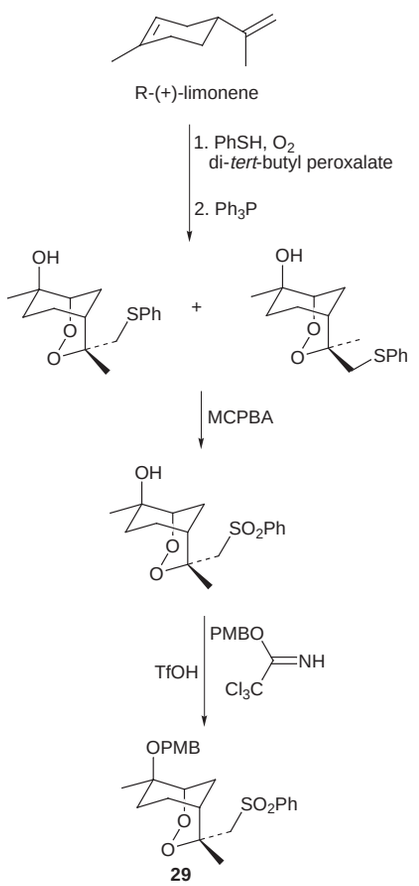
4.1 Oxidation of sulfides and sulfoxides

Many of the oxidising systems discussed for the preparation of sulfoxides and selenoxides, give sulfones and selenones as by-products of over-oxidation. Relatively little new work has been done on the oxidation of sulfides to sulfones and the corresponding transformation of selenides to selenones has received even less attention. The oxidation of dialkyl sulfoxides to the corresponding sulfones has recently been achieved using hydrogen peroxide and titanium containing zeolites.[249] The first report of the oxidation of episulfides to episulfones has recently been made. The oxidation employs an Oxone®–trifluoroacetone reagent system and works particularly well for bicyclic systems but not, surprisingly, for cyclohexene thiirane (Scheme 133).[250] A discussion of novel episulfone substitution and ring-opening reactions *via* α-sulfonyl carbanion intermediates has been published.[251]



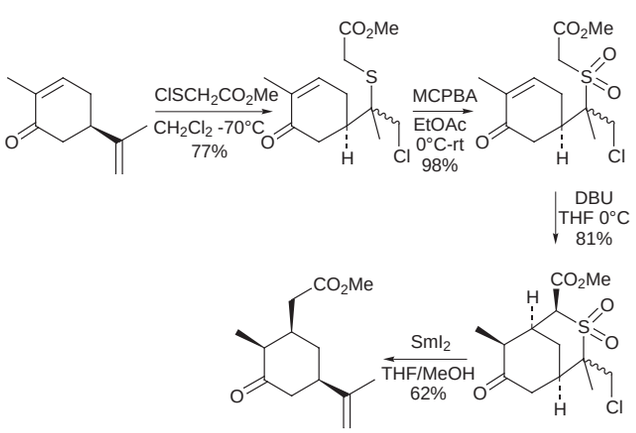
Scheme 133

Sulfone endoperoxide **29**, prepared by thiol–oxygen co-oxidation of 1,5-dienes, peracid oxidation to the sulfone, and protection of the hydroxy group, has been found to have *in vitro* anti-malarial activity comparable to that of artemisinin (Scheme 134).[252,253] Other related sulfone trioxanes have also been prepared but have significantly lower anti-malarial activity.[254]



Scheme 134

A temporary sulfone tether has been used to stereospecifically deliver a methoxycarbonylmethylene group to the enone moiety in (−)-carvone in an intramolecular Michael addition (Scheme 135).[255] The tether is initially introduced by sulfenylation of the isopropenyl olefin followed by oxidation of the sulfide to the corresponding sulfone.

