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Sulfur is More Than the Fat Brother of Oxygen. An Overview of Organosulfur Chemistry

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Abstract A survey of the structure and synthetic applications of organosulfur compounds is given. The emphasis is on the key features of organosulfur chemistry.

Keywords Structure · Reactivity · Chirality · Reagents

Abbreviations

LG	leaving group
LDBB	lithiated 4,4′-di-*tert*-butyl-biphenyl
LDMAN	lithiated 1-dimethylaminonaphthaline
MO	molecular orbital
TBS	*tert*-butyl(dimethyl)silyl
TOMAC	methyl(trioctyl)ammonium chloride

1 Introduction

Replacing oxygen by sulfur in a functional group does not just correspond to a small step in the periodic table, but may well lead to another world of chemistry. The differences in chemical reactivity and stability can be explained by the change in atomic radii, in electronegativity, and in polarizability between oxygen and sulfur. On the other hand, as VIA (group 16) elements oxygen and sulfur have the same number of outer-shell electrons and so there are also many similarities.

The difference in covalent radii of oxygen (70.2 pm) and sulfur (104.9 pm) clearly shows for carbon as bonding partner (covalent radius 77.2 pm) that an organosulfur compound will have a weaker σ bond and also overlap of p_z orbitals in a π bond will be less efficient in a thiocarbonyl as compared to a carbonyl group [1, 2]. In fact, the dissociation energy of the single bond of carbon with oxygen (355–380 kJ/mol) [3] and of the C – S single bond (255 kJ/mol) [4] quantitatively reflects the change in bonding efficiency. The analogous situation is seen for the dissociation energies of the double bond of carbon with oxygen (678.3 kJ/mol) and with sulfur (377 kJ/mol) [5, 6].

The electronegativities are a reflection of electron affinities, ionization potentials and bond energies. Table 1 shows the pertinent data for carbon, oxygen and sulfur. The data clearly demonstrate the familiar situation that in a carbon–oxygen bond the polarization will be with a partial electropositive charge on carbon and with a partial negative charge on oxygen. In contrast, a comparison of the data as given by different methods gives no clear picture of the polarization of the C – S bond. However, the data of the Sanderson scale of electronegativities are of particular interest as this scale is based on the "compactness" of an atom's electron cloud and so represents the polarizability of the atom [2]. This is obviously quite pronounced for sulfur and is an important feature to account for charge stabilization on adjacent centers and for leaving group abilities.

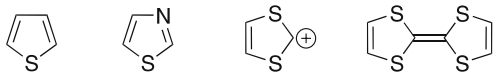
Whatever the direction of the polarization of a C – S bond may be, the polarization is not pronounced and the ionic character of organosulfur compounds is lessened as compared to their oxygen congeners. Therefore, hy-

Table 1 Electronegativities of carbon, oxygen and sulfur on different scales [2, 7]

Element	Pauling	Mulliken	Allred and Rochow	Sanderson
C	2.50	2.63	2.50	2.746
O	3.44	3.17	3.17	3.654
S	2.58	2.41	2.44	2.957

drogen bonding is much less important for sulfur compounds, for example in contrast to alcohols the sulfur in thiols is poor at hydrogen bonding. On the other hand, this makes thiocarboxylic acids and thiols stronger acids than their oxygen analogues.

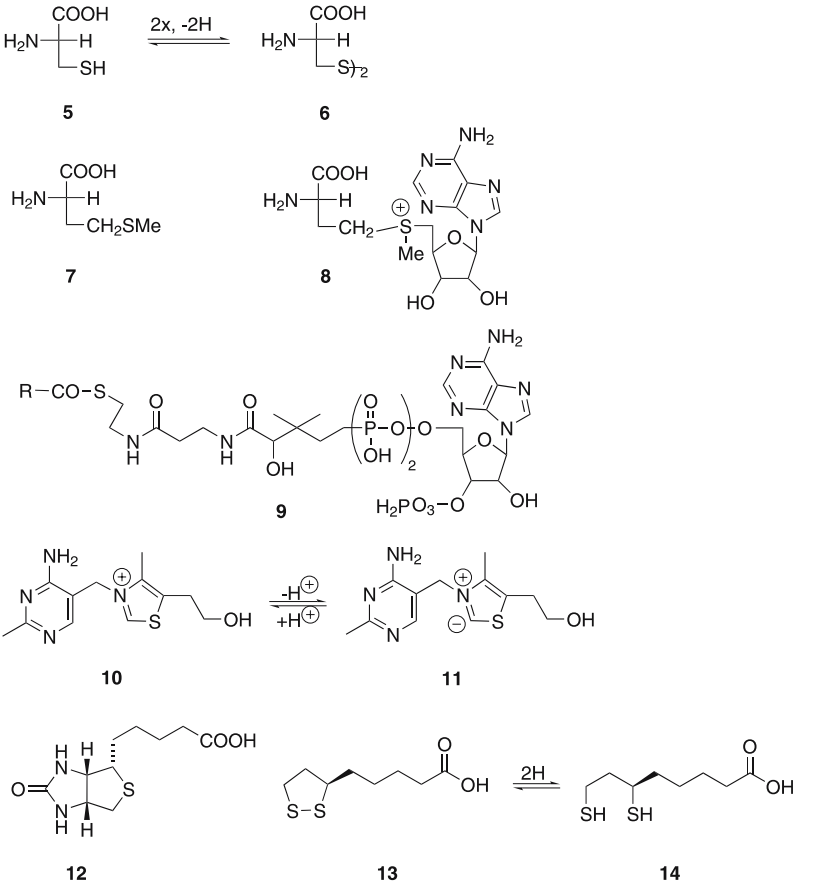
Sulfur plays an important role as a ring member in hetarenes. Actually, thiophene **1** (resonance energy 113 kJ/mol) is less aromatic than benzene, but, interestingly, more aromatic than its oxygen congener furan (resonance energy 75 kJ/mol) [8, 9]. This can be understood in terms of the low electronegativity of sulfur which allows more efficient integration of the nonbonding electron pair into the aromatic system. An explanation involving the d-orbitals of sulfur appears not to be in line with the recent experimental evidence and with MO calculations [8, 9]. Thiazole **2** is another sulfur-containing hetarene with a rich chemistry [10]. Also 1,3-dithiolium salts **3** are aromatic and are of particular interest as starting materials for tetrathiafulvalenes **4** which are superior electron-donating components for charge-transfer complexes and salts with high electrical conductivity ("organic metals") [11–13] (Scheme 1).



1 **2** **3** **4**

Scheme 1 Aromatic sulfur-containing hetarenes and the related tetrathiafulvalene system

Also the importance of organosulfur compounds for the chemistry of life should be noted. Key examples include amino acids such as cysteine **5** with its dehydrogenation product cystine **6** and methionine **7**, the thioester acetyl coenzyme A **9** (R = CH_3), thiamine (Vitamin B_1) **10**, biotin **12** (Vitamin H) or α-lipoic acid **13**. Thus, amino acid **7**, coupled to adenosine as in **8** ("*S*-adenosylmethionine"), is nature's iodomethane or diazomethane equivalent for methyl transfer reactions. Similarly, what an acyl chloride or anhydride is in an organic laboratory, is acyl coenzyme A **9** for acyl transfer reactions in nature. Thiamine **10** gives an example for the use of umpolung chemistry in nature when deprotonation on C-2 of the heteroaromatic ring converts an electrophilic into a nucleophilic center as in **11**. Lipoic acid **13** is involved in biochemical redox chemistry taking up hydrogen from an alcohol to give a carbonyl product [14–16] (Scheme 2).

