REVIEW

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

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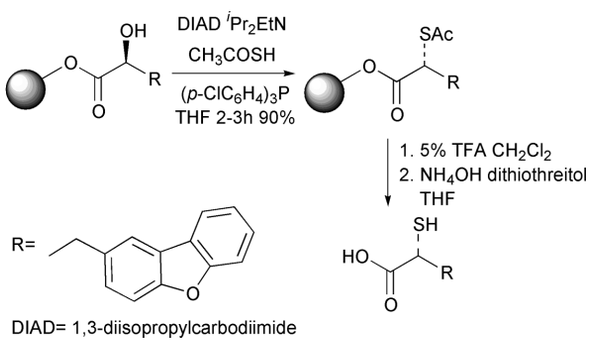
1 Introduction

This review continues a series that began in 1994 and deals with new approaches to the synthesis of thiols and selenols, disulfides and diselenides, sulfides and selenides, sulfoxides and selenoxides, and sulfones and selenones. Each section has been organised so as to deal initially with general routes or reactions that give simple, unfunctionalised compounds, before dealing with processes that give products with greater functionality. Within each section, reactions have been grouped, where possible, according to reaction type, although on occasion reactions that give a particular class of products have been collected together. Cyclic systems are covered alongside analogous acyclic systems.

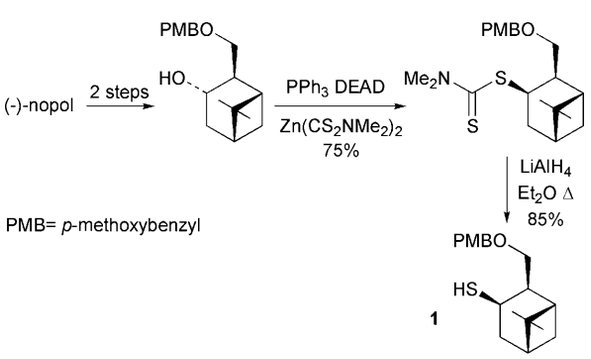
As with previous reviews in the series, emphasis has been placed on new reactions and strategies, stereo- and enantioselective reactions, and emerging areas of interest such as solid-phase chemistry and solid-supported reagents.

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

2.1 Preparation of thiols, disulfides, selenols, and diselenides. Thioesters and thiocarbamates are common precursors to thiols. Thiol inhibitors of metallo-β-lactamases have been prepared *via* the corresponding thioacetates.[1] Bacterial resistance to β-lactam antibiotics is in part due to the increasing incidence of metallo-β-lactamases (MBLs). A solid-phase Mitsunobu reaction has been used for the preparation of a series of thiol inhibitors of the metallo-β-lactamase IMP-1, one of the more threatening MBLs (Scheme 1).[1] Enantiomerically pure thiol **1**, prepared from (−)-nopol in four steps, has been used in the synthesis of both isomers of *trans*-1-mercaptocyclohexan-2-ol from cyclohexene oxide (Scheme 2).[2] The diastereoisomeric hydroxy sulfides obtained from the ring-opening reaction are oxidised diastereoselectively to the corresponding sulfoxides which can then be separated by chromatography. Thermolysis of the sulfoxides results in elimination to give the corresponding sulfenic acids which can be trapped with 3,5-dimethylthiophenol to give the unsymmetrical disulfides. Reduction then gives the enantiomerically pure *trans*-1-mercaptocyclohexan-2-ols (Scheme 3).[2] The palladium-catalysed enantioselective rearrangement of racemic *O*-allylic thiocarbamates to *S*-allylic thiocarbamates has been used for the asymmetric synthesis of allylic thiols (Scheme 4).[3]

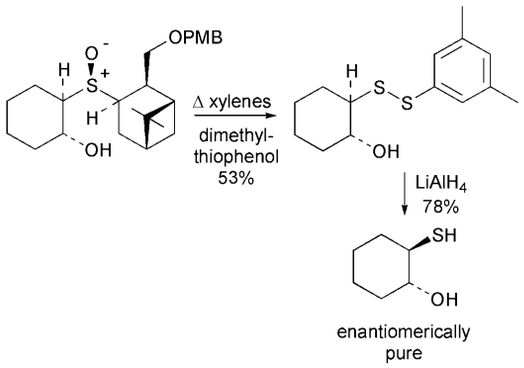


Scheme 1

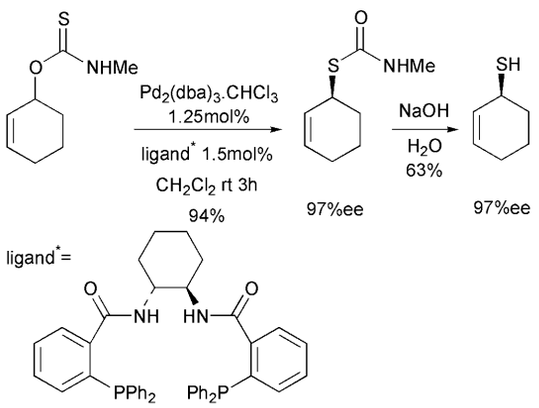


Scheme 2

An extensive study on the conversion of aryl methyl sulfides to the corresponding arenethiols using sodium alkanethiolates has been reported.[4] A short asymmetric synthesis of homocystine and homocysteine has been described which uses



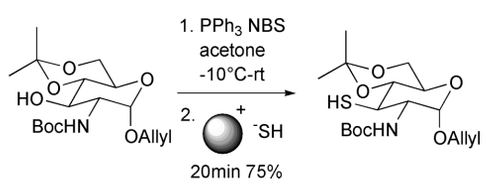
Scheme 3



Scheme 4

Schöllkopf's reagent and employs trityl protection for the thiol group.[5]

A previously reported polymer-supported hydrosulfide reagent reacts with activated alcohols to give thiols in excellent yields.[6] The reagent has been shown to be compatible with a range of functional groups and several common protecting groups (Scheme 5).

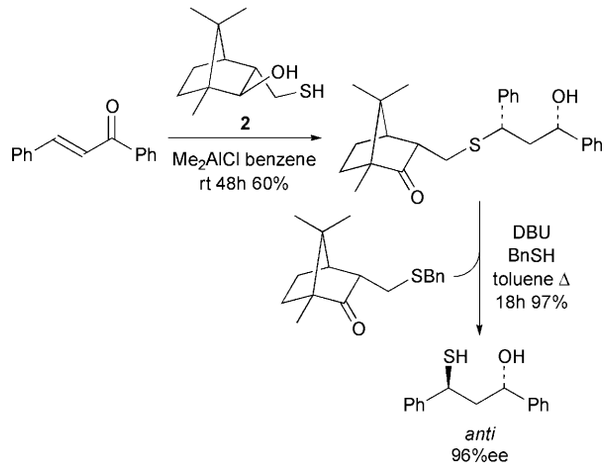


Scheme 5

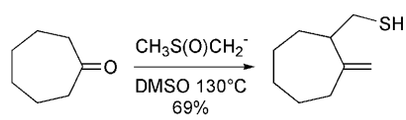
β-Amino tertiary thiols have been prepared by the ring-opening of thiiranes with secondary amines.[7] The reaction proceeds in excellent yield when the procedure is carried out neat. A highly enantioselective synthesis of 1,3-hydroxy thiols has been described which employs the camphor-derived hydroxy thiol **2**, in a tandem Michael addition–Meerwein–Ponndorf–Verley reduction strategy (Scheme 6).[8]

Finally, the direct preparation of γ-unsaturated thiols from ketones using methanesulfinyl carbanion in DMSO has been reported.[9] The reaction has been shown to proceed *via* the [2,3]-sigmatropic rearrangement of intermediate β-unsaturated sulfinyl carbanions (Scheme 7).

Symmetrical aryl and alkyl disulfides are readily prepared by the oxidation of the corresponding thiols. New reagent systems for this transformation include benzyltriphenylphosphonium dichromate;[10] aqueous hydrogen peroxide in trifluoroethanol;[11] trichloronitromethane;[12] ammonium persulfate under solvent-free conditions;[13] and clay-supported ammonium nitrate under microwave irradiation.[14] The direct conversion of alcohols to symmetrical disulfides using dicyclohexylcarbodiimide and



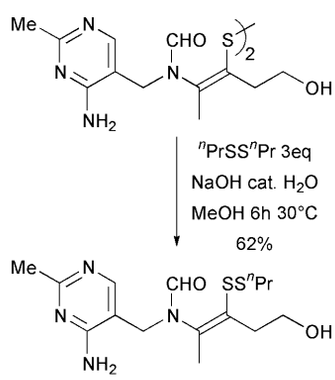
Scheme 6



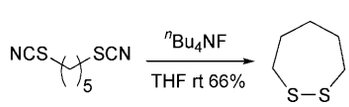
Scheme 7

benzyltriethylammonium tetrathiomolybdate has also been reported.[15]

Unsymmetrical disulfides bearing extensive functionality have been prepared by a base-induced cross-reaction with symmetrical disulfides (Scheme 8).[16] Finally, cyclic disulfides have been prepared in good yield from bisthiocyanates by treatment with fluoride sources (Scheme 9).[17]



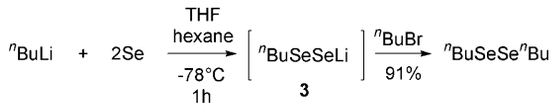
Scheme 8



Scheme 9

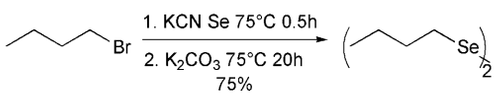
The preparation of fluorous diaryl diselenides has recently been described.[18] On reduction with tributylstannane, fluorous selenols are formed and these are effective in inhibiting undesirable radical rearrangements by fast trapping of radical intermediates. The fluorous diselenide can be recovered after the reaction by continuous fluorous extraction.[18]

A recent report details the preparation of previously unknown diselenolates, such as **3**, by insertion of two selenium atoms into the C–Li bond or by insertion of selenium into metal selenolates.[19] Preliminary studies have found these species to be relatively stable and to react with alkyl halides to give diselenides (Scheme 10). A detailed mechanistic study of the reaction of aryl and alkyl selenocyanates with base has led to an efficient new synthesis of symmetrical diselenides from alkyl bromides.[20] The approach is based on the sequential reaction of



Scheme 10

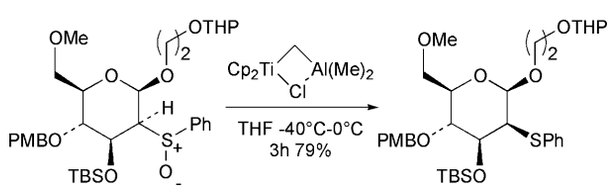
potassium selenocyanate, formed *in situ* by the reaction of selenium with potassium cyanide, with alkyl bromides followed by reaction of the resultant alkyl selenocyanate with potassium carbonate (Scheme 11).[20]



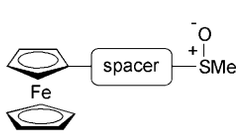
Scheme 11

Finally, a convenient and stereoselective route to divinyl diselenides has been reported which involves the hydrozirconation of terminal alkynes, reaction with elemental selenium and aerial oxidation.[21]

2.2 Synthesis of sulfides and selenides. *2.2.1 Simple sulfides and selenides.* Arguably the simplest route to sulfides involves the deoxygenation of sulfoxides. The deoxygenation of sulfoxides and selenoxides with the Tebbe and Pestasis reagents has recently been reported.[22] The reaction conditions have been found to tolerate a wide range of functionality and protecting groups (Scheme 12). Diaryl sulfoxides are smoothly reduced to the corresponding sulfides with ferrocene and trifluoroacetic anhydride.[23] Interestingly, this process has been used as a method for the evaluation of molecular wires. For example, in systems such as **4**, through-bond electron transfer from the ferrocenyl group is responsible for the deoxygenation of the tethered sulfoxide. The efficiency of this process therefore reflects the electron-transfer properties of the spacer group.[23] The deoxygenation of dialkyl and diaryl sulfoxides with 2,6-dihydroxypyridine has also been reported.[24]



Scheme 12



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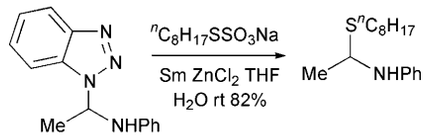
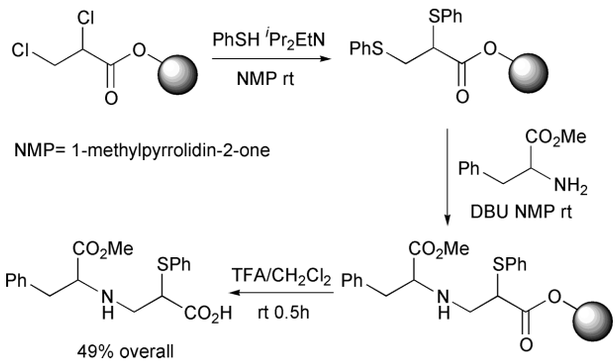
The displacement of leaving groups with sulfur nucleophiles is one of the more common methods for the preparation of sulfides. Unsymmetrical α-amino sulfides have been prepared by the samarium–zinc chloride mediated addition of sodium alkyl thiosulfates to 1-(α-aminoalkyl)benzotriazoles under aqueous conditions (Scheme 13).[25] The sequential nucleophilic substitution of immobilised 2,3-dichloropropionic acid has been employed in the solid-phase synthesis of α-sulfanyl β-amino propionic acid derivatives (Scheme 14).[26] The reduction of diaryl sulfides and selenides with ytterbium metal, conveniently activated by the addition of a trace of methyl iodide, gives ytterbium(III) chalcogenolate complexes.[27] These complexes react with epoxides by Lewis acidic activation and subsequent delivery of a nucleophile (Scheme 15).