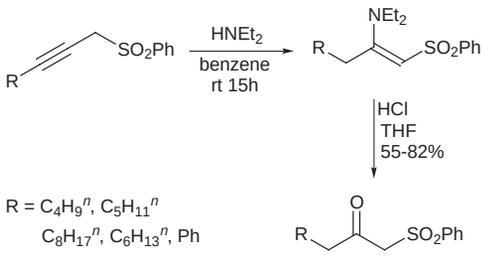


Scheme 135

4.2 Non-oxidative routes to sulfones

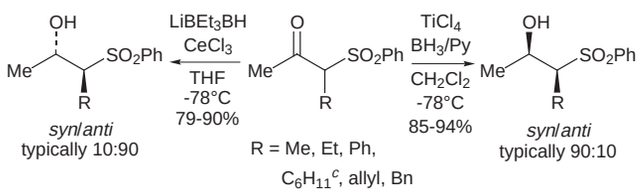
4.2.1 Functionalised sulfones

The addition of diethylamine to acetylenic sulfones followed by hydrolysis gives 1-phenylsulfonyl ketones in good yield

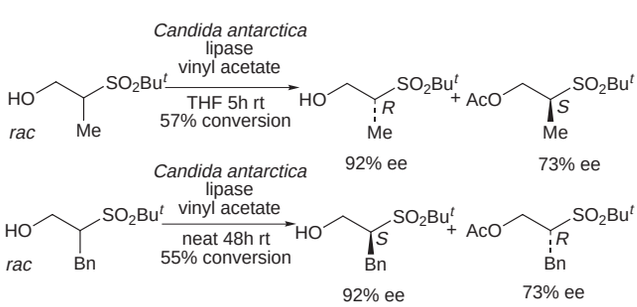


Scheme 136

(Scheme 136).[256] The reduction of α-alkyl-β-keto sulfones under various conditions allows access to both *syn*- and *anti*-α-alkyl-β-hydroxy sulfones (Scheme 137).[257] The lipase catalysed resolution of racemic α-hydroxymethyl sulfones by esterification with vinyl acetate has been studied.[258] Changing the alkyl substituent at the chiral centre from methyl to benzyl leads to a complete reversal in selectivity (Scheme 138). Baker's yeast mediated kinetic resolution of racemic α-phenylsulfonylcyclopentanones has been employed in an approach to 4-(phenylsulfonylmethyl)carboxylic acids in either enantiomeric series (Scheme 139).[259] The overall sequence corresponds to the introduction of a phenylsulfonylmethyl group at an unactivated centre in the original carboxylic acid. Stereoselective baker's yeast reduction has also been used in a route to enantiomerically pure (1*R*,2*R*)- and (1*S*,2*S*)-2-alkyl-1-phenylsulfonylcyclopropanes (Scheme 140).[260] The 1,2-shift of a phenylsulfonyl group has been observed on the treatment of 1,1-bis(phenylsulfonyl)cyclopropanes with fluoride ion.[261] Alkynyl phenylsulfonyl cyclopropanes and epoxides have been prepared by the conjugate addition of either dimethylsulfoxonium methylide or Bu′OOLi to enyne sulfones (Scheme 141).[262]