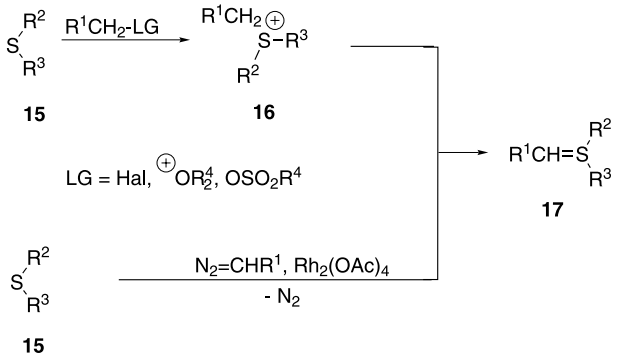


Scheme 2 Sulfur-containing biomolecules

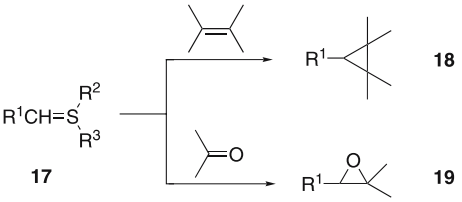
2 Sulfur Ylides

Oxonium salts are in the first place strong alkylating agents [17]. Their sulfur analogues **16** are obtained easily because of the strong nucleophilicity of the sulfide sulfur and they also act as alkyl transfer reagents [18, 19], but their most noteworthy feature is their acidity allowing ready *S*-ylide formation to **17** by base treatment; alternatively, carbene transfer to the parent sulfide **15** is a possible route to *S*-ylides **17** [20] (Scheme 3) [21].

The *S*-Ylides **17** thus formed play an important role in formal methylene transfer to alkenes giving cyclopropanes **18** or to carbonyl compounds giving epoxides **19** [22, 24, 25] (Scheme 4). Interestingly, the reaction of aryldiazomethanes, sulfides and aldehydes shows high diastereoselectivity for *trans*-1,2-disubstituted oxiranes **19** [24].

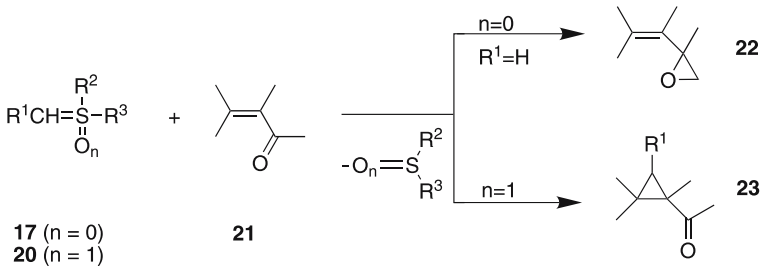


Scheme 3 *S*-Ylide formation from sulfides via sulfonium salts or via carbene transfer



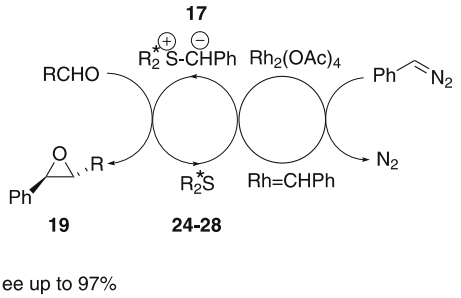
Scheme 4 Cyclopropane or oxirane formation using *S*-Ylides

An interesting dichotomy is observed for α,β-unsaturated carbonyl compounds **21** which give vinyloxiranes **22** or acylcyclopropanes **23** depending on the type of *S*-Ylide used [22] (Scheme 5). In particular, the highly reactive dimethyl-methylen-sulfurane **17** (R^1 = H, R^2 = R^3 = Me) attacks the carbonyl group to give a vinyloxirane **22** while less reactive *S*-Ylides, especially sulfoxonium ylides **20**, add to the C = C unit to give vinyloxiranes.



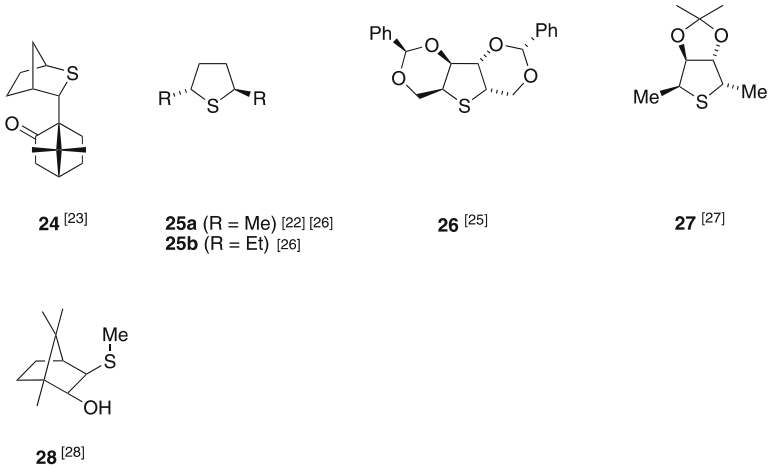
Scheme 5 Acylcyclopropanes or vinyloxiranes from α,β-unsaturated carbonyl compounds and *S*-Ylides

Recently, efficient asymmetric versions of oxirane formation via *S*-Ylides **17** and aldehydes were developed in particular by the Aggarwal [23], Goodman [26] and Metzner groups [27, 28] (Scheme 6). Here, a sulfide with



Scheme 6 Catalytic cycle for enantioselective oxirane formation from aldehydes and chiral *S*-Ylides **24–28**

a chiral carbon backbone is used and allows us to generate oxiranes with high enantioselectivity in a catalytic cycle. Scheme 7 shows sulfides **24–28** as examples of useful sources of chiral information in the enantioselective process.

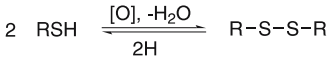


24 [23] **25a** (R = Me) [22] [26] **25b** (R = Et) [26] **26** [25] **27** [27] **28** [28]

Scheme 7 Examples of useful chiral sulfides

3 Oxidation

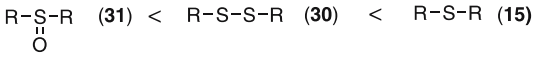
The ready oxidation of sulfur(II) compounds by appropriate reagents is a key feature of organosulfur chemistry. Thus, the reversible oxidation of a thiol **29** to a disulfide **30** is an essential structural element in many biomolecules as mentioned above of the pair cysteine **5**/cystine **6** and in redox chemistry (cf. **13/14**; Scheme 8) [30].



29 **30**

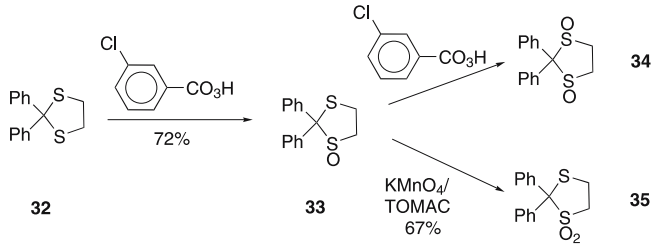
Scheme 8 Thiol/disulfide redox system

The oxidation of sulfides to sulfoxides and sulfones is now usually carried out with *m*-chloroperbenzoic acid. An approximate order of increasing ease of oxidation is given in Scheme 9 [31].