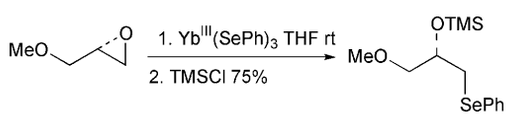
The direct preparation of enantiomerically pure sulfides and selenides from camphor-derived ketones has been reported.[28]



Scheme 13

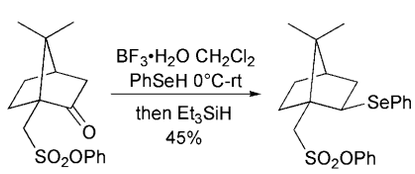


Scheme 14



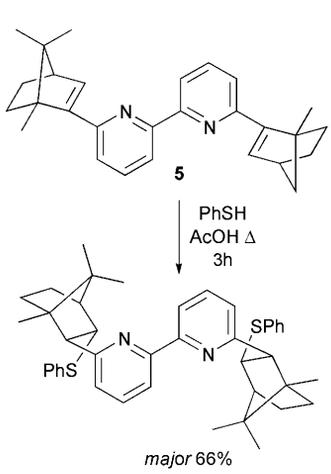
Scheme 15

The Lewis acid-mediated addition of thiols and selenols to the carbonyl group, followed by *in situ* reduction of the intermediate thionium or selenonium ion, selectively gives *exo*-sulfides and selenides in modest yield (Scheme 16).[28]



Scheme 16

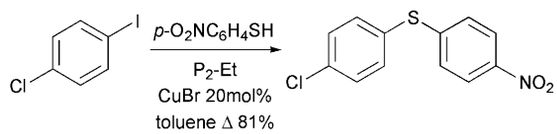
The *anti*-Markovnikov addition of arene- and alkane-thiols to simple alkenes has been achieved using a zeolite catalyst. Steric constraints in the zeolite pore have been used to explain the observed selectivity.[29] The addition of thiophenol to bis-alkene **5** has been employed in the synthesis of novel camphor-derived pyridyl and 2,2′-bipyridyl sulfide ligands (Scheme 17).[30]

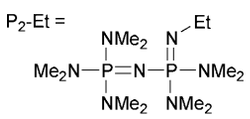


Scheme 17

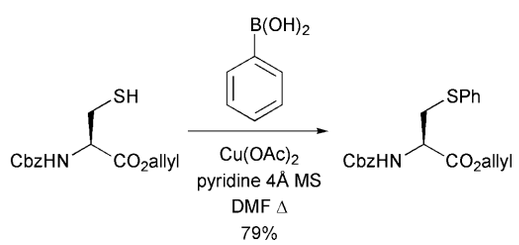
Diaryl and aryl alkyl sulfides have been prepared by a variety of metal-mediated cross-coupling processes. The coupling of aryl iodides and arene thiols in the presence of catalytic copper

bromide and a phosphazene base gives diaryl sulfides in good yield (Scheme 18).[31] The reaction is highly chemoselective in that the presence of hydroxy groups and other halides is tolerated. The cross-coupling of arylboronic acids and alkanethiols mediated by copper(II) acetate, gives aryl alkyl sulfides in good yield (Scheme 19).[32] The palladium-catalysed coupling of primary and secondary thiols with aryl iodides has been employed in the solid-phase synthesis of aryl alkyl sulfides (Scheme 20).[33] Diaryl diselenides have been prepared by a nickel(II)-catalysed coupling of diaryl diselenides with aryl iodides in the presence of a polymer-supported borohydride reducing agent (Scheme 21).[34] The palladium-catalysed coupling of aryl and alkyl halides with phenyl tributylstannyl selenide gives the corresponding unsymmetrical phenyl selenides in good yield (Scheme 22).[35] Interestingly, an alkyl iodide possessing β-hydrogens has also been employed successfully in the reaction. In an extension of the reaction, the butylseleno group has also been transferred from tin.[35] A series of enantiomerically pure, ferrocenyl-oxazoline-derived aryl selenide ligands, such as **6**, have been prepared and employed successfully in palladium-catalysed allylic alkylations.[36]

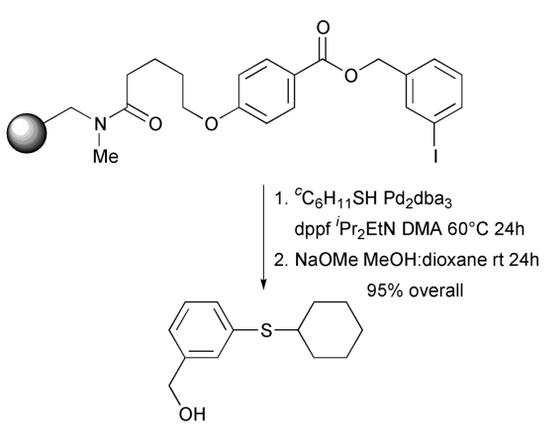




Scheme 18



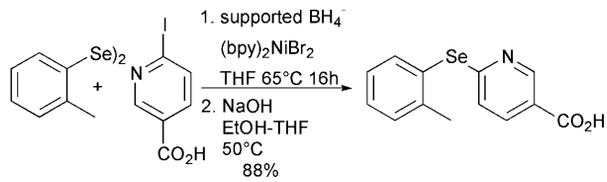
Scheme 19



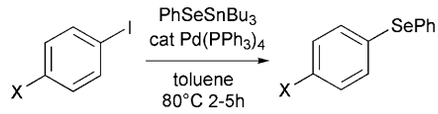
dppf = 1,1'-bis(diphenylphosphino)ferrocene
DMA = *N,N*-dimethylacetamide

Scheme 20

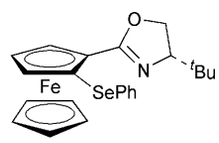
Diaryl sulfides have also been prepared from arenethiols and aryl halides using caesium fluoride on alumina under microwave irradiation.[37] A novel class of spirocyclic cocaine analogues has been prepared by an approach which includes the Suzuki coupling of a cocaine-derived vinyl triflate with 2-methylsulfanylphenylboronic acid.[38] The regioselective synthesis of



Scheme 21



Scheme 22



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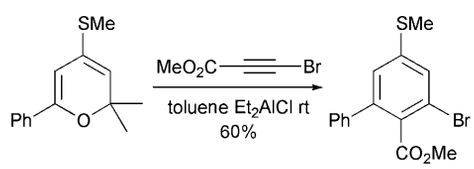
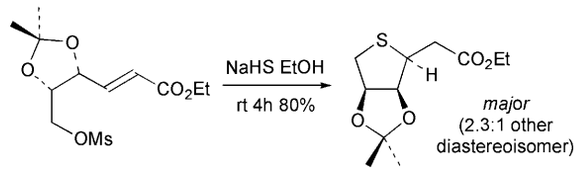
substituted aryl sulfides *via* carbonyl–alkyne exchange reactions of 2,2-dimethyl-2,3-dihydro-4*H*-pyran-4-thione-derived dienes has been reported (Scheme 23).[39]



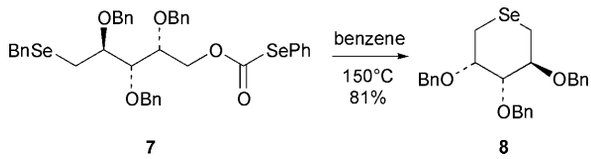
Scheme 23

A variety of interesting approaches to 'simple' cyclic sulfides has been reported. Michael addition of hydrogen sulfide anion to substrates derived from L-erythrose and D-mannose, followed by sequential intramolecular mesylate displacement, has been employed in the synthesis of thiosugars (Scheme 24).[40] An efficient method for the preparation of selenosugars has recently been developed. Thermolysis of selenocarbonate **7**, derived from D-arabinose, gives selenopentopyranose **8** *via* nucleophilic attack of the benzylseleno moiety with subsequent loss of carbon dioxide and benzeneselenolate (Scheme 25).[41] Functionalised thiopyran derivatives have been prepared from homoallylic thiols and aldehydes in a highly diastereoselective, indium chloride-mediated cationic cyclisation (Scheme 26).[42] The first synthesis of 11-thia steroids involves the intramolecular Diels–Alder reaction of an *in situ* generated *o*-quinodimethane species, with an alkene connected by a sulfur-containing tether (Scheme 27).[43] The decomposition of 1,3-dipole precursor **9** in the presence of α,β-unsaturated camphorsultam amide dipolarophiles gives *anti*-tetrahydrothiophene cycloadducts with good diastereoselectivity (Scheme 28).[44] The enantioselective desymmetrisation of *meso*-compounds is an attractive strategy in asymmetric synthesis. Recently, an exciting preliminary study into the desymmetrisation of *meso*-cyclic disulfides by desulfurisation with enantiomerically pure aminophosphines has appeared.[45] Although the product cyclic sulfides are obtained in low enantiomeric excess, the approach shows considerable potential as a new strategy for the preparation of enantiomerically enriched compounds of this type (Scheme 29).[45]

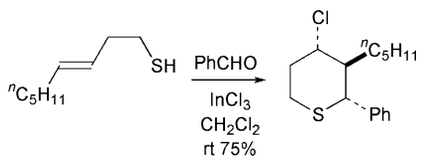
A new family of selenium-based 'safety-catch' linkers has been reported for carboxylic acids, alcohols and amines.[46] The linker is in fact a masked allyl ester, carbonate, or carbamate. Oxidation to the selenoxide and elimination generates the allyl moiety and palladium-catalysed deprotection employing a polymer-bound tin hydride can then be carried out



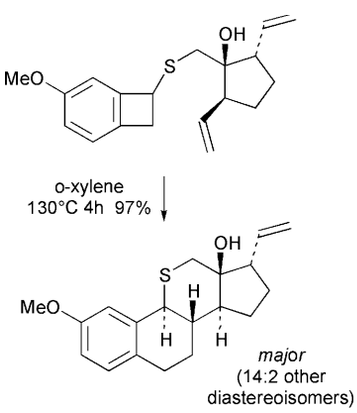
Scheme 24



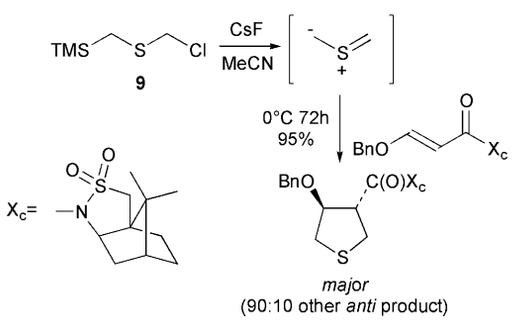
Scheme 25



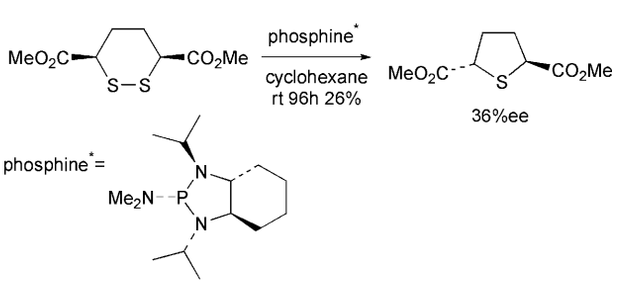
Scheme 26



Scheme 27



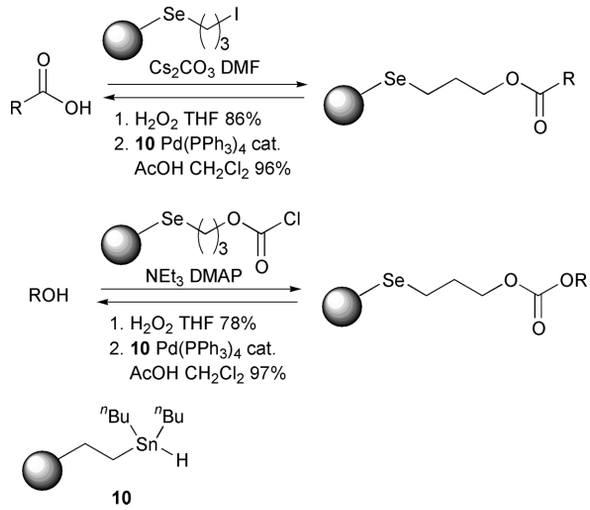
Scheme 28



Scheme 29

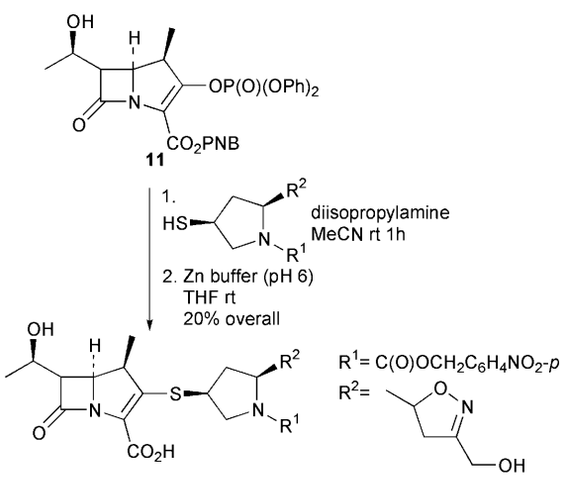
(Scheme 30).[46] The linker has been employed in a solid-phase semi-synthesis of vancomycin.