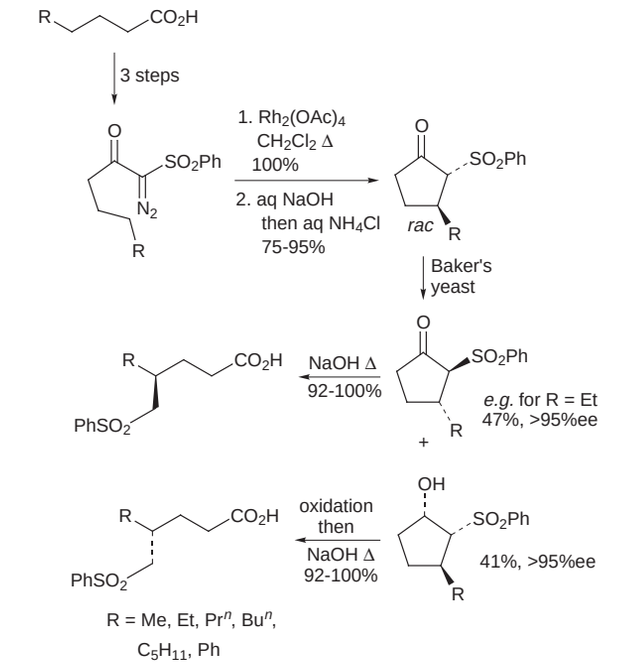
Scheme 137



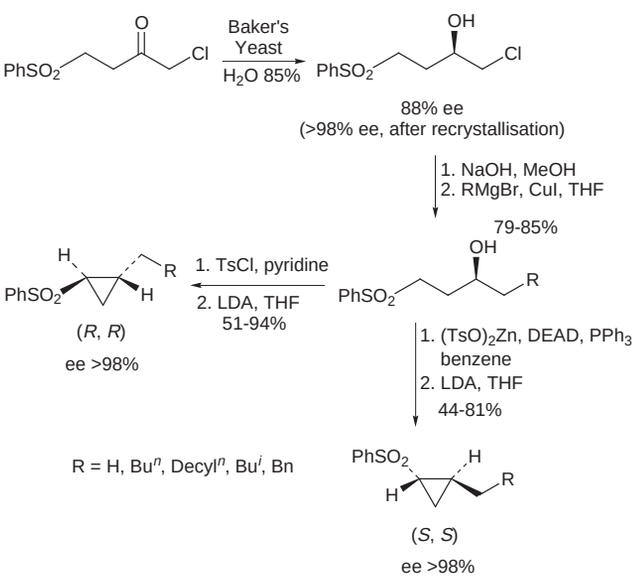
Scheme 138

Functionalised sulfones have also been prepared by the reduction of α-bromo sulfones using $NaBH_4$ and catalytic diphenyl diselenide.[263] In a related reaction, reduction of 2,5-dibromo-2,5-bis(phenylsulfonyl)hexane with samarium(II) iodide results in an interesting intramolecular coupling reaction to give *trans*-2-iodo-1,2-dimethyl-1-phenylsulfonylcyclobutane in quantitative yield (Scheme 142).[263] The palladium catalysed reaction of carbonates derived from γ-hydroxypropenyl sulfones, with β-keto esters and 1,3-diketones provides convenient access to tetrasubstituted dihydrofurans *via* a tandem γ-allylic substitution and cyclisation process. In most cases the reaction shows good diastereoselectivity for the *trans*-sulfone product (Scheme 143).[264]

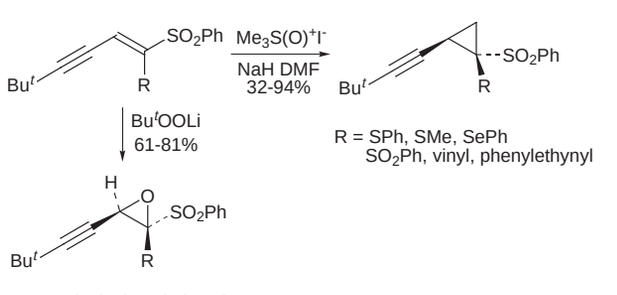
Radical addition to vinyl sulfones provides an effective route