Scheme 9 Relative ease of oxidation of different substrates

This implies that in the competition experiment of sulfide **15** vs. sulfoxide **31** oxidation in a thioacetal *S*-oxide **33** the *S*,*S*′-dioxide **34** is formed preferentially. Selective oxidation of a sulfoxide unit to a sulfone is possible using hydroperoxides [32, 33], peracids in an alkaline medium [34, 35] or in particular permanganate [36, 37]. Scheme 10 shows an example where compound **35** with a sulfone unit in a thioacetal is generated; a reasonable yield is achieved using phase transfer catalysis.

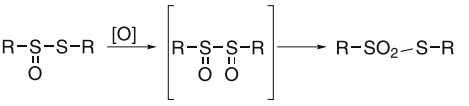


Scheme 10 Selective oxidation of a thioacetal *S*-oxide

Use of alternative oxidizing agents such as hydrogen peroxide/acetic acid may lead to preferential oxidation of disulfides over sulfides [31].

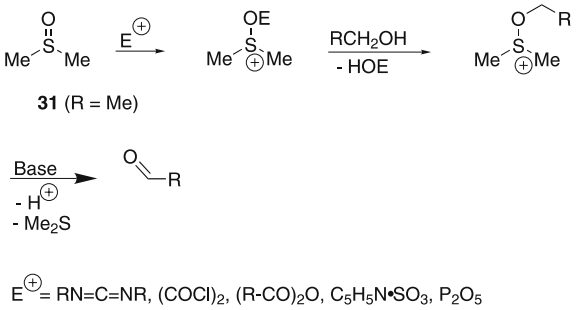
In the oxidation of disulfide *S*-monoxides **36** a possible *S*,*S*′-dioxide **37** usually rapidly rearranges to give the *S*,*S*-dioxide **38** (thiosulfonate *S*-ester; Scheme 11) [38, 39].

Among the sulfoxides, dimethyl sulfoxide (31, R = Me) has found wide application as an oxygen carrier in reagent systems for the oxidation of alcohols, particularly of primary alcohols to aldehydes [40] (Scheme 12). Sulfone chemistry is the main focus in "The Smiles Rearrangement and the Julia-Kocienski Olefination Reaction" by K. Plesniak, A. Zarecki and J. Wicha, in this volume.



36 37 38

Scheme 11 Oxidation of disulfides to thiosulfonates

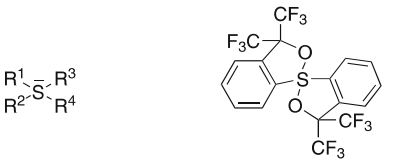


31 (R = Me)

$E^{\oplus}$ = RN=C=NR, $(COCl)_2$, $(R\text{-}CO)_2O$, $C_5H_5N{\bullet}SO_3$, P_2O_5

Scheme 12 Electrophile-assisted oxidation of primary alcohols by dimethyl sulfoxide

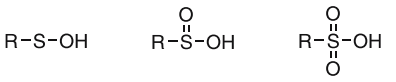
An apparent violation of the octet rule can be seen in sulfuranes **39** where the central sulfur atom shows a decet structure. Such species have been discussed for a long time as reaction intermediates, but with first reports in 1971 [41, 42] stable sulfuranes of type **40** could be prepared and their chemistry be studied in detail [43] (Scheme 13).



39 **40**

Scheme 13 Sulfuranes

Apart from disulfide formation, another formal oxidation pathway of thiols involves increasing incorporation of oxygen to give sulfenic acids **41**, sulfinic acids **42** and finally sulfonic acids **43** (Scheme 14).



41 **42** **43**

Scheme 14 Formal oxidation products of thiols

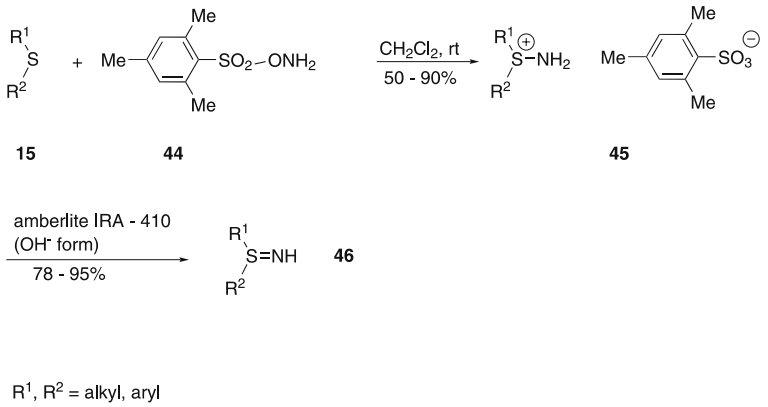
Sulfenic acids **41** are inherently unstable [44], but play a role in biochemical pathways [45, 46]. Sulfinic acids **42** [47] as well as sulfonic acids **43** and their derivatives [48] play an important role as synthetic intermediates.

4
Higher Oxidation States Involving Nitrogen

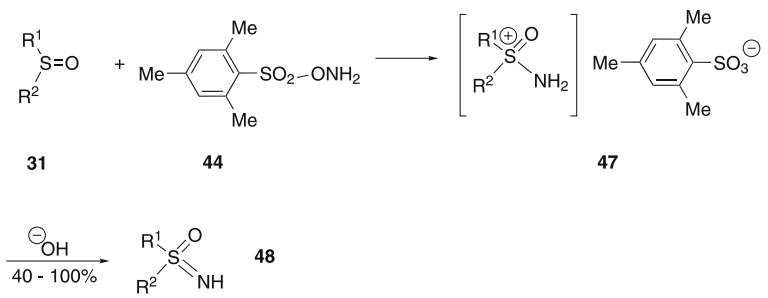
Sulfilimines (Chemical Abstracts nomenclature) or the preferred simpler name sulfimines **46** (IUPAC nomenclature) are the nitrogen analogues of sulfoxides **31** [49, 50]. The synthesis of sulfimines is usually achieved by imination of sulfides **15** using haloamines or -amides, azides or in particular *O*-mesitylenesulfonyl-hydroxylamine (**44**, MSH; Scheme 15) [51].

The MSH method is also useful to obtain sulfoximines **48** from sulfoxides **31** in usually excellent yields [52, 53] (Scheme 16).

Because of their possible chirality (vide infra), sulfoximines **48** have been recognized as an interesting class of synthetic intermediates or as chiral ligands [54].



Scheme 15 Formation of sulfimines by imination of sulfides with MSH (**44**)



Scheme 16 Formation of sulfoximines by imination of sulfoxides with MSH

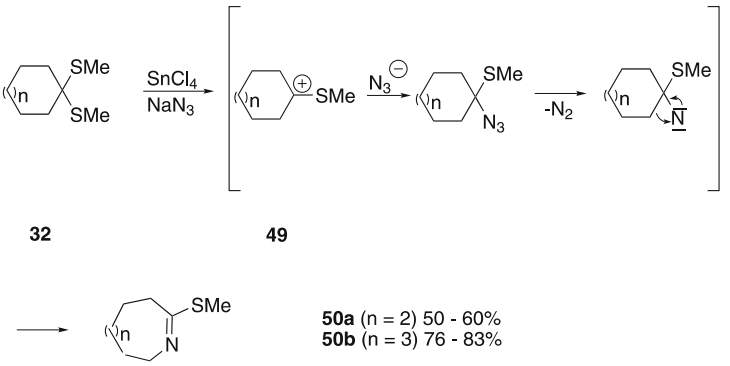
The S – N bond in sulfilimines or sulfoximines is not as strong as the S – O bond in sulfoxides or sulfones. In particular, S – N bond cleavage by reduction or by hydrolysis is a ready reaction [50, 53].