2.2.2 Functionalised sulfides and selenides. The Michael addition of thiols or thiolates to electron-deficient alkenes is



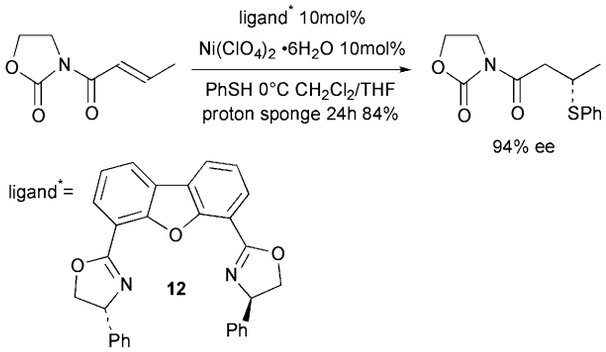
Scheme 30

a commonly used strategy for the synthesis of functionalised sulfides. New sulfur-containing carbapenem antibiotics have been prepared by the Michael addition–elimination of proline-derived thiols to enolphosphate **11** (Scheme 31).[47] The first report of an asymmetric thiol conjugate addition mediated by a chiral Lewis acid has appeared.[48] The Lewis acid employed is a nickel(II) aqua complex of chiral ligand **12**. Excellent enantioselectivities were obtained for a variety of thiols, although only one Michael acceptor was used and this substrate contained an achiral oxazolidinone auxiliary for coordination to the Lewis acid (Scheme 32).[48] An interesting tandem Michael addition–Meerwein–Ponndorf–Verley reduction employing *exo*-10-mercaptobornan-2-ol has been reported.[49] Lewis acid mediated Michael addition of the enantiomerically pure thiol to acyclic α,β-unsaturated ketones, followed by 1,7-hydride shift gives reduction products in high yield and with high diastereoselectivity (Scheme 33 and Scheme 6). Reductive or oxidative desulfurisation can then be used to remove the sulfur tether.[49]

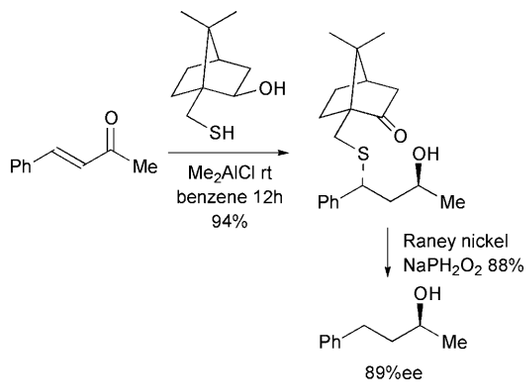


Scheme 31

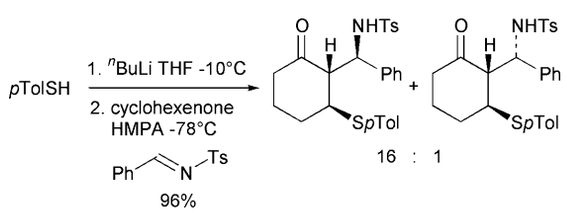
Sequential processes triggered by thiolate or selenolate Michael additions are becoming increasingly sophisticated and several new examples have been reported. A highly stereoselective Michael–imino aldol condensation triggered by thiolate anions has been described (Scheme 34).[50] The Michael–aldol tandem cyclisation of ω-oxo-α,β-unsaturated esters mediated by lithium phenylmethanethiolate allows functionalised carbocycles to be prepared with excellent stereoselectivity.[51] Finally, a full report of the stereoselective lithium thiolate, or selenolate, triggered, tandem Michael–aldol reaction has



Scheme 32



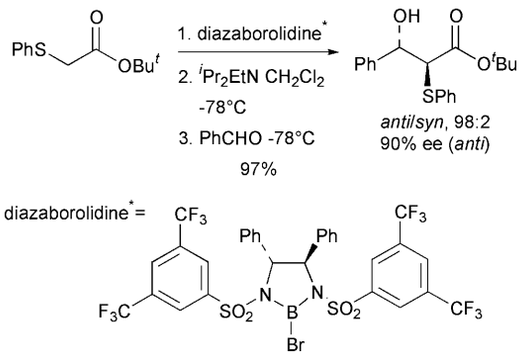
Scheme 33



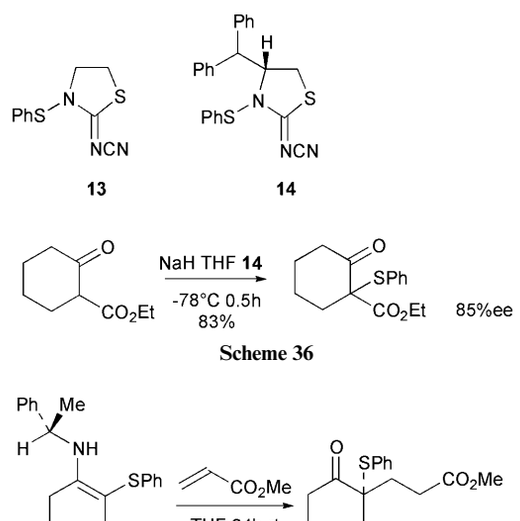
Scheme 34

recently appeared.[52] Interestingly, the magnesium selenolate-mediated tandem Michael–aldol reaction has been shown to be *anti*-selective.[53] This is in marked contrast to analogous lithium thiolate-mediated processes which are *syn*-selective.

The enantioselective aldol reaction of phenylthioacetate esters with aldehydes mediated by a chiral diazaborolidine has been reported.[54] The sulfide aldol adducts are obtained with high *anti*-selectivity and in high enantiomeric excess (Scheme 35). A method for the conversion of aldehydes to the corresponding one-carbon homologated α-sulfanyl aldehydes has been reported.[55] 3-Phenylsulfanyl-2-(*N*-cyanoimino)thiazolidine, **13**, is an interesting new sulfenylating agent for the α-sulfenylation of carbonyl compounds.[56] An enantiomerically pure version of the reagent **14** has been developed and used in asymmetric sulfenylation reactions. High enantioselectivities have been observed for some cyclic ketones although selectivities have been found to depend markedly on ring-size and on the anion-stabilizing group (Scheme 36).[56] Enantiomerically pure enamine **15**, readily prepared by condensation of 2-phenylsulfanylcyclohexanone with (*S*)-1-phenylethylamine, reacts with electron-deficient olefins in an asymmetric Michael addition (Scheme 37).[57] The sulfide Michael adducts were obtained in good yield and high enantiomeric excess. On treatment with catalytic rhodium(II) acetate, α-diazo thiol esters decompose to give thio-substituted ketenes which undergo facile [2 + 2] cycloaddition with alkenes, alkynes and imines, to give α-thio-substituted cyclobutanones, cyclobutenones, and β-lactams, respectively (Scheme 38).[58] Finally, the reaction of selenothioic *S*-esters with trialkyl phosphites gives α-phosphoryl sulfides in good yield (Scheme 39).[59]

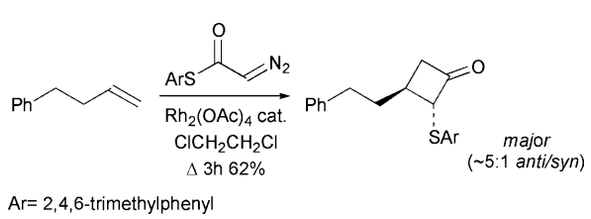


Scheme 35

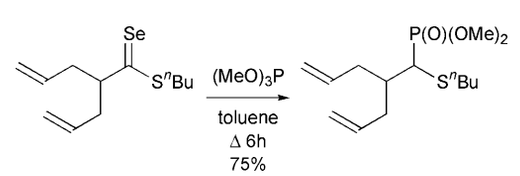


Scheme 36

Scheme 37



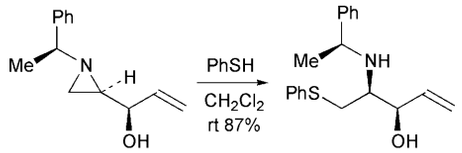
Scheme 38



Scheme 39

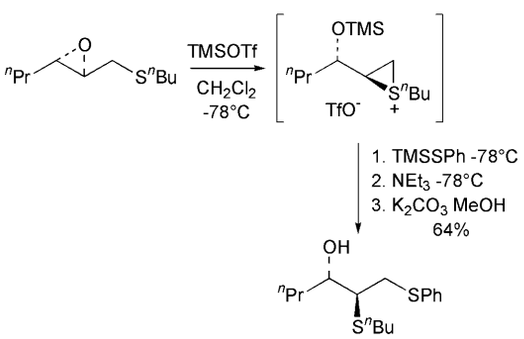
The ring-opening of cyclopropanes with sulfenyl chlorides has been described.[60] The product distribution was found to depend markedly on the reaction conditions and the substitution on the cyclopropane. β-Arylsulfanyl ketones have been prepared by the reaction of α-benzotriazolylalkyl phenyl sulfides with enamines.[61] The regioselective ring-opening of unactivated, enantiomerically pure aziridines with thiols has been used for the preparation of functionalised β-amino sulfides (Scheme 40).[62]

The intermediacy of thiiranium ions is often invoked to explain the stereoselectivity observed in a variety of approaches

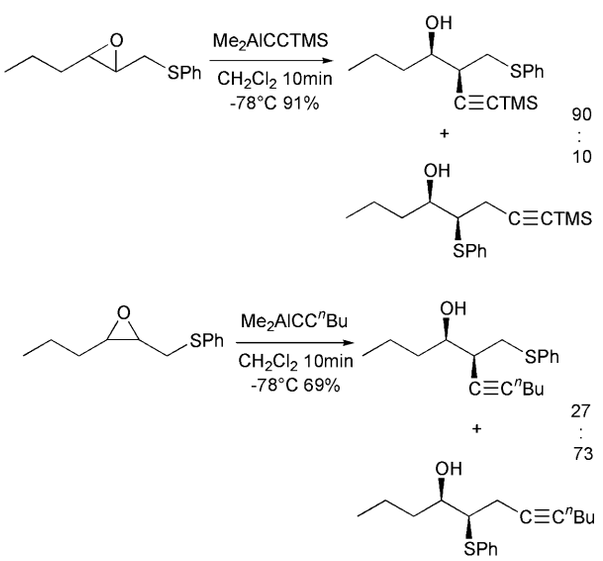


Scheme 40

to functionalised sulfides. 3-Hydroxy-1,2-dithioethers have been prepared from 2,3-epoxy sulfides with full regio- and stereocontrol by Lewis acid-induced thiiranium ion formation followed by ring-opening with thiolate nucleophiles (Scheme 41).[63] Treatment of 2,3-epoxy sulfides with alkynylaluminiums gives alkynylation products arising from ring-opening of an intermediate thiiranium ion (Scheme 42).[64] The product distribution depends markedly on the stereochemistry of the epoxide substrate. Unusual heterocyclic systems such as 1,8-dioxaspiro-[4.5]decanes have been prepared in a stereochemically controlled manner using an approach involving phenylsulfanyl migration.[65] Treatment of diol **16** with toluene-*p*-sulfonic acid gives the spirocyclic ether **17** *via* the formation of a thiiranium ion intermediate (Scheme 43). Studies on the stereoselective formation of functionalised tetrahydrofurans and tetrahydropyrans using similar strategies have also been described.[66,67] In a related study, thiols **18** and **19** were found to undergo very different reactions triggered by the acid-catalysed formation of a thiiranium ion intermediate.[68] For short-chain thiols, cyclisation occurs to give spirocyclic sulfides. For longer-chain thiols, elimination to give allylic sulfides is observed (Scheme 44).[68]

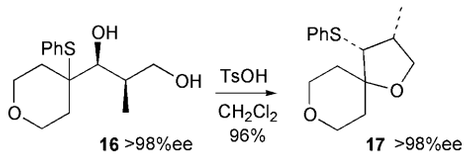


Scheme 41

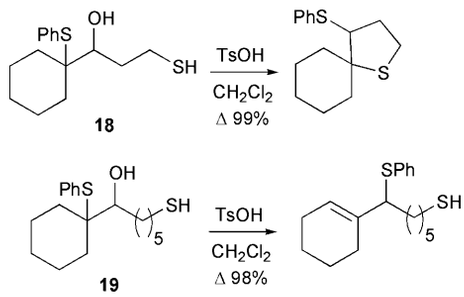


Scheme 42

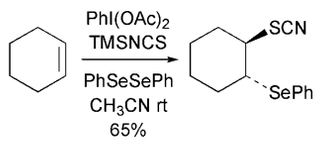
The hypervalent iodine-mediated thiocyano-phenylselenenylation of alkenes using *in situ* generated bis(thiocyanato)iodobenzene has been reported (Scheme 45).[69] The oxyselenenylation of diolefins using a photosensitised