Scheme 139

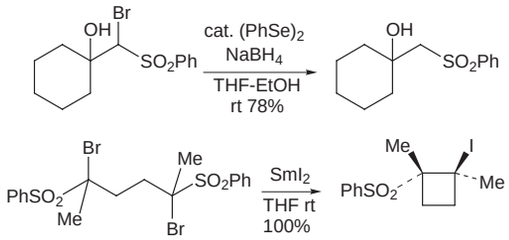


Scheme 140

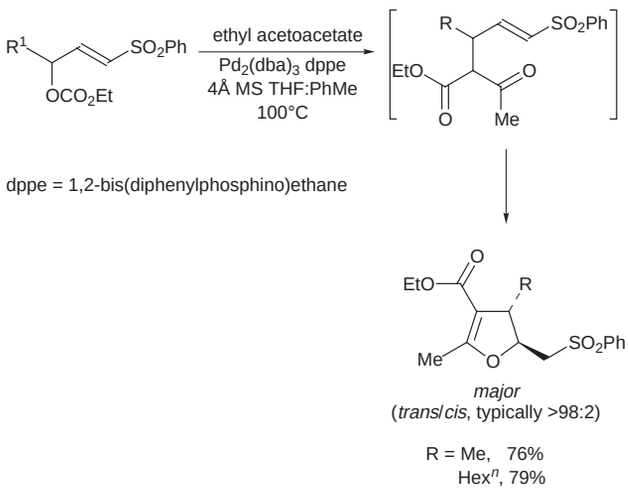


Scheme 141

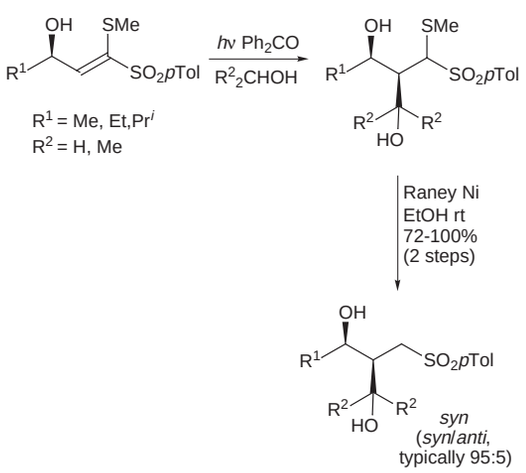
to functionalised sulfones. High 1,2-asymmetric induction was achieved in the 1-hydroxyalkyl radical addition to acyclic 3-hydroxy-1-methylthio-1-(*p*-tolylsulfonyl)alk-1-enes. The addition is highly *syn*-selective regardless of initial olefin geometry. Reductive desulfurisation then gives the corresponding sulfone adducts in excellent overall yield (Scheme 144).[265] Similar 1,2-



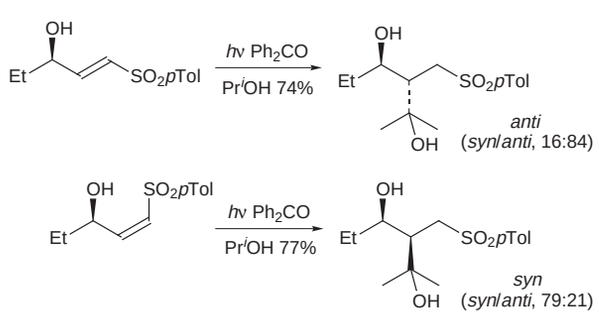
Scheme 142



Scheme 143

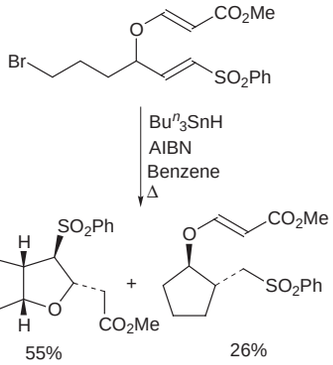


Scheme 144



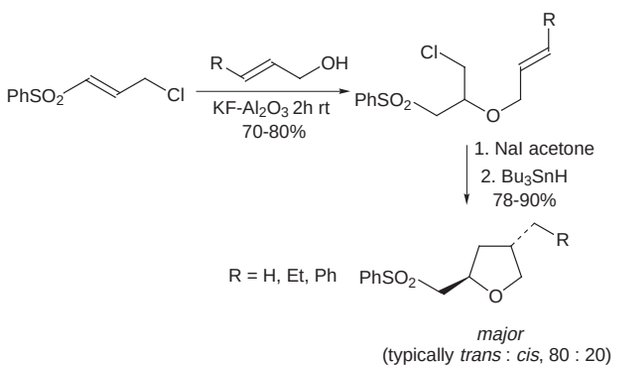
Scheme 145

induction was achieved in radical additions to α,β-unsaturated sulfones lacking the thiomethyl group (Scheme 145).[266] An interesting sequential approach to various bicyclic oxygen heterocycles involving radical addition to vinyl sulfones has been reported.[267] Initial 5-*exo*-*trig* radical addition to the vinyl