5
Sulfur May Stabilize Carbenium Ions

Even though the difference in electronegativities between carbon and sulfur is negligible, a non-bonding electron-pair in a sulfide unit will exert a stabilizing electron-donating (+ M) effect on a neighboring carbon with a positive charge; alternatively, the stabilizing effect may be ascribed to the polarizability of the sulfur atom (Scheme 17).

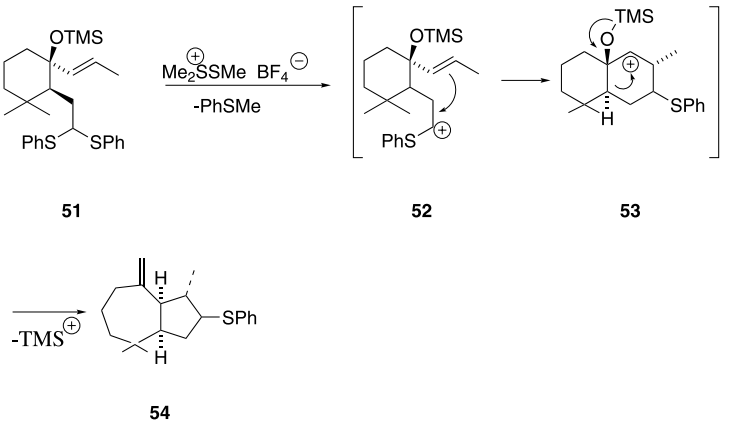
Scheme 17 Sulfur as electron donor to a carbenium ion

Trost noted that thioacetals **32** provide ready access to sulfur-stabilized carbenium ions **49** ("thionium ions") [55] and that these species display enhanced carbonyl reactivity; so they were addressed as "super carbonyl" groups. Thus, in cyclic thioacetals **32** one sulfur unit is removed by the action of tin(IV) chloride (Scheme 18).



Scheme 18 Thioacetals as super carbonyl groups: sulfur substitution by azide and Curtius-type rearrangement

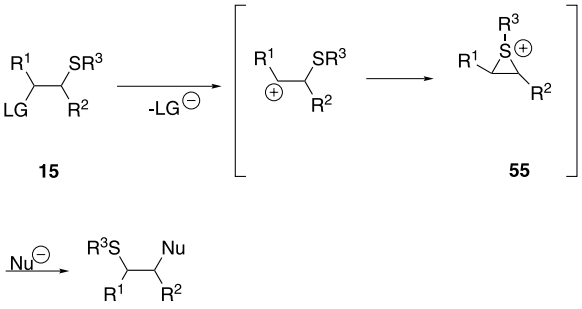
An illustrative example of the carbenium-stabilizing effect of sulfur is provided by a key reaction step in Overman's synthesis of Shahamin K [56]. Treatment of the hydroxyaldehyde derivative **51** with dimethyl(methylthio)-sulfonium tetrafluoroborate (DMTSF) leads apparently to *S*-methylation and from there to elimination of thioanisole to give an *S*-stabilized carbenium ion



Scheme 19 Sulfur-induced pinacol rearrangement in the synthesis of Shahamin K

52 which is attacked by the alkene unit to trigger a pinacol rearrangement in **53** (Scheme 19).

The electron-donating effect of sulfur is also a key feature in 1,2-sulfur shifts (cf. "1,2-Sulfur Migrations" by A. Sromek and V. Gvorgyan, in this volume) which occur via thiiranium intermediates **55** securing the stereoselective nature of the process (Scheme 20).

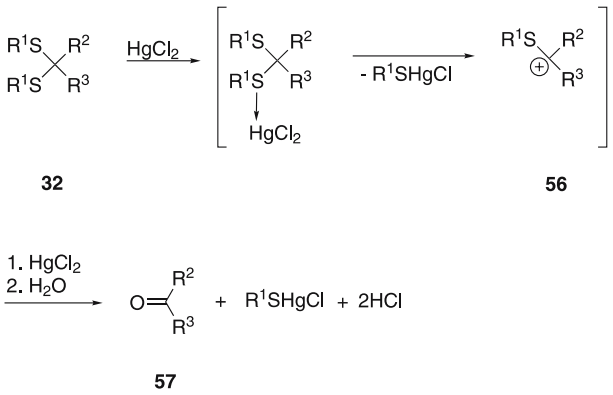


Scheme 20 1,2-Shifts of sulfide groups via thiiranium ions

6
Association with Non-Carbon Electrophiles

Because of the size of the atom, non-bonding electron-pairs on sulfur are softer (more polarizable) than those on oxygen. Consequently, electron-pairs on sulfur are better nucleophiles, but less basic. Following the HSAB principle, sulfur compounds tend to associate preferentially with soft Lewis acids rather than with the hard proton. This is, for example, significant in the for-

mal hydrolysis of thioacetals **32** which, in contrast to acetal hydrolysis, does not work with simple acid catalysis. Instead, soft Lewis acids, especially thiophilic mercury(II) salts, have to be employed. Oxidative methods based on the formation of sulfur(IV) intermediates offer an environmentally benign and often chemically more efficient alternative [57–59] (Scheme 21). As the reaction proceeds via a cationic intermediate **56**, carbenium-stabilizing groups R^2, R^3 will favor hydrolysis to give finally aldehydes or ketones **57**.

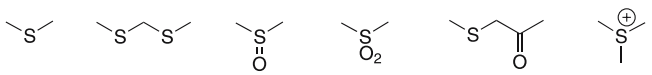


Scheme 21 Hydrolysis of a thioacetal

A specific interaction is observed between thiols **29** and gold. Actually, thiol molecules are adsorbed readily from solution onto gold creating a dense monolayer with the organic tail pointing outwards from the surface [60, 61].

7
Sulfur May Stabilize Carbanions

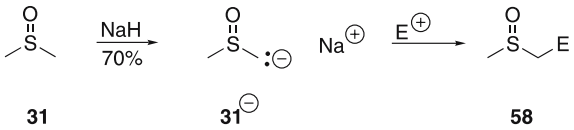
A sulfide, sulfoxide or sulfone group will acidify hydrogen on the adjacent carbon atom. This effect has been explained by resonance-stabilization of the carbanion involving d-orbitals on sulfur, but the polarizability of the sulfur group is now considered to give a better description [62] and also electronegativities have to be taken into account [63]. Actually, the stabilizing effect of a phenyl sulfonyl group is comparable to that of a cyano group, though smaller than that of a carbonyl or nitro function [64]. α-Phenylthio substitution increases the acidity of cyclohexanone by 3 pK units [65]. In Scheme 22



Scheme 22 Order of increasing acidities for some sulfur functionalities

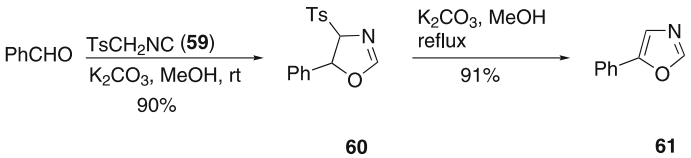
an approximate order of increasing acidities is given for some important sulfur functionalities [66–68].