Scheme 43



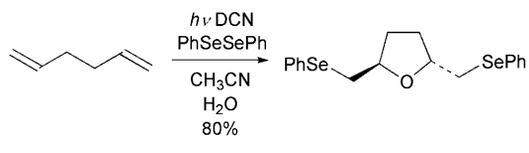
Scheme 44



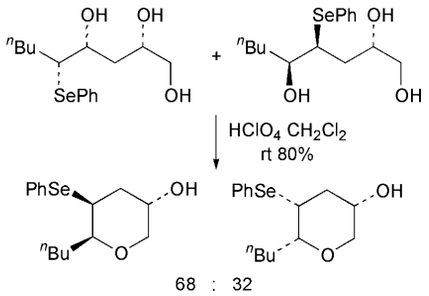
Scheme 45

electron transfer (PET) approach for the activation of diphenyl diselenide, selectively gives *trans*-dialkyl cyclic ethers (Scheme 46).[70] Complexes formed between aryl selenocyanates and metal triflates have been employed in selenoetherification and selenolactonisation reactions.[71] A detailed study of selenoetherification reactions that form tetrahydrofuran and -pyran rings has been carried out (Scheme 47).[72] The thermodynamic tetrahydropyran products have been shown to form from a mixture of the kinetic tetrahydrofuran products. The stereochemistry of the reaction is believed to be lost due to equilibration of the intermediate seleniranium ion *via* a dissociation–association mechanism.[72] The selenolactonisation of unsaturated carboxylic acids has been carried out using a solid-supported selenium electrophile and gives polymer-bound selenides in good yield (Scheme 48).[73] The selenium-linkage can be cleaved reductively or oxidatively, *via* selenoxide elimination. A general approach to bicyclo[3.3.1]nonan-9-ones has been reported which involves the selenium-mediated cyclisation of alkenyl-substituted β-dicarbonyls.[74] The use of a selenium bromide resin not only induces efficient cyclisation but also leads to the immobilisation of the bicyclic products for further solid-phase manipulations (Scheme 49).[74] The same selenenyl bromide resin has been employed in a solid-phase approach to benzopyrans.[75,76] A selenium-based linker has been employed in the solid-phase synthesis of carbohydrates:[77] selenoglycosylation using the tributyltin ether of a resin-bound selenol was employed for the immobilisation of the sugar (Scheme 50). A 1,2-seleno migration was then used to shift the linkage to the 2-position of the sugar, thus allowing further glycosylation reactions to be carried out. The selenium-based linkage was finally cleaved either oxidatively or reductively, in the latter case to give 2-deoxyglycosides.[77]

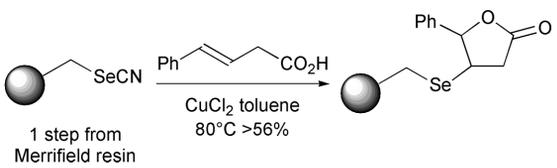
Further advancements in the asymmetric oxyselenenylation of olefins have been reported. The process has been the subject



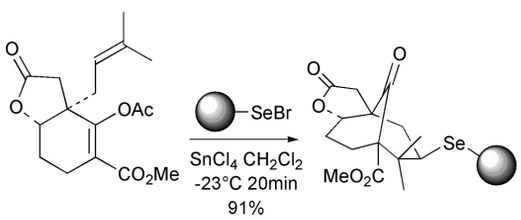
Scheme 46



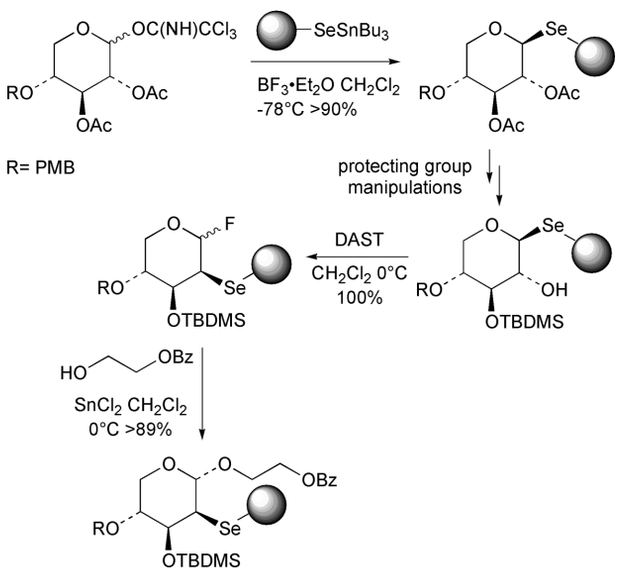
Scheme 47



Scheme 48



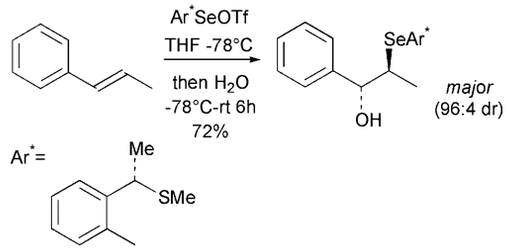
Scheme 49



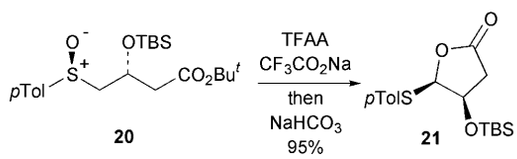
Scheme 50

of extensive calculations which have resulted in a model for the prediction of stereoselectivities.[78] In the design of new asymmetric selenenylating agents, the importance of a nearby heteroatom for interaction with the selenium centre is now well appreciated. The first synthesis of a sulfur-containing diselenide and the corresponding selenenyl triflate (the active selenenylating agent) has been reported.[79] Preliminary studies showed slightly improved diastereoselectivities in selected asymmetric selenomethoxylation reactions when compared to reactions with related reagents containing oxygen and nitrogen heteroatoms (Scheme 51).[79]

Several new variants on the Pummerer reaction of sulfoxides have been described. The diastereoselective Pummerer-type cyclisation of sulfoxide **20** gives the *cis*-β-hydroxy-γ-sulfanyl-γ-butyrolactone **21** in high yield (Scheme 52).[80] An asymmetric Pummerer cyclisation has recently been employed in an

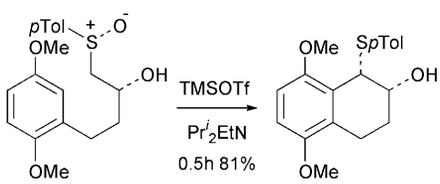


Scheme 51



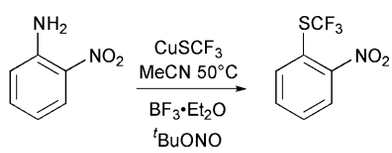
Scheme 52

approach to anthracyclinones (Scheme 53).[81] The stereochemistry of the process has been shown to be controlled by the β-hydroxy group rather than by the stereochemistry at sulfur. In a related process, high diastereoselectivities have been observed in the Lewis acid-mediated Friedel–Crafts alkylation of aromatics with menthol-derived α-chloro-α-phenylsulfanylacetates.[82]



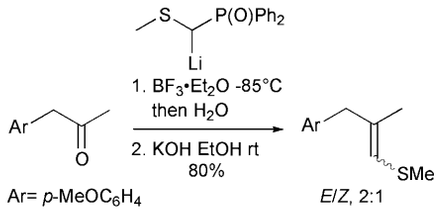
Scheme 53

The development of methods for the preparation of partially fluorinated sulfides remains a popular area of research. The one-pot conversion of anilines to trifluoromethyl sulfides has been reported.[83] *In situ* diazotisation in the presence of copper trifluoromethanethiolate gives the corresponding sulfide in moderate yield (Scheme 54). Trifluoromethyl aryl sulfides have also been prepared by reaction of silver(I) trifluoromethanethiolate with activated aromatic halides, in the presence of potassium iodide or tetrabutylammonium iodide.[84] α-Phenylsulfanyl esters are fluorinated in the α-position on treatment with *p*-methyliodobenzene difluoride.[85] In some cases, treatment with two equivalents of reagent gave α-difluorinated adducts. The analogous reaction of α-phenylsulfanyl amides gives products arising from α-fluorination, Pummerer-induced cyclisation or sulfoxidation depending upon the nature of the substrate.[86]



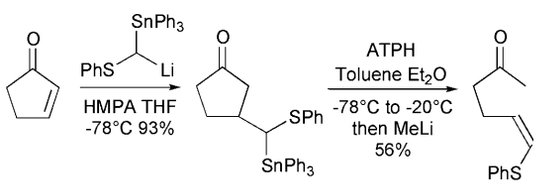
Scheme 54

2.2.3 Vinylic and acetylenic sulfides and selenides. The Horner–Wittig reaction of α-lithio(methylsulfanylmethyl)-diphenylphosphine oxide with ketones gives methyl vinyl sulfides (Scheme 55).[87] For enolisable or bulky ketones, it has been reported that yields can be improved by the addition of boron trifluoride–diethyl ether. A new conjugate addition, enone fragmentation procedure has been developed which allows the synthesis of acyclic vinyl sulfides from cyclic enones.[88] The reaction involves the conjugate addition of



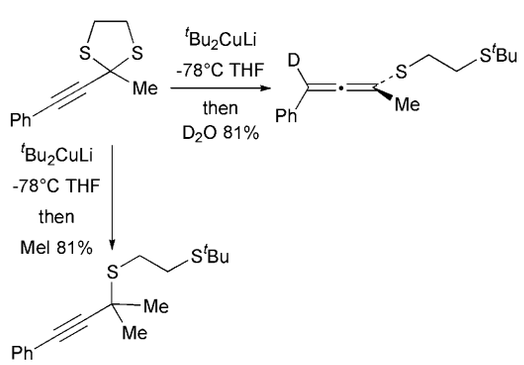
Scheme 55

triphenylstannyl(phenylsulfanyl)methyllithium to enones followed by fragmentation of the resulting γ-stannyl ketone adducts by treatment with aluminium tris(2,6-diphenylphenoxide) and methyllithium (Scheme 56).[88] Propargylic thioacetals (propargyl = prop-2-ynyl) react with organocuprates to give either allenyl or propargylic sulfides depending upon the nature of the electrophilic quench employed (Scheme 57).[89] Transmetallation of the organocopper intermediates with zinc bromide and palladium-catalysed coupling with aryl and alkynyl halides was also reported. The addition of arene/alkane thiolate and selenolate nucleophiles to alkynylphosphonates gives the corresponding (*Z*)-β-organosulfanyl and organoselanyl vinyl phosphonates selectively and in moderate yield.[90]



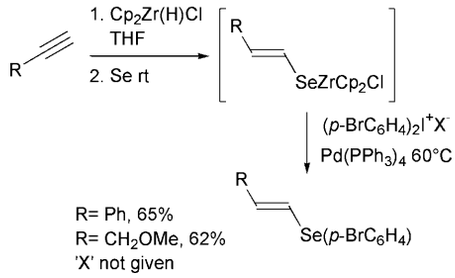
ATPH= aluminium tris(2,6-diphenylphenoxide)

Scheme 56

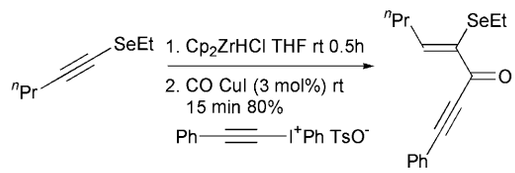


Scheme 57

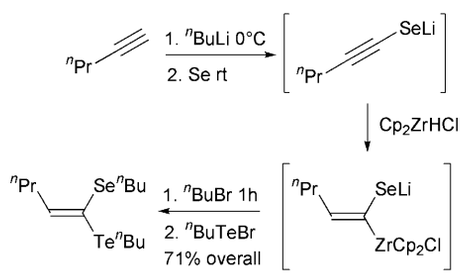
A stereoselective synthesis of (*E*)-aryl vinyl selenides *via* the reaction of elemental selenium with vinyl zirconocenes has been reported.[91] The palladium-catalysed coupling of the intermediate vinylselenozirconocenes with diaryliodonium salts gives (*E*)-aryl vinyl selenides in good yield (Scheme 58).[91] In a related study, (*E*)-α-selenylvinylzirconiums formed by the hydrozirconation of alkynyl selenides, have been found to undergo copper-catalysed carbonylative cross-coupling with alkynyliodonium tosylates (Scheme 59).[92] (*Z*)-Selenyl-α,β-unsaturated ketones have also been prepared by the palladium-catalysed cross-coupling of (*E*)-α-selenylvinylstannanes with acyl halides.[93] The hydrozirconation of acetylenic selenides can give a mixture of regioisomers. In stark contrast, the hydrozirconation of *in situ* generated alkynyl selenolates has been found to proceed regiospecifically.[94] This approach has been employed in the synthesis of ketene telluro(seleno) acetals which are important precursors for the preparation of vinyl selenides (Scheme 60).[94] α-Chalcogeno ketenes, generated *in situ* from α-chalcogeno acid chlorides, react with carboxyphosphoranes to give 4-phenylchalcogeno allenic ethyl esters in good yield (Scheme 61).[95] A highly selective three-component coupling