Scheme 146

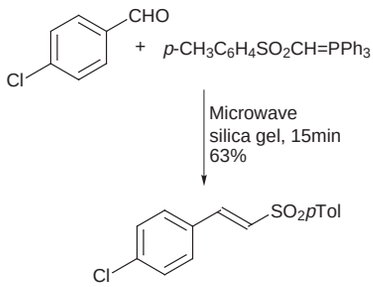
sulfone, followed by either a second 5-*exo*-*trig* cyclisation or hydrogen atom capture by the intermediate α-sulfonyl radical, gives the observed product mixtures (Scheme 146).[267] A radical cyclisation approach to substituted tetrahydrofurans has been reported which involves the 5-*exo*-*trig* radical cyclisation of halo(allyl)sulfones to give *trans*-2,4-disubstituted tetrahydrofurans as the major products (Scheme 147).[268]



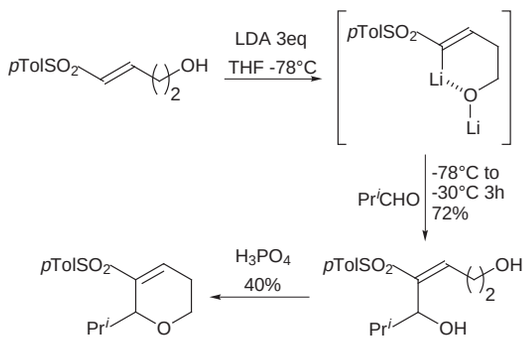
Scheme 147

4.2.2 Vinyl sulfones

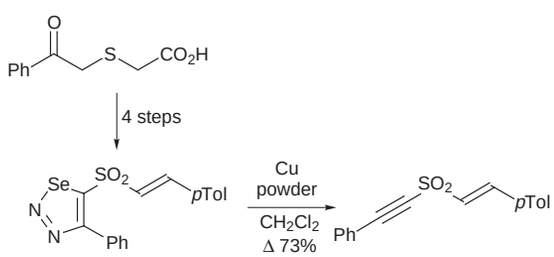
trans-Disubstituted vinyl sulfones have been prepared *via* the Wittig reaction of aromatic aldehydes with (*p*-tolylsulfonylmethylene)triphenylphosphorane under microwave irradiation (Scheme 148).[269] Vinyl sulfones having pendant hydroxy groups can be regioselectively lithiated α to sulfur. The resulting anions react efficiently with electrophiles to give the expected sulfone adducts which upon treatment with phosphoric acid give dihydropyran sulfone derivatives (Scheme 149).[270] Enyne sulfones have been prepared *via* the pyrolysis of 4-aryl-1,2,3-selenadiazol-5-yl *p*-tolylvinyl sulfones, prepared in turn from phenacylsulfanylacetic acid (Scheme 150).[271] Treatment of bridged vinyl sulfones with either *n*-butyllithium or LDA results in smooth β-metallation and subsequent reactions with electrophiles are then possible. When toluene-*p*-sulfonyl fluoride is employed as the electrophile in the aza-bridged series, the bis-sulfone product was subsequently employed as a key intermediate in the synthesis of epibatidine.[272] After hydrogenation and asymmetric elimination of the 7-azabicyclo[2.2.1]heptane bis-sulfone with a chiral base derived from ephedrine, the desired vinyl sulfone was obtained in moderate enantiomeric excess (Scheme 151).[273] Dienyl and enynyl sulfones have been prepared by the ring-opening of oxanorbornenic derivative **30** with an alkynyllithium, followed by reduction and isomerisation (Scheme 152).[274] Chiral manganese salen complexes have been used in the catalytic asymmetric epoxidation of cyclic 2-sulfonyl-1,3-dienes. The presence of the sulfone moiety leads to a significant increase in observed enantioselectivities compared to unsubstituted cyclic dienes (Scheme 153).[275] Finally, enantiomerically enriched alk-2-ynyl toluene-*p*-sulfinates,