The deprotonation of sulfonium salts **16** was discussed above as an entry to *S*-Ylides **17**. Sodium methylsulfinylmethylide ("dimsyl sodium") has been found to be formed easily from dimethyl sulfoxide and reacts with electrophiles to give products **58** (Scheme 23), but is also often used as a base [69].



Scheme 23 Formation of sodium methylsulfinylmethylide and reaction with electrophiles

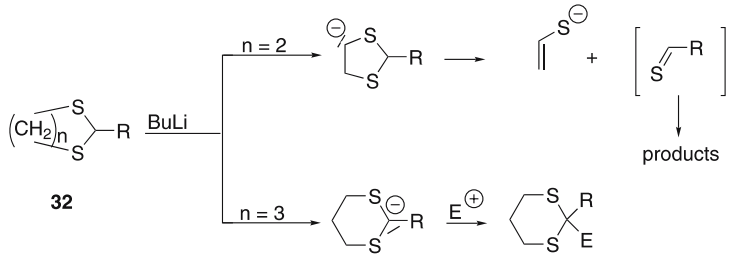
Obviously, it is an advantage for synthetic applications if an acidifying sulfur functionality is combined with another electron-withdrawing group. So there is a rich chemistry of sulfonate- or sulfonamide-stabilized carbanions [70]. Similarly, tosylmethyl isocyanide (**59**, TosMIC) [71, 72] has found a plethora of synthetic applications. Scheme 24 shows an example of oxazole **61** formation [71].



Scheme 24 Deprotonation of "TosMIC" and use in heterocyclic synthesis

Corey and Seebach noted that, in contrast to acetals, in spite of their moderate acidity thioacetals **32** can be deprotonated and readily react with various types of electrophiles [59, 73–75]. It was emphasized that the thioacetal reaction represents an excellent example of umpolung chemistry as the normal a^1 reactivity of a carbonyl carbon is reversed into d^1 in its thioacetal anion [76, 77]. Cyclic thioacetals of the 1,3-dithiane type (**32**, $n = 3$) usually give the best results [57, 75], whereas the anions of 1,3-dithiolanes (**32**, $n = 2$) tend to give preferentially ring opening by a 1,3-anionic cycloreversion and should be avoided [36, 37, 78] (Scheme 25).

2-Silyl-thioacetals **62** are useful building blocks in a domino process involving a 1,4 silyl migration homo-Brook rearrangement [79] in **63** and giving carbo- or heterocycles; best results are obtained for synthesis of cyclopentanes **65** [80] (Scheme 26).



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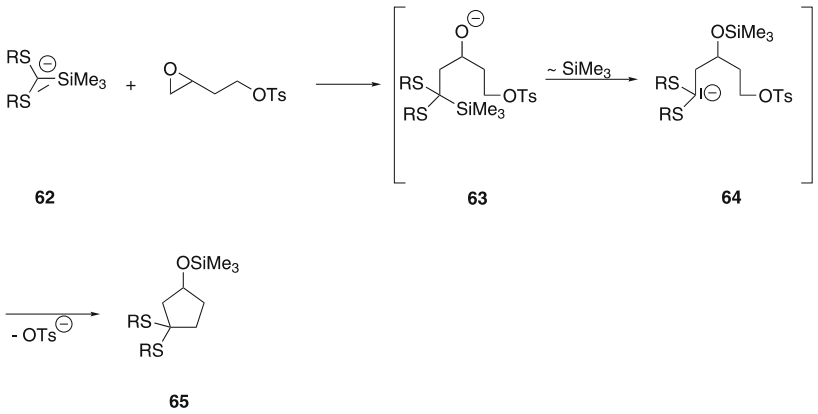
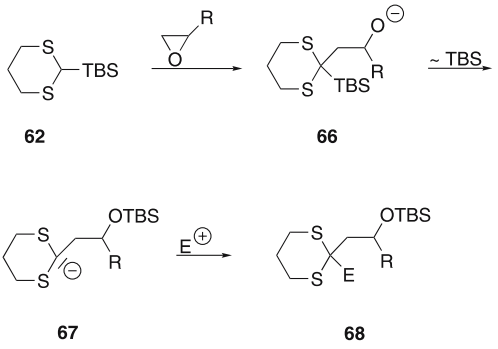
Scheme 25 1,3-Anionic cycloreversion of 1,3-dithiolanes vs. use of 1,3-dithianes in umpolung chemistry



62 63 64 65

Scheme 26 2-Silylthioacetals in a cyclopentane-forming domino process

This type of thioacetal-supported domino process has been successfully applied to secure formation of a second carbanion **67** from 1,3-dithianes **62** [81] (Scheme 27).



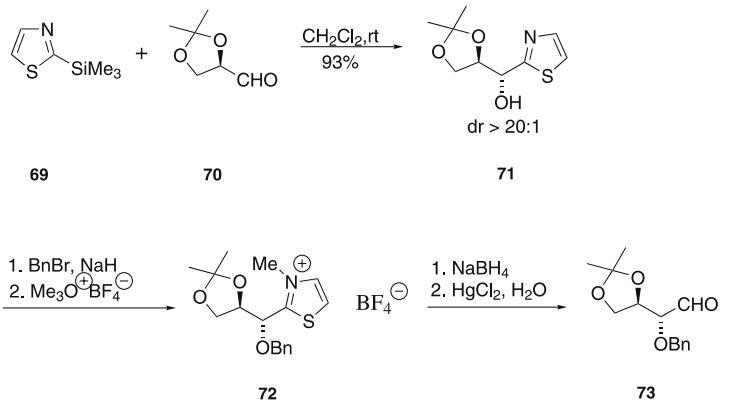
62 66 67 68

Scheme 27 "Linchpin chemistry" using a silyl migration to achieve a formal second thioacetal deprotonation

Elegant applications of this reaction principle in natural product synthesis have been published under the trademark of "linchpin chemistry" [81]. Many more applications of thioacetals in natural product synthesis have been reported [82].

In place of thioacetals, also thioacetal *S*,*S*-dioxides of type **35** have been used as d^1 synthons [83].