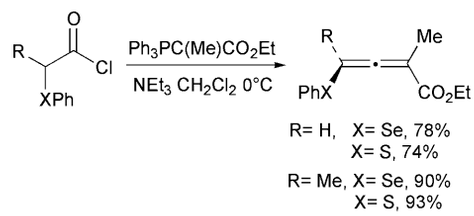
Scheme 58



Scheme 59

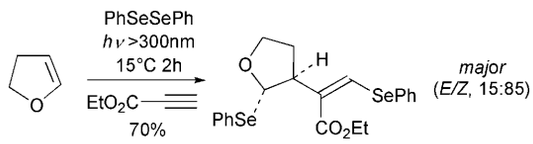


Scheme 60



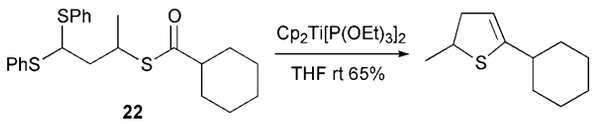
Scheme 61

of ethyl propiolate, alkenes, and diphenyl diselenide, initiated by visible-light irradiation, has been reported.[96] The reaction proceeds by the regioselective addition of the phenylseleno radical to the alkyne, followed by reaction of the resultant stabilised β-(phenylseleno)vinyl radical with the olefin (Scheme 62).[96]

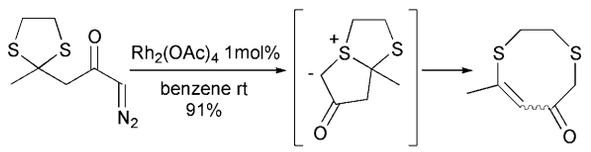


Scheme 62

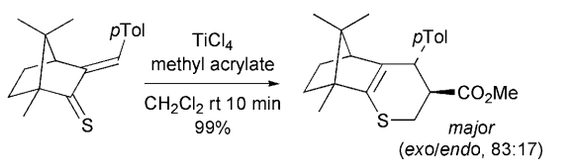
The intramolecular carbonyl olefination of thiol ester **22** with a low-valent titanium species gives 2,3-dihydrothiophene derivatives in good yield (Scheme 63).[97] Cyclic vinyl sulfides have also been prepared by the 3-, 4- and 5-carbon ring expansions of diazoketones bearing dithioacetal rings (Scheme 64).[98] The reactions proceed *via* intermediate bicyclic sulfonium ylides. The Diels–Alder reactions of enantiomerically pure camphor-derived thiabutadienes give dihydrothiopyran cycloadducts with high diastereoselectivity (Scheme 65).[99] Recent studies have shown 1-phenylseleno-2-(*p*-tolylsulfonyl)ethyne to be an excellent dienophile and dipolarophile.[100] Interestingly, the regiochemistry of Diels–Alder reactions of this species with substituted dienes was found to be different to those involving



Scheme 63

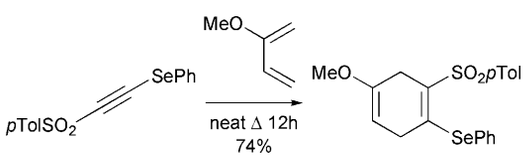


Scheme 64

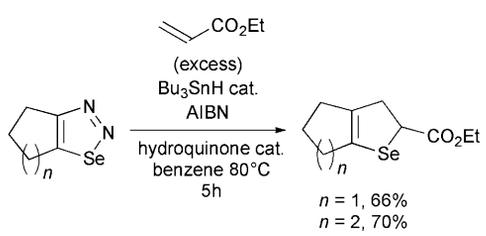


Scheme 65

simple acetylenic sulfones (Scheme 66).[100] The treatment of 1,2,3-selenadiazoles with a catalytic amount of tributyltin hydride and AIBN in the presence of an excess of olefin, gives dihydroselenophenes in good yield (Scheme 67).[101] The reaction proceeds *via* tributyltin radical-promoted denitrogenation to give a vinyl radical, which then adds to the olefin, followed by intramolecular cyclisation.

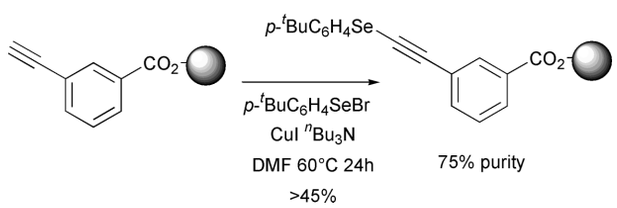


Scheme 66



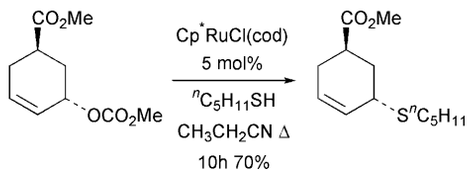
Scheme 67

Finally, the copper-mediated coupling of areneselenyl bromides with solid-supported terminal alkynes has been employed in the synthesis of selenium-containing acetylenic retinoids (Scheme 68).[102]

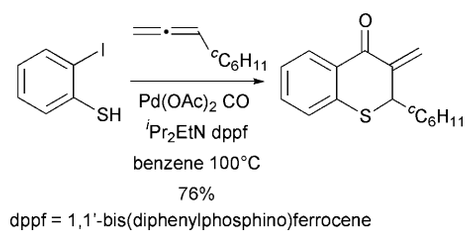


Scheme 68

2.2.4 Allylic, homoallylic and benzylic sulfides and selenides. The transition metal-catalysed reaction of allyl derivatives with nucleophiles is now a well established method in organic synthesis. However, the use of sulfur nucleophiles is often problematic due to catalyst poisoning. The first ruthenium-catalysed allylation of arene- and alkane-thiols has recently been reported.[103] Interestingly, the reaction proceeds efficiently with allylic alcohols in addition to allylic carbonates, trifluoroacetates and acetates. The reaction has been shown to proceed *via* a π-allylruthenium complex (Scheme 69).[103] The palladium-catalysed, carbonylative heteroannulation of iodothiophenols and allenes has been reported and proceeds to give thiochroman-4-one derivatives in good yield and with excellent regioselectivity (Scheme 70).[104] The first synthesis of α,β-acetylenic thioketones and aldehydes and their subsequent trapping with dienes to give allylic sulfide, cycloadducts, has been described.[105]

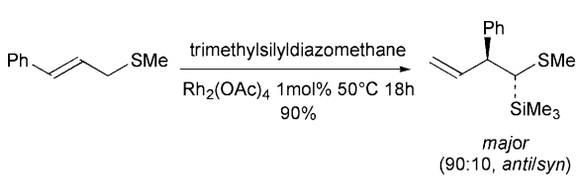


Scheme 69

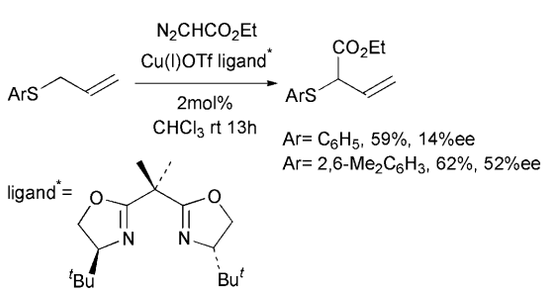


Scheme 70

The [2,3]-sigmatropic rearrangement of allylic sulfur ylides, prepared by the reaction of trimethylsilyldiazomethane with allyl sulfides in the presence of rhodium acetate under convenient reaction conditions, gives α-trimethylsilyl homoallylic sulfides with high diastereoselectivity (Scheme 71).[106] The use of a range of chiral metal catalysts gave only low enantioselectivities. An extensive study into the asymmetric copper-catalysed [2,3]-sigmatropic rearrangement of sulfur ylides derived from allylic sulfides has shown that enantioselectivities depend markedly on the steric and electronic characteristics of the substrate (Scheme 72).[107]

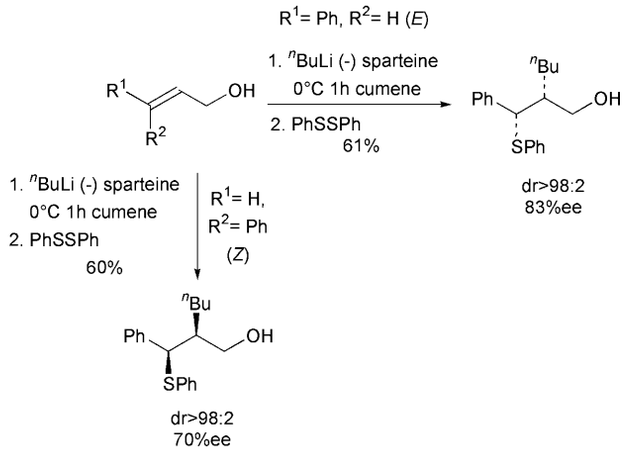


Scheme 71



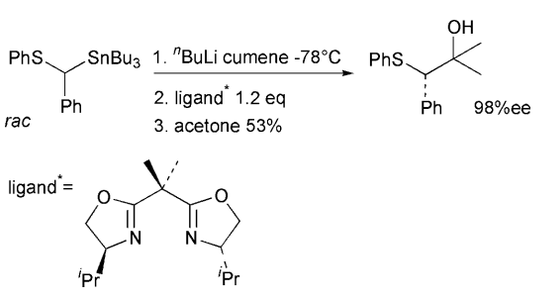
Scheme 72

The enantioselective carbolithiation of cinnamyl derivatives using a stoichiometric or catalytic amount of (−)-sparteine and primary or secondary alkyllithiums has been reported.[108] The enantiofacial selectivity in the formation of the intermediate benzylic organolithiums depends upon the stereochemistry of the initial double bond. Quenching with disulfide electrophiles gives benzylic sulfides in good yield and with high enantioselectivity (Scheme 73).[108] An alternative approach to

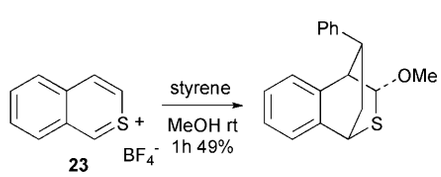


Scheme 73

enantiomerically enriched benzyl sulfides *via* α-lithio aryl benzyl sulfides has been described.[109] α-Lithiosulfides are configurationally unstable even at low temperatures. However, the use of a stoichiometric amount of a chiral bisoxazoline ligand has allowed excellent enantioselectivities to be achieved in the reactions of α-lithio aryl benzyl sulfides with electrophiles (Scheme 74). A racemic carbanion is initially formed which then undergoes either a dynamic kinetic or a dynamic thermodynamic resolution.[109] The 2-benzothiopyrylium salt **23** undergoes a [4 + 2]-type cycloaddition on treatment with alkenes to give sulfur-containing heterocycles (Scheme 75).[110] 2-Halobenzyl alk-1-ynyl sulfides undergo an unusual cyclisation under basic conditions to give dihydrothiophenes (Scheme 76).[111] Interestingly, the halide substituent appears to be crucial to the success of the reaction. The 6-*endo* radical cyclisation of benzylic sulfide **24** proceeds efficiently to give cyclic sulfide **25** in good yield (Scheme 77).[112] The mode of cyclisation is controlled by the stabilising effect of sulfur on the intermediate radical. Allylic, propargylic, benzylic, and alkynyl bromides react with dialkyl and diaryl diselenides in the presence of $SnCl_2$ and catalytic copper halides to give the corresponding unsymmetrical selenides in good yield (Scheme 78).[113] The reaction is thought to involve the formation of a dicopper(selenolate) intermediate. Allylic selenides have been prepared by the reduction of diaryl and dialkyl diselenides with cadmium(II) chloride and samarium metal, followed by the addition of allylic bromides.[114]



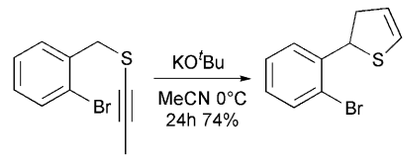
Scheme 74



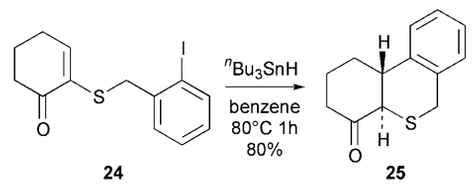
Scheme 75

3 Synthesis of sulfoxides and selenoxides

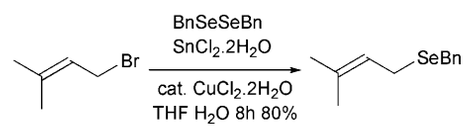
As in previous reviews in this series, this section is dominated by methods for the preparation of sulfoxides. There are, however,



Scheme 76

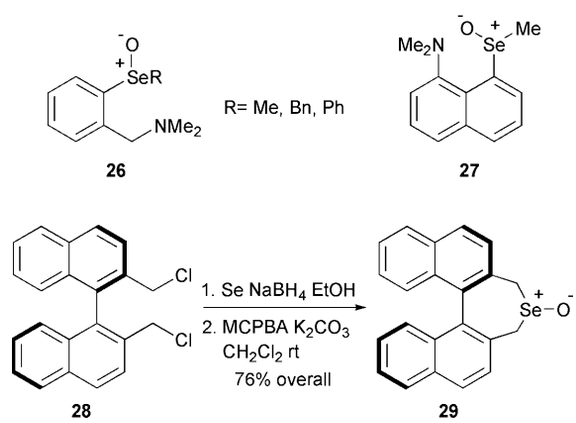


Scheme 77



Scheme 78

some reports detailing the synthesis of selenoxides. The chemistry of thiophene and selenophene 1-oxides and 1,1-dioxides, including routes to such compounds, has recently been reviewed.[115] Racemic alkyl aryl selenoxides **26**, configurationally stabilised by the intramolecular coordination of an amino group to the selenium atom, have been resolved by chiral chromatography.[116] This is the first reported isolation of enantiomerically pure aryl alkyl selenoxides. A similar resolution of selenoxide **27** has also been described.[117] Finally, enantiomerically pure binaphthyl-based selenoxide **29** has been prepared by treatment of the dichloride **28** with sodium selenide followed by oxidation under standard conditions (Scheme 79).[118]