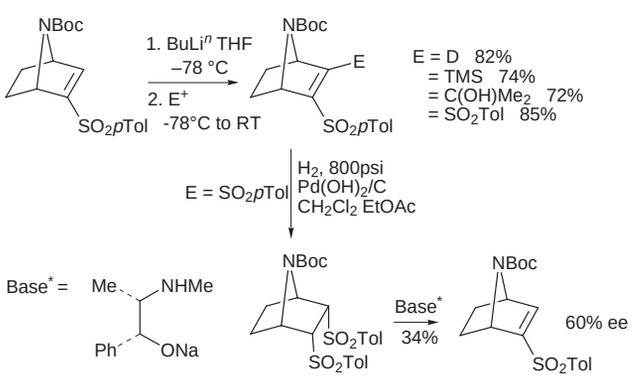
Scheme 148



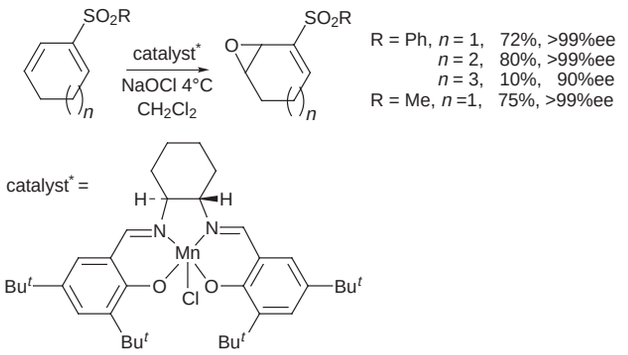
Scheme 149



Scheme 150

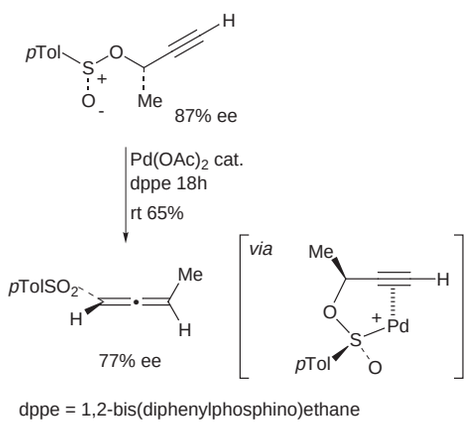


Scheme 151



Scheme 153

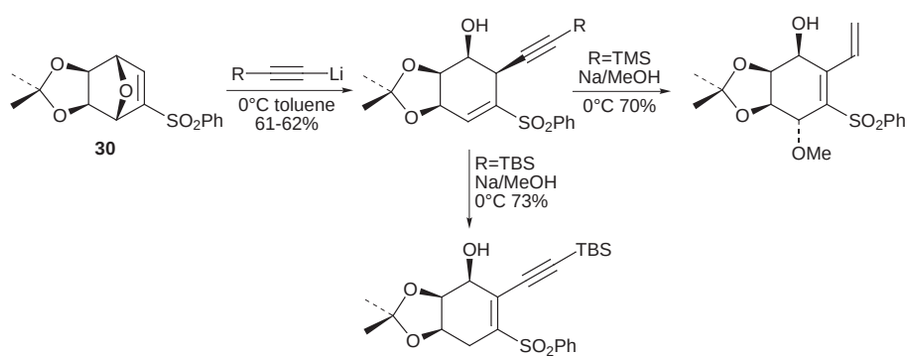
chiral at both the α-carbon and the sulfur atom are transformed into chiral allenyl sulfones on treatment with palladium acetate, with only a small loss in stereochemical integrity. To explain the stereochemical observations, a mechanism has been proposed involving coordination of palladium to the sulfinate sulfur and the alkyne, conjugate addition of palladium to the triple bond to give an allenylpalladium species, and reductive elimination to give the product allenyl sulfones (Scheme 154).[276]