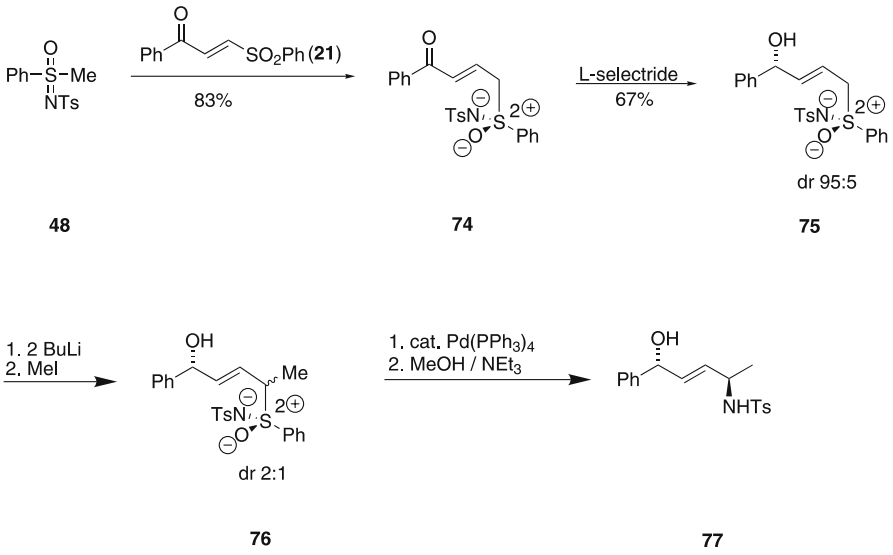
Also other heterocyclic formyl anion equivalents than thioacetals or congeners have been employed [59, 84]. Thus, Dondoni has developed use of 2-lithio-1,3-thiazole or of the corresponding trimethylsilyl derivative **69** as formyl equivalent allowing chain extension of aldehydes such as **70** (Scheme 28) [85, 86]. The heterocyclic auxiliary can be removed by alkylation with Meerwein reagent, reduction with sodium borohydride and mercury chloride-assisted hydrolysis to give aldehyde **73**.



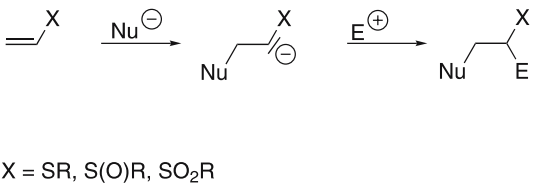
Scheme 28 Chain elongation of 2,3-O-isopropylidene-D-glyceraldehyde with a thiazole reagent

The acidity in the α position to a sulfide, sulfoxide or sulfone function is also seen for sulfoximines and has allowed quite a few synthetic applications [53, 87–89]. Even tandem diastereoselective reactions are possible as shown by the Michael-addition of deprotonated sulfoximine **48** to a sulfonyl-substituted enone **21** and subsequent highly diastereoselective reduction to hydroxyalkenyl-sulfoximine **75**. After methylation to **76**, treatment with a palladium catalyst resulted in reorganization of the *N*-tosyl-sulfoximine unit to an *N*-benzensulfinyl-tosylamide and eventually to tosylamide **77** [90] (Scheme 29).

The stabilizing effect of sulfur functionalities on carbanions is not only important in deprotonation chemistry, but also as an electronic effect in the stabilization of reactive intermediates. Thus, sulfanyl, sulfinyl or sulfonyl substituents on a C = C bond make the alkene electron deficient and encourage nucleophilic addition (Michael addition; cf. Scheme 30) [91].

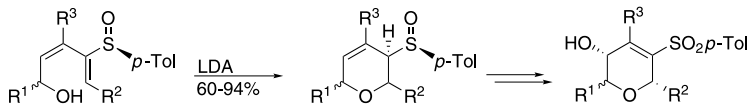


Scheme 29 Diastereoselective synthesis of 1,4-aminoalcohols via 1,4-stereochemical control using sulfoximines



Scheme 30 Michael-type addition reactions to vinyl sulfides, sulfoxides or sulfones

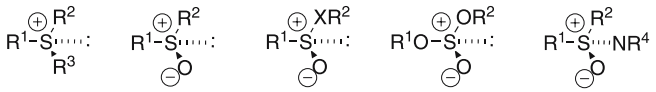
An application giving eventually functionalized dihydropyrans is shown in Scheme 31 [92].



Scheme 31 Cyclization of sulfinyl-substituted dienols to dihydropyrans

8
Chiral Sulfur

Sulfur exhibits pyramidal bonding in sulfonium salts **16**, sulfoxides **31**, sulfinic acid **42** and derivatives, sulfurous acid derivatives **78**, and sulfox-

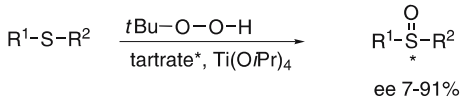


16 31 42 78 48

Scheme 32 Chiral sulfur functionalities

imines **48**. Thus, these compounds are chiral by substitution with unequal residues ($R^1 \neq R^2$, and for sulfonium salts also $\neq R^3$ Scheme 32).

Access to optically active sulfoxides **31** is mainly by oxidation of sulfides **15** in the presence of an optically active catalyst or by nucleophilic substitution on an optically active sulfinate **79** [93]. In the former route, modified Sharpless conditions are employed (Scheme 33) [94, 95]; alternatively, 1,1′-bis-2-naphthol is used [96]. However, the approach is limited to alkyl aryl sulfoxides (**31**; R^1 = alkyl, R^2 = aryl) and even here the efficiency in terms of optical yield is variable [97].



ee 7-91%

15 31

Scheme 33 Oxidation of sulfides to optically active sulfoxides in the presence of D- or L-tartrate

Because of the lack of a general asymmetric oxidation method, carbanion chemistry involving the displacement of a chiral leaving group is often chosen to obtain optically active sulfoxides **31** [93] even though the chiral auxiliary has to be applied in stoichiometric amounts and again only alkyl aryl sulfoxides are obtained with reasonable ee's. Here, the Andersen procedure where an organometallic reagent attacks menthyl *p*-toluenesulfinate **79** is the most popular as separation of sulfinate diastereomers by fractional crystallization is usually convenient [98–100] (Scheme 34).

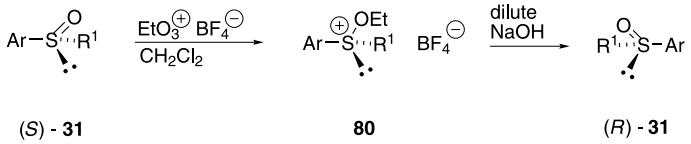
79 31

40-88%
ee 85-98%

R=Me, Et, *i*Pr, Ph, tBuOOCCH$_2$

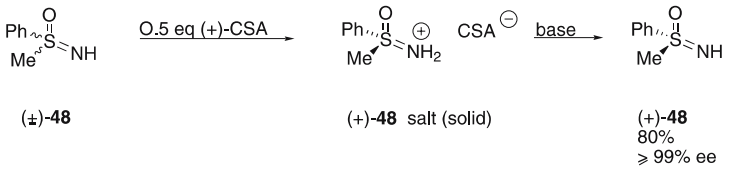
Scheme 34 Non-racemic *p*-tolyl alkyl sulfoxides from menthyl *p*-toluenesulfinate

The Andersen procedure normally provides products with sulfur in the *S* configuration. If the enantiomer is desired, the Johnson approach of alkylation to **80** and hydrolysis by aqueous base allows inversion of configuration (Scheme 35) [100, 101].



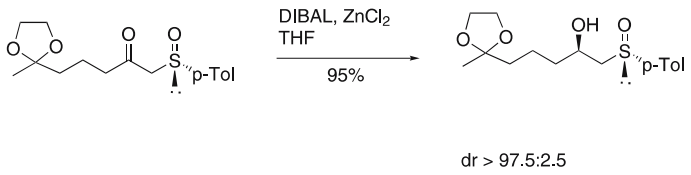
Scheme 35 Inversion of configuration in a sulfoxide

Convenient access is available to an optically pure sulfoximine **48** by fractional crystallization with (+)-camphorsulfonic acid (CSA); the (+)-enantiomer of *S*-methyl-*S*-phenylsulfoximine forms a solid salt with CSA that can be cleaved by base to give the pure (+) form while the (–) form can be isolated from the filtrate (Scheme 36) [102, 103].