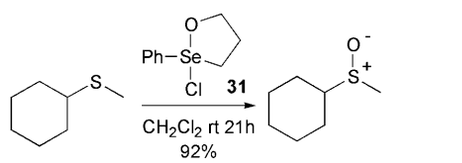
Scheme 79

A new method for the determination of the absolute stereochemistry of sulfoxides has been developed and involves the preparation of diastereoisomeric *N*-(methoxyphenylacetyl)-sulfoximides.[119]

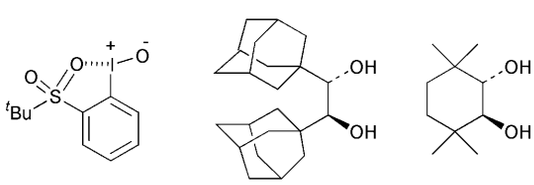
3.1 Oxidation of sulfides and selenides. *3.1.1 Achiral oxidising systems.* A recent review of metal-catalysed oxidations includes a discussion of sulfoxidations.[120] Mechanistic studies into the oxidation of sulfides using oxo(salen)chromium(V) complexes have been described.[121] The mechanisms of sulfoxidations catalysed by high-valent intermediates of heme enzymes have also been investigated.[122] The catalytic effect of Lewis acids on the permanganate oxidation of sulfides has been the subject of a recent kinetic study.[123] Silica gel and alumina

have been used to mediate the oxidation of sulfides and sulfoxides using *tert*-butyl hydroperoxide or Oxone®.[124]

Benzyltriphenylphosphonium dichromate[10] and iodosylarene **30**,[125] are new, general reagents for the oxidation of dialkyl, aryl alkyl and dialkyl sulfides. The sulfoxidation of dialkyl and aryl alkyl sulfides has been reported using several new systems including urea–hydrogen peroxide complex under solvent-free conditions;[126] a hexamethylenetetraamine–bromine complex;[127] and trimethylsilyl chloride with KO_2.[128] In the latter report, the sulfoxidation is proposed to occur *via* the generation of a trimethylsilylperoxide radical. The reaction can be carried out at low temperature, with little over-oxidation to the sulfone and with good chemoselectivity.[128] Phenylselenurane **31** has been found to selectively oxidise dialkyl sulfides to sulfoxides under mild conditions (Scheme 80).[129] Aryl alkyl sulfides remain unchanged by the reagent, presumably due to electronic factors.

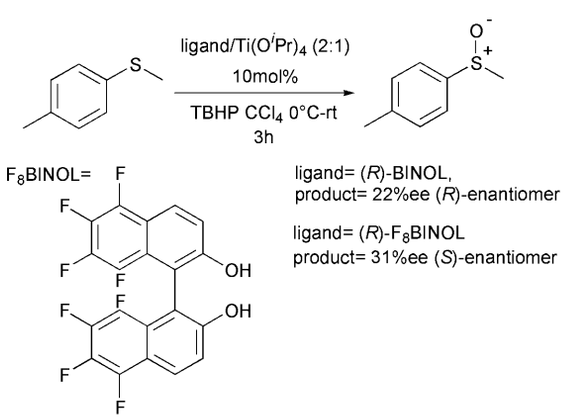


Scheme 80



30 **32** **33**

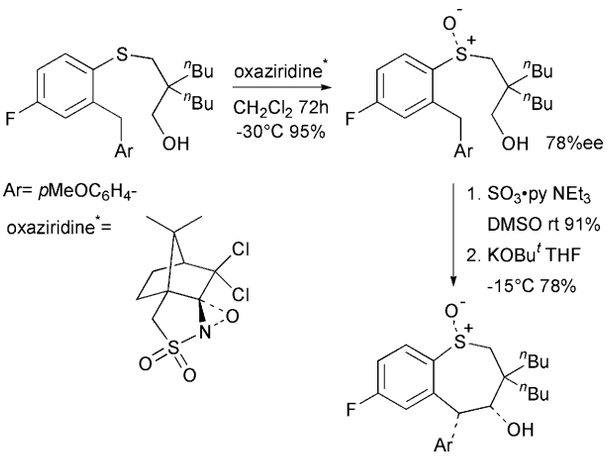
3.1.2 Stereoselective oxidising systems. Several new studies on 'classic' titanium-based systems for the asymmetric oxidation of sulfides to sulfoxides have been reported. F_8BINOL is an interesting BINOL derivative, showing increased configurational stability and possessing significantly more acidic hydroxy donor groups. Enantiomerically pure F_8BINOL has been found to display reversed selectivity in some titanium(IV)-mediated sulfoxidations when compared to analogous systems derived from BINOL (Scheme 81).[130] The nature of previously described titanium(IV) sulfoxidation catalysts derived from titanium(IV) isopropoxide and C_3-symmetric tris(hydroxyalky)-amine ligands has been probed using NMR techniques and electrospray ionisation mass spectrometry.[131] New C_2-symmetrical enantiomerically pure diols, **32** and **33**, have been prepared and screened as ligands in the titanium(IV)-mediated asymmetric oxidation of aryl alkyl sulfides.[132] The new ligands were found to be much less effective than previously employed diol ligands.



Scheme 81

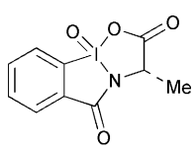
The vanadium-mediated asymmetric oxidation of 1,2-bis-(arylsulfanyl)ethanes using hydrogen peroxide and an enantiomerically pure Schiff-base ligand has been reported.[133] Although mixtures were obtained, C_2-symmetrical bis-(sulfoxide) products were obtained in reasonable yield and often in high enantiomeric excess.[133]

An enantioselective approach to pharmaceutically important benzothiepines has been developed which involves asymmetric sulfoxidation of a precursor aryl alkyl sulfide using Davis' conditions (Scheme 82).[134] The sulfoxide stereochemistry is then used to control the stereochemistry of the key cyclisation step. A full account of the development of catalytic asymmetric sulfoxidation using enantiomerically pure camphorsulfonyl imines and hydrogen peroxide has appeared.[135] This sulfoxidation process is currently believed to proceed *via* oxygen-transfer to the prochiral sulfide from an α-hydroperoxyamine intermediate.



Scheme 82

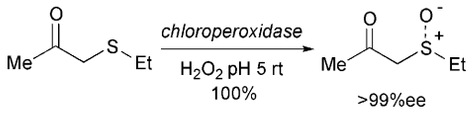
The asymmetric sulfoxidation of aryl alkyl sulfides in water using iodoxybenzene, magnesium bromide and (+)-dibenzoyl-D-tartaric acid gives product sulfoxides in moderate enantiomeric excess.[136] Enantiomerically pure amino acid-derived benziodazole oxides, such as **34**, have been found to oxidise prochiral sulfides in high chemical yield but with low enantioselectivity.[137]



34

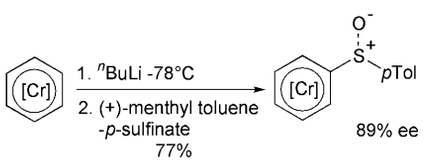
Several new developments in the area of enzymatic sulfoxidation have been described. The asymmetric sulfoxidation of thioanisole using peroxidase–glucose oxidase bienzymatic systems has been reported.[138] This approach takes advantage of the *in situ* generation of H_2O_2 from glucose and oxygen by glucose oxidase. A recent report details studies on sulfoxidation using vanadium bromoperoxidase from *Ascophyllum nodosum*.[139] An enzymatic sulfoxidation approach has recently been employed in the synthesis of all the stereoisomers of methionine and ethionine sulfoxides.[140] Finally, the asymmetric sulfoxidation of β-sulfanyl carbonyl compounds with chloroperoxidase proceeds in excellent yield and with high enantioselectivities for substrates bearing small alkyl substituents (Scheme 83).[141]

3.2 Non-oxidative routes to sulfoxides and selenoxides. The reaction of sulfinyl chlorides with *N*-methylephedrine gives diastereoisomeric sulfinates in varying diastereoisomeric ratios.[142] After purification, these sulfinates react with Grignard

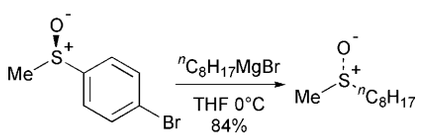


Scheme 83

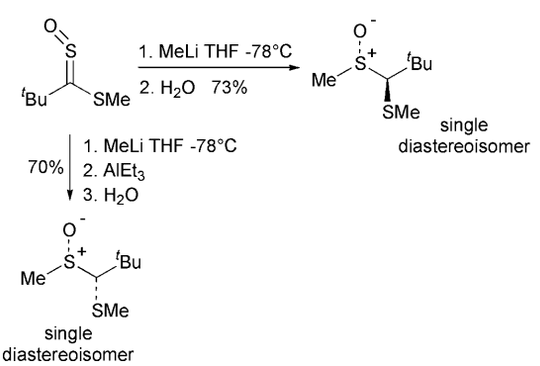
reagents in Andersen-type reactions to give enantiomerically enriched sulfoxides.[142] The preparation of sulfinyl-substituted arene–chromium tricarbonyl complexes *via* the reaction of the anion derived from benzene–chromium tricarbonyl and enantiomerically pure sulfinyl transfer reagents has been reported (Scheme 84).[143] The displacement of substituted benzene anions from aryl alkyl sulfoxides using Grignard reagents proceeds with clean inversion at sulfur.[144] The approach has been used in a convenient route to enantiomerically enriched alkyl methyl sulfoxides (Scheme 85). The addition of alkyllithiums to aliphatic sulfines generates lithiated α-sulfanyl carbanions which can be protonated with high diastereoselectivity (Scheme 86).[145] Interestingly, addition of triethylaluminium is thought to generate an aluminium 'ate' complex with inversion of configuration at the α-carbon. Subsequent quenching gives the opposite diastereoisomer with complete selectivity.[145]



Scheme 84



Scheme 85

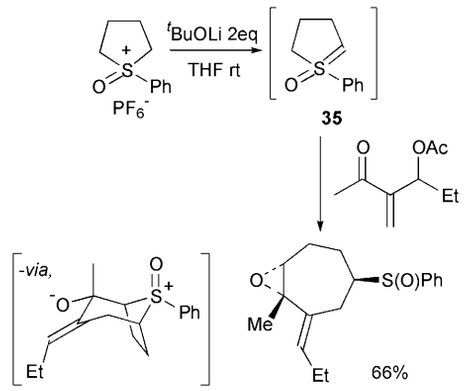


Scheme 86

Aryl methyl sulfoxides have been resolved by formation of inclusion compounds with dehydrocholic acid.[146] In an interesting study, a variety of sulfoxides have been prepared essentially enantiomerically pure by kinetic resolution using an electrochemical–enzymatic system employing DMSO-reductase.[147] Sulfoxides are deoxygenated with high enantioselectivity by the enzyme. The enzyme is then re-reduced by an electron carrier, which in turn is recycled at the electrode surface.[147]

The reaction of cyclic oxosulfonium ylide **35** with Baylis–Hillman derivatives gives sulfoxide-containing cycloheptene oxides *via* an interesting sequential process involving Michael addition, acetate elimination and epoxide formation (Scheme 87).[148]

Finally, the preparation of symmetrical diaryl sulfoxides

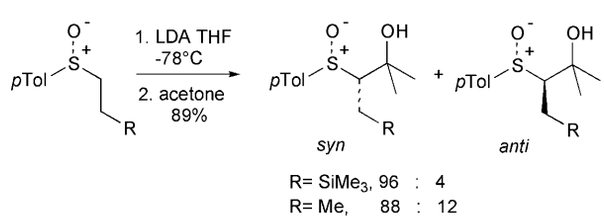


Scheme 87

from the reaction of thionyl chloride with arenes, catalysed by trifluoromethanesulfonic acid, has been reported.[149]

3.2.1 Functionalised sulfoxides and selenoxides. Studies on the synthesis of episulfoxides by rhodium-catalysed 'SO' transfer from (*E*)-stilbene episulfoxide to strained alkenes have been described in full.[150]

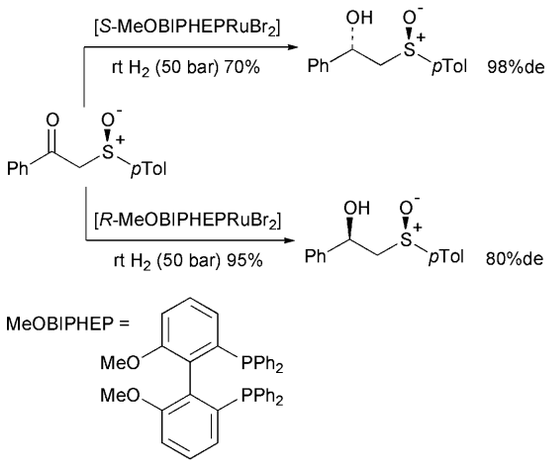
β-Hydroxy sulfoxides have been prepared in a one-pot procedure from cyclic epoxides by ring-opening with thiols in hexafluoropropan-2-ol, and subsequent *in situ* oxidation.[151] Interestingly, the epoxide substrates need no additional protic or Lewis acid activation. α-Sulfinyl carbanions derived from β-silylethyl sulfoxides react with electrophiles with improved *syn*-selectivity when compared to the selectivities obtained using unfunctionalised α-sulfinyl anions (Scheme 88).[152] The silicon group is thought to interact with the carbonyl group of the electrophile, stabilising the transition state leading to the *syn* diastereoisomer. Similar interactions have been invoked in the conjugate addition reactions of these anions to α,β-unsaturated esters.[153] The ruthenium-catalysed hydrogenation of enantiomerically pure β-keto sulfoxides gives β-hydroxy sulfoxides with only moderate diastereoselectivity.[154] When chiral ruthenium catalysts were used, the diastereoselectivity was much higher and was found to be independent of the stereochemistry at sulfur (Scheme 89).[154] Enantiomerically pure β-keto sulfoxides have been prepared by the addition of the α-sulfinyl anion derived from (*R*)-methyl *p*-tolyl sulfoxide to nitriles.[155]