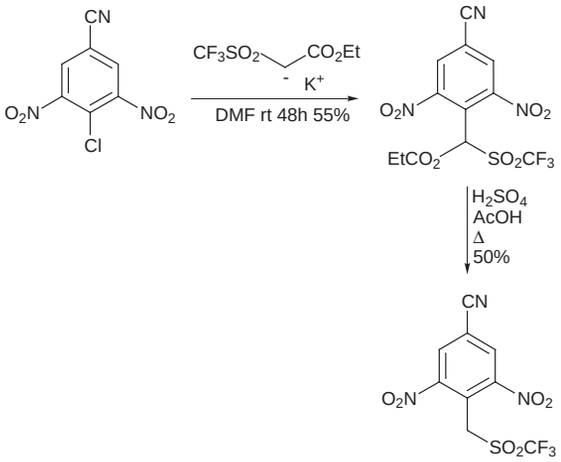
Scheme 154

4.2.3 Allylic and benzylic sulfones

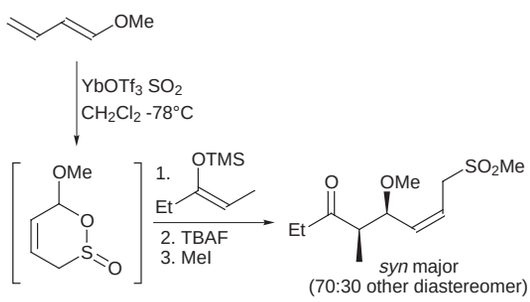
Allylic sulfones can be conveniently prepared *via* the zinc-mediated coupling of allyl bromides with alkyl or arylsulfonyl chlorides.[277] Benzylic trifluoromethyl sulfones have been prepared by the reaction of electron-deficient aromatic halides with the anion of ethyl (trifluoromethylsulfonyl)acetate followed by decarboxylation (Scheme 155).[278] An unusual sequence corresponding to the overall oxyallylation of trimethylsilyl enol ethers, involves the Diels–Alder reaction of dienes with sulfur dioxide followed by Lewis acid decomposition of the cycloadduct. The methoxonium ion produced can be trapped with nucleophiles to give allylic sulfone products



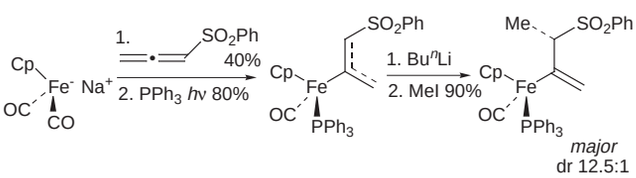
Scheme 152



Scheme 155

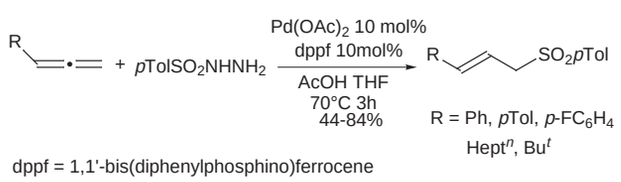


Scheme 156



Scheme 157

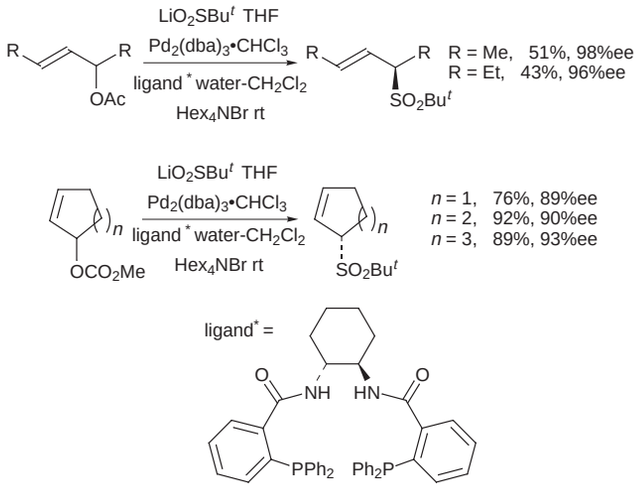
(Scheme 156).[279] The deprotonation and alkylation of chiral-at-iron allyl and vinyl sulfones occurs regio- and stereoselectively although the products observed depend greatly on the electrophile used (Scheme 157).[280] The palladium catalysed hydrosulfination of allenes using tosylhydrazine and a palladium(II) catalyst gives allylic sulfones in moderate to good yield (Scheme 158).[281] In addition, acyclic and cyclic *tert*-butyl sulfones have been stereoselectively prepared *via* palladium catalysed reaction of the corresponding acetates or carbonates with 2-methylpropane-2-sulfinate in the presence of a *P*,*P*-chiral ligand (Scheme 159).[160]



Scheme 158

5 Conclusions

The importance of organo-sulfur and -selenium chemistry in organic synthesis can not be overstated. The emergence of new stereoselective reactions and efficient asymmetric processes suggest further advances are imminent.



Scheme 159

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