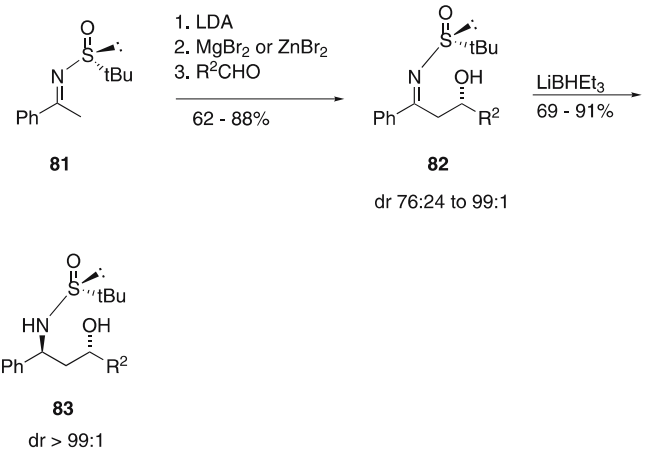
Scheme 36 (+)-*S*-Methyl-*S*-phenylsulfoximine by crystallization with CSA

There are numerous examples where chiral sulfur functionalities serve as the auxiliary in asymmetric synthesis [104]. Very often, based on the Andersen approach, non-racemic *p*-tolyl-substituted sulfoxides are applied [105, 106]. Thus, it has been shown that a sulfoxide group as a chiral sulfur auxiliary allows a diastereoselective reduction of a neighboring oxo group [107] (Scheme 37).



Scheme 37 Sulfoxide-directed diastereoselectivity in ketone reduction

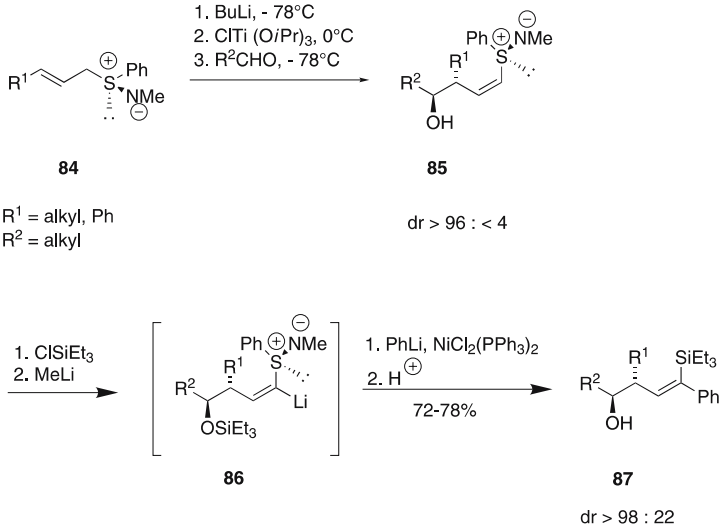
The Davis [108] and Ellman [109, 110] groups have demonstrated that chiral sulfinylimines **81** are very useful auxiliaries allowing various synthetic transformations with full control of the configuration. Thus, sulfinylimines **81** with α-hydrogen can be used as chiral aza-enolates in a modified aldol



Scheme 38 Aza-aldol reaction with diastereoselective control by a sulfinylimine group

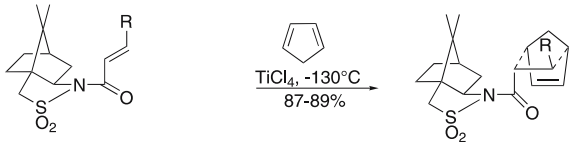
reaction to provide hydroxyalkylimines **82**; further highly diastereoselective reduction yields 1,3-aminoalcohols **83** [111] (Scheme 38).

Presently, sulfoximines **48** may be the most popular example of a sulfur-based functional group which is used in asymmetric synthesis [53]. Thus, the titanates of non-racemic *trans*-allyl sulfoximines **84** add aldehydes in a highly regio- and diastereoselective fashion to give *anti*-(*Z*)-configured homoallylic alcohols **85** [112]; subsequent silylation and deprotonation, followed by a nickel-catalyzed substitution initiates a 1,5 silicon migration and provides homoallylic alcohol **87** with a vinyl silane moiety [113] (Scheme 39).



Scheme 39 Reaction of the anions of allyl sulfoximines with aldehydes

In asymmetric versions of the Diels–Alder reaction, Oppolzer found a practical control element which at the same time activates the dienophile and is based on the presence of a sultam unit as in **88** [114] (Scheme 40). In the presence of a Lewis acid and at low temperatures excellent diastereomeric excess in [4 + 2] cycloadduct **89** (dr up to 99 : 1) could be achieved.

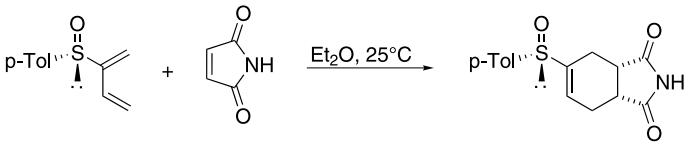


88 **89**

R=H, Me

Scheme 40 The Oppolzer sultam as a chiral auxiliary in Diels–Alder reactions

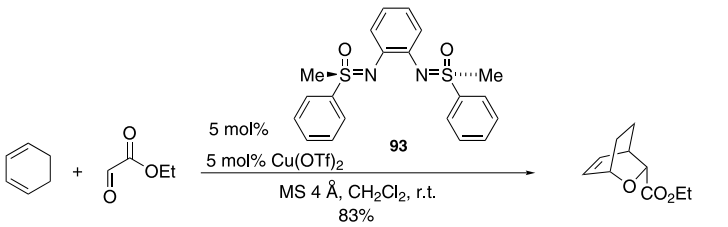
A chiral sulfoxide substituent in the 1- or 2-position of a diene gives a chiral 4π component of a Diels–Alder reaction [115]. Thus, reaction of the optically pure dienylsulfoxide **90** with maleimide **91** gives cycloadduct **92** as a single enantiomer [116] (Scheme 41).



90 **91** **92**

Scheme 41 [4 + 2] Cycloaddition of an optically pure dienylsulfoxide

A non-racemic sulfur functionality is also a useful feature in a catalyst for [4 + 2] cycloaddition; very good results were obtained with the C2-symmetric bis(sulfoximine) copper(II) complex **93** [117] (Scheme 42).



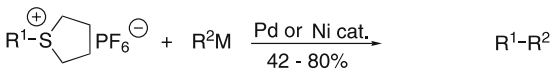
98% ee, endo:exo 99:1

Scheme 42 Enantioselective catalysis of a [4 + 2] cycloaddition by a C2-symmetric sulfoximine ligand

9
Sulfur as the Leaving Group

The main goal in doing organosulfur chemistry is usually to achieve a specific transformation with ease and elegance, but once this has been achieved there is often no more need for the presence of sulfur and the sulfur has to be removed—preferably in a way that will generate another useful functionality. The main routes to remove sulfur are substitution, elimination, oxidation and reduction.