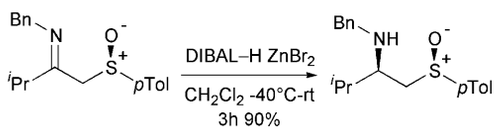
Scheme 88

The reduction of enantiomerically pure α-sulfinyl ketimines with DIBAL-H and zinc bromide proceeds with essentially complete diastereoselectivity to give *syn*-β-amino sulfoxides in high yield (Scheme 90).[156] A $LiClO_4$-mediated one-pot synthesis of β-amino sulfoxides and sulfones has been reported which involves the addition of α-lithiated sulfoxides and sulfones to *in situ* prepared iminium ions (Scheme 91).[157] In a related process, enantiomerically pure β-amino sulfoxides have been prepared by a double asymmetric induction process involving the condensation of enantiomerically pure α-lithio sulfoxides with enantiopure *N*-sulfinylimines.[158]

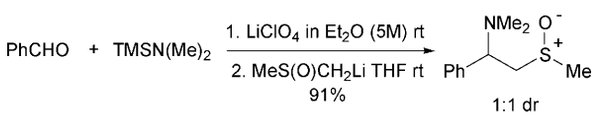
The sulfoxide moiety is one of the most important stereocontrol elements in organic synthesis. The previously reported sulfoxide-directed stepwise reduction of a β,δ-dioxo sulfoxide has been employed in the synthesis of (−)-colletol and (+)-colletodiol.[159] The *tert*-butylsulfinyl group has been used as an efficient stereocontrol element in Pauson–Khand reactions



Scheme 89

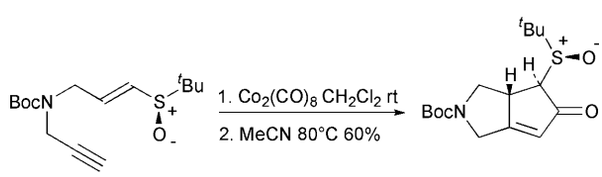


Scheme 90

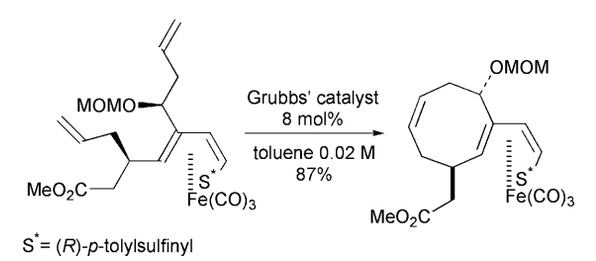


Scheme 91

(Scheme 92).[160] The olefin geometry in the starting vinyl sulfoxide appears to have little effect on the stereochemical outcome of the reaction and hence olefin mixtures have been used.[160] Ring-closing metathesis of enantiomerically pure 1-sulfinyl iron(0) diene complexes bearing two appropriate olefinic tethers has allowed the synthesis of 6-, 7-, 8- and 9-membered carbocycles in excellent yields (Scheme 93).[161] It is as yet unclear what role the sulfinyl-diene iron tricarbonyl moiety plays in the cyclisation reaction, but it would appear likely that it acts as a conformational restraint.

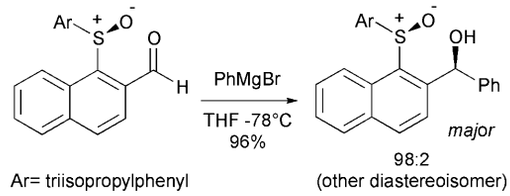


Scheme 92



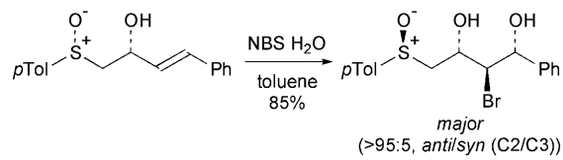
Scheme 93

The addition of organometallic nucleophiles to 1-[(2,4,6-triisopropylphenyl)sulfinyl]-2-naphthaldehyde proceeds with high diastereoselectivity through a non-chelated transition state (Scheme 94).[162] The high selectivities appear to arise from the tendency of the sulfoxide substrate to exist as one major rotamer about the C–S bond. Bromohydrin formation from β-hydroxy-γ,δ-unsaturated sulfoxides has been shown to proceed stereoselectively due to participation of the sulfoxide



Scheme 94

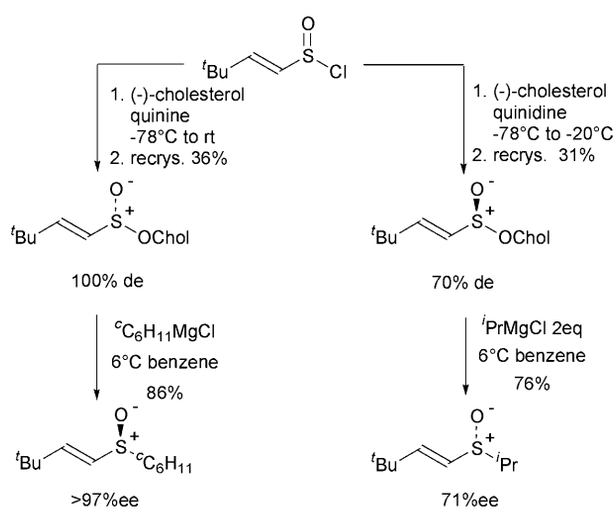
moiety.[163] Opening of the intermediate bromonium ion by the sulfoxide oxygen, followed by hydrolysis of the cyclic sulfoxonium intermediate proceeds with clean inversion at sulfur (Scheme 95).[163]



Scheme 95

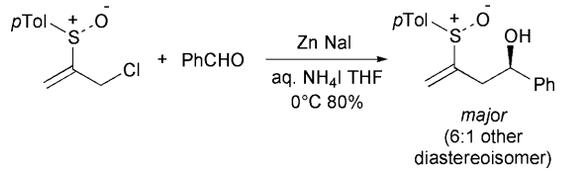
Finally, a full discussion of the use of enantiomerically pure vinyl sulfoxides as temporary stereocontrol elements in 5-*exo*-*trig* radical cyclisation–elimination reactions has appeared.[164]

3.2.2 Unsaturated sulfoxides and selenoxides. The reaction of (*E*)-3,3-dimethylbut-1-enylsulfinyl chloride and (−)-cholesterol in the presence of quinine or quinidine allows access to either diastereoisomeric sulfinate ester *via* a combination of kinetic resolution and fractional recrystallisation (Scheme 96).[165] Subsequent reaction with Grignard reagents in an Andersen-type procedure gives the expected enantiomerically enriched vinyl sulfoxides. The procedure is, however, far from general, as only a single α,β-unsaturated sulfinyl chloride has been used.[165]

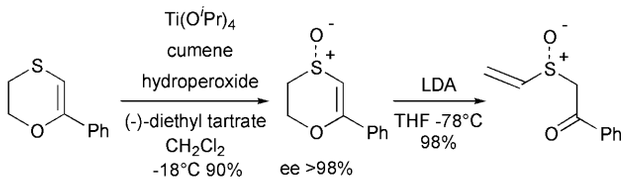


Scheme 96

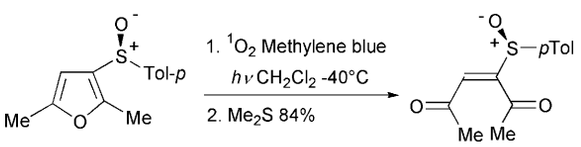
The allylation of aldehydes under aqueous Barbier conditions using an enantiomerically pure 2-sulfinylallyl chloride gives β-hydroxy vinyl sulfoxides with moderate diastereoselectivity (Scheme 97).[166] Enantiomerically pure α-vinylsulfinyl ketones have been prepared by a novel route involving the asymmetric sulfoxidation of substituted oxathiines (Scheme 98).[167] The resultant enantiomerically enriched sulfoxides then undergo efficient ring-cleavage on treatment with base to give the product β-keto vinyl sulfoxides.[167] The chemoselective, and highly efficient photooxidation of enantiomerically pure 3-(*p*-tolylsulfinyl)furans gives the 'unmasked' 1,4-dicarbonyl compounds in good yield (Scheme 99).[168] Cyclic vinyl sulfoxides are produced from the Diels–Alder reactions of sulfinyldienes.



Scheme 97



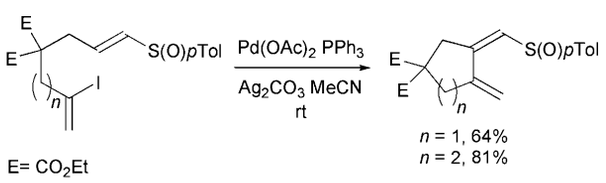
Scheme 98



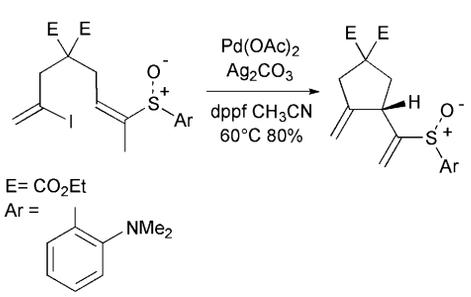
Scheme 99

The hetero-Diels–Alder reaction of enantiomerically pure sulfinyldienes with thioketones gives thiopyran cycloadducts with complete regioselectivity but poor facial selectivity.[169]

1-Sulfinylalka-1,3-dienes have been prepared by the intramolecular Heck reactions of vinyl sulfoxides bearing tethered vinyl iodides (Scheme 100).[170] The 2-(*N*,*N*-dimethylamino)-phenylsulfinyl group has been employed as a highly effective stereocontrol element in related intramolecular Heck reactions to give vinyl sulfoxides (Scheme 101).[171] The palladium-catalysed, sequential ring-opening–cyclisation of enantiomerically pure (β-sulfinyl)vinylcyclopropane derivative **36** and acrylonitrile gives the functionalised cyclopentane derivative **37** in moderate yield and diastereoisomeric excess (Scheme 102).[172] The intramolecular alkylation of enantiomerically pure α-lithio vinyl sulfoxides gives cyclic vinyl sulfoxides in good yield and with no racemisation at sulfur (Scheme 103).[173] Interestingly, the corresponding (*Z*)-vinyl sulfoxides give the same products *via* rapid double-bond isomerisation, again with no racemisation at sulfur.[173]

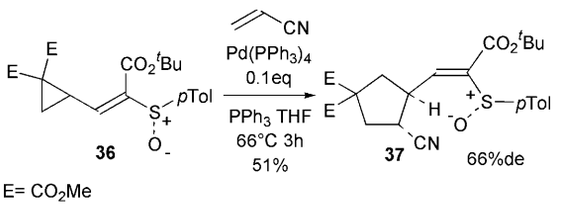


Scheme 100

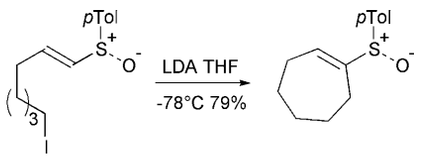


Scheme 101

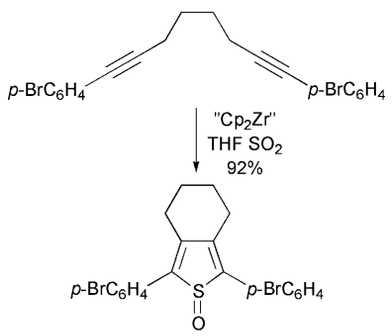
A new method for the synthesis of thiophene 1-oxides has been reported which involves the reaction of zirconocenes, formed *in situ* from 1,6-diynes, with sulfur dioxide (Scheme 104).[174]



Scheme 102

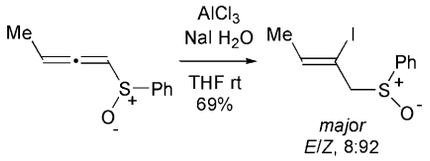


Scheme 103



Scheme 104

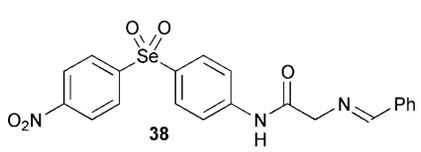
Finally, the Lewis acid-mediated hydrohalogenation of allenic sulfoxides in the presence of water gives 2-haloallyl sulfoxides in good yield (Scheme 105).[175]



Scheme 105

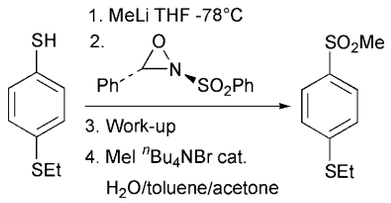
4 Synthesis of sulfones and selenones

The chemistry of selenones continues to receive little attention although a recent study has detailed the preparation of diaryl selenones **38**, and their antibacterial properties have been evaluated.[176]



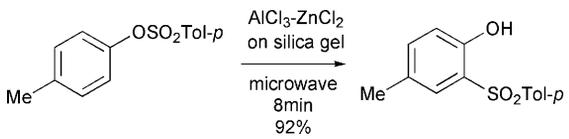
4.1 Oxidation of sulfides and sulfoxides. The oxidation of diaryl and dialkyl sulfoxides to the corresponding sulfones using hydrogen peroxide and methyltrioxorhenium as catalyst has been the subject of a kinetic investigation.[177]

4.2 Non-oxidative routes to sulfones. *4.2.1 Simple sulfones.* The oxidation of aryl thiolates using Davis' benzaldehyde-derived oxaziridine gives sulfinate anions which can be alkylated to give aryl sulfones.[178] In several cases, the oxidation shows surprising chemoselectivity (Scheme 106). The thia-Fries rearrangement of arylsulfonates typically requires extremely forcing conditions and thus has found few applications. New conditions employing a supported $AlCl_3$–$ZnCl_2$ mixture in the absence of solvent and under microwave irradiation give high



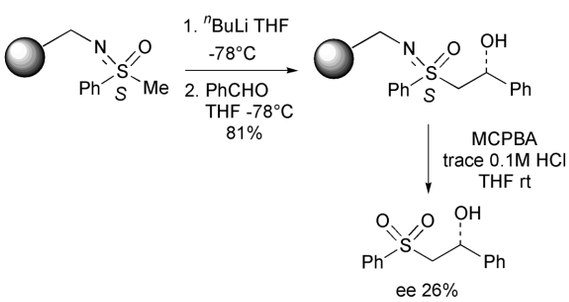
Scheme 106

yields of aryl sulfones after short reaction times (Scheme 107).[179] A new, catalytic reagent system for the arylsulfonylation of arenes has been developed and employs bismuth(III) chloride and trifluoromethanesulfonic acid.[180]

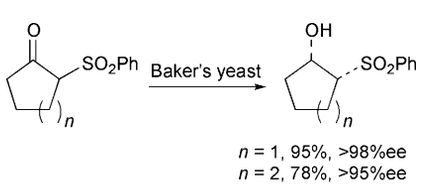


Scheme 107

4.2.2 Functionalised sulfones. A sulfoximide linker has recently been developed for the solid-phase synthesis of sulfones.[181] Oxidation of the sulfoximide linker with MCPBA results in cleavage from the support with subsequent generation of the corresponding sulfone. The methodology has been applied to the synthesis of β-hydroxy sulfones (Scheme 108). Efficient dynamic kinetic resolution of 2-phenylsulfonylcyclopentanone and -cyclohexanone has been reported using baker's yeast reduction (Scheme 109).[182] The approach proved less efficient for larger ring derivatives. The copper-catalysed addition of Grignard reagents to enantiomerically pure vinylsulfonyl dioxazaborocanes, such as **39**, has been reported.[183] Subsequent oxidative cleavage of the carbon–boron bond in the adducts gives β-hydroxy sulfones in high enantiomeric excess (Scheme 110).



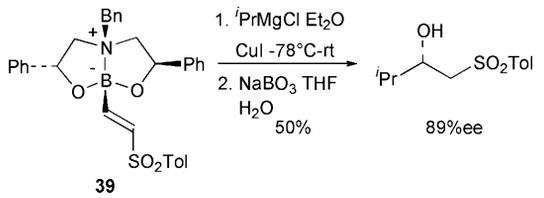
Scheme 108



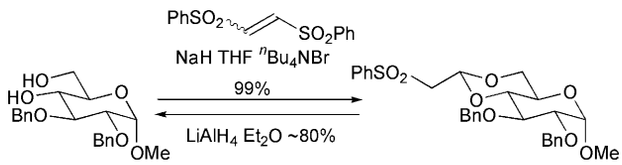
Scheme 109

Phenylsulfonylethylidene (PSE) acetals have recently been reported as a new protecting group for diols in carbohydrate chemistry.[184] The group is introduced by an addition–elimination–addition to 1,2-bis(sulfonyl)ethene (Scheme 111).

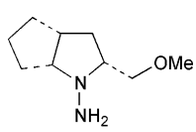
A full report of studies into the synthesis of β-amino sulfones by the aza-Michael addition of enantiopure ammonia equivalents, such as **40**, to vinyl sulfones, has appeared.[185] After reductive cleavage of the stereocontrol element, subsequent α-alkylation gives α-substituted β-amino sulfones. The addition



Scheme 110

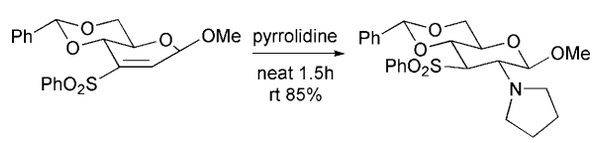


Scheme 111



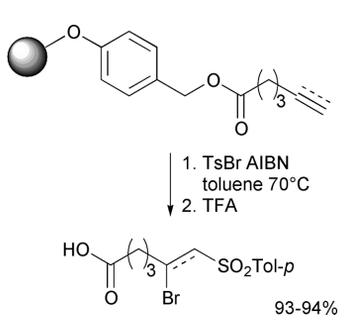
40

of amines to carbohydrate-derived vinyl sulfones has been reported and may provide a useful approach to the synthesis of deoxyaminosugars (Scheme 112).[186]



Scheme 112

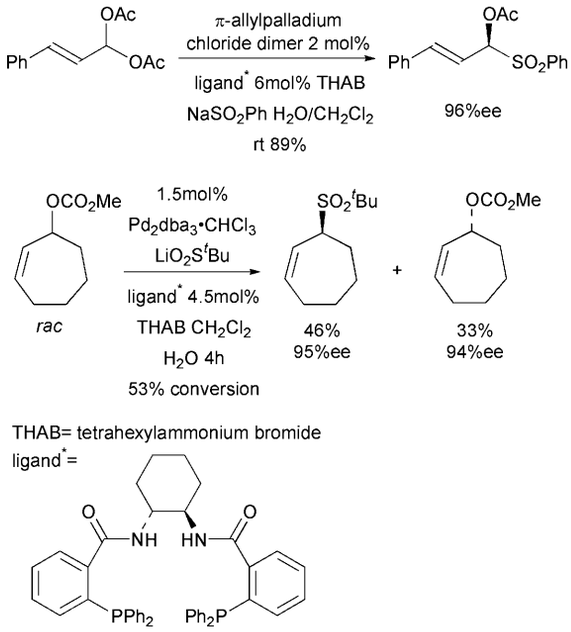
The successful addition of toluenesulfonyl radicals to solid-supported, unactivated alkenes and alkynes has recently been reported.[187] The method provides a convenient approach to β-bromo-alkyl and -alkenyl sulfones (Scheme 113).



Scheme 113

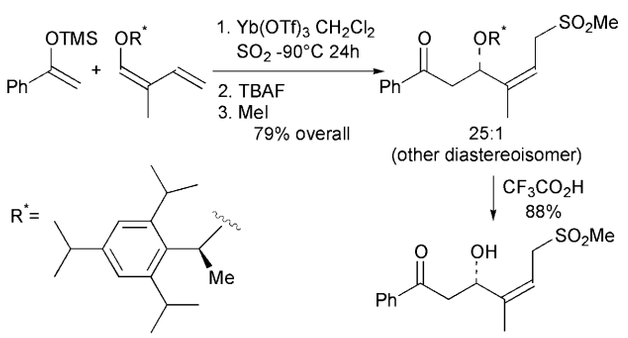
4.2.3 Allylic, homoallylic, benzylic and vinylic sulfones. Palladium-catalysed asymmetric allylic alkylation is now a well established method in organic synthesis. Recent studies employing sulfinate nucleophiles have been described. The palladium-catalysed asymmetric allylic alkylation reaction employing allylic geminal diesters and sulfinate nucleophiles gives α-acetoxy allylic sulfones in high enantiomeric excess and excellent yield (Scheme 114).[188] The product α-acetoxy sulfones are useful 'chiral aldehyde' equivalents. The palladium-mediated kinetic resolution of racemic cyclic and acyclic allylic carbonates with sulfur nucleophiles has also been reported.[189] The methodology allows the synthesis of allylic sulfones and sulfides in high enantiomeric excess (also Scheme 114).

An asymmetric version of the previously reported four component coupling of 1-alkoxyalka-1,3-dienes, silyl enol ethers, sulfur dioxide and alkyl iodides has been described.[190] The process employs an auxiliary-bearing diene and gives functionalised allylic sulfones with good selectivity (Scheme

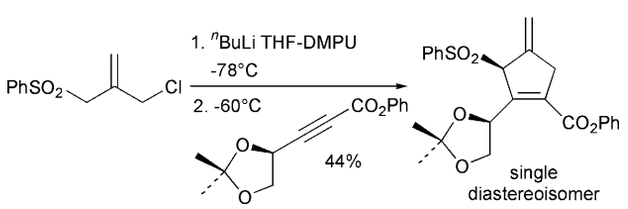


Scheme 114

115). A Michael-initiated cyclisation reaction employing 2-(chloromethyl)-3-phenylsulfonylprop-1-ene and γ-alkoxy-α,β-alkynoates has been reported (Scheme 116).[191] The γ-alkoxy group was found to be necessary for successful cyclisation. The 1,3-asymmetric induction in the Michael addition arises from a preferred facial approach arising in part from an interaction between the lithium cation and the phenyl group of the ester.[191] A solid-phase route to cyclobutylidenes has been reported and involves the α,α-dialkylation of a polymer-bound phenyl allyl sulfone with 2-chloromethyloxirane (Scheme 117).[192] The product cyclobutylidenes were obtained from the resin using a palladium-mediated S_N2' nucleophilic displacement of the polymeric phenyl sulfinate group.[192]



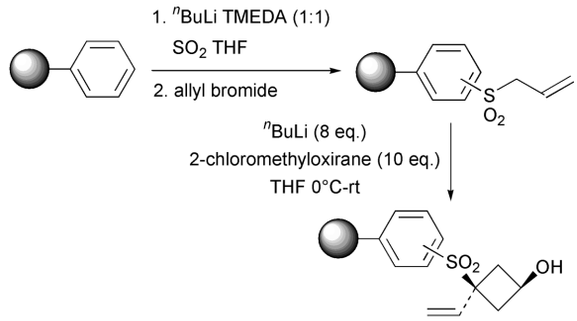
Scheme 115



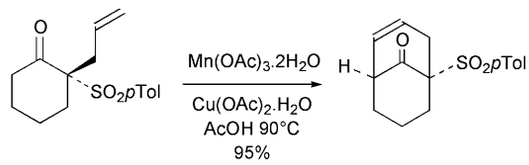
Scheme 116

The manganese(III)-mediated oxidative radical cyclisations of enantiomerically enriched 2-allyl-2-(*p*-tolylsulfonyl)cyclohexanones give bicyclic homoallylic sulfones in excellent yield (Scheme 118).[193]

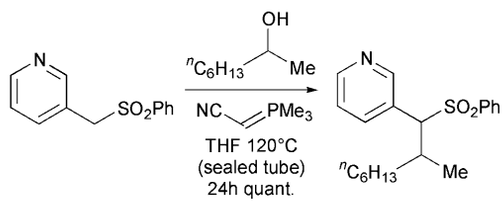
Arylmethyl phenyl sulfones have been used successfully as carbon nucleophiles in Mitsunobu-type alkylations using new Mitsunobu reagents such as cyanomethylene trimethylphosphorane (Scheme 119).[194]



Scheme 117

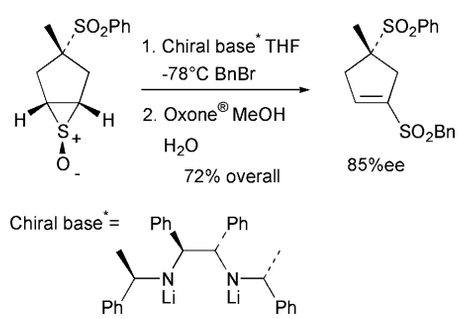


Scheme 118



Scheme 119

The enantioselective rearrangement of ring-fused episulfoxides mediated by chiral lithium amide bases has been reported.[150] After rearrangement and oxidation at sulfur, vinyl sulfone products are obtained in high enantiomeric excess (Scheme 120). Unfortunately, as the authors point out, difficulties in accessing episulfoxide substrates are likely to limit the utility of the methodology for the immediate future.[150]



Scheme 120

5 Conclusion

Advances in the synthesis of organosulfur and selenium compounds continue to be made at an impressive pace. The development of stoichiometric and catalytic metal-mediated reactions is one particular area that is providing efficient, new approaches to important compound types. Significant progress has also been made in the development of new and improved asymmetric methods for the synthesis of organosulfur and selenium compounds. Perhaps one of the most interesting current areas of research in this area, however, involves the often quite ingenious application of 'classical' organosulfur and selenium chemistry to problems in relatively new areas such as solid-phase synthesis.

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