In substitution reactions, the excellent polarizability makes thiolates and their oxygen-substituted congeners good leaving groups. A current field of application is CC bond formation by reaction of a sulfur-functionalized substrate and an organometallic compound [118, 119]. Thus, Stille-, Suzuki-, and Negishi-type cross-coupling reactions are possible between thiolane-derived sulfonium salts **94** and organotin compounds, boronic acids, or organozinc compounds in the presence of palladium or nickel catalysts [120] (Scheme 43).



94 **95**

R^1 = Ar, Hetaryl, Bn
R^2 = Alkenyl
M = Sn, B, Zn

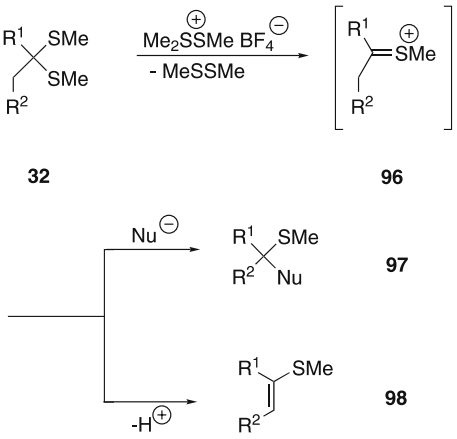
Scheme 43 Cross-coupling of sulfonium salts with organometallics

Trost found that reaction of thioacetals **32** with dimethyl(methylthio)sulfonium fluoroborate (DMTSF) offers an efficient way to substitute one alkylthio group via an intermediate thionium salt **96**; from here, substitution by nucleophiles or elimination are possible giving products **97** and **98**, respectively [121] (Scheme 44; cf. also Scheme 18).

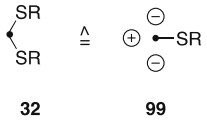
Combined with the possibility to deprotonate thioacetals and add electrophiles to the resulting carbanion (vide supra), the reaction of Scheme 44 implies that a thioacetal is the equivalent of a dianion-cation [121] (Scheme 45).

For alkene-forming elimination reactions, a study of vinyl sulfone **102** formation from a series of 2-substituted sulfones **100** has allowed to determine the relative order of sulfur-based leaving groups (Scheme 46) [122].

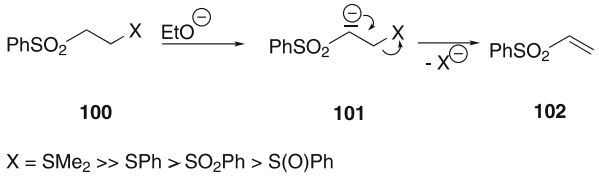
A sulfone unit may also be employed in thermal elimination reactions as shown by the pyrolysis of a dihydroisothianaphthene dioxide **103** to give the highly reactive o-quinodimethane **104** (Scheme 47) [123].



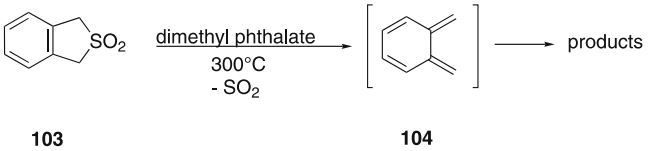
Scheme 44 Reaction of thioacetals with dimethyl(methylthio)sulfonium fluoroborate (DMTSF)



Scheme 45 Thioacetals as dianion-cation equivalent



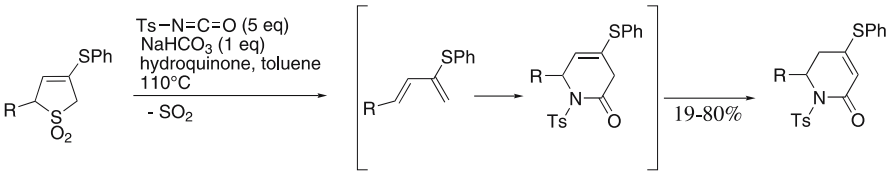
Scheme 46 Relative leaving-group abilities of sulfur-based functions in vinyl sulfone formation



Scheme 47 Elimination of sulfur dioxide from a cyclic sulfone

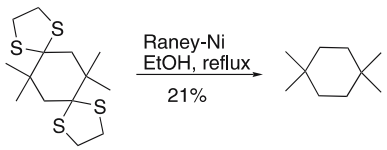
Similarly, sulfur dioxide extrusion from 3-sulfolenes **105** generates reactive dienes **106** which can, for example, be employed in aza-Diels–Alder reactions to give pyridine derivatives **108** via **107** [124] (Scheme 48).

In the reduction of carbonyl compounds to alkanes, use of thioacetals **32** sometimes shows advantages over Wolff–Kishner procedures [125]; in Scheme 49 an example of a two-fold reduction is given.



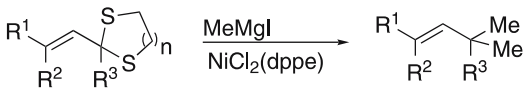
105 106 107 108

Scheme 48 Extrusion of sulfur dioxide from 3-sulfolenes as a route to aza-Diels–Alder chemistry



Scheme 49 Alkane formation by reduction of thioacetals

The classical reduction of thioacetals **32** is nicely complemented by procedures of reductive alkylation giving compounds with quaternary carbons in good yields (Scheme 50) [126, 127].

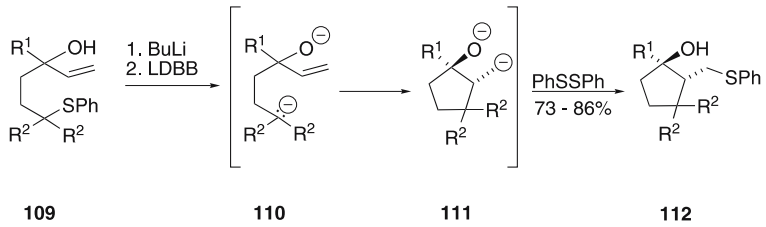


n=1,2
R^1, R^2, R^3=H, alkyl, aryl

Scheme 50 Nickel-catalyzed reductive alkylation of allylic thioacetals

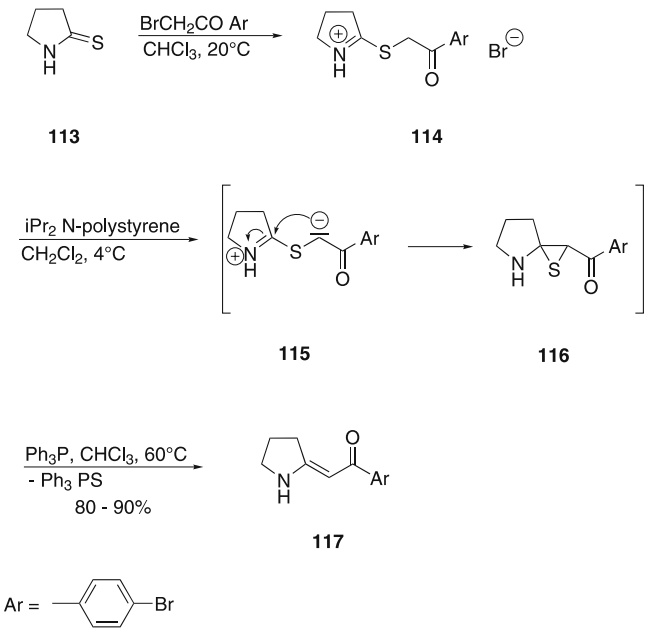
Cohen found that treatment of sulfide or thioacetal units by the radical anion of 1-dimethylamino-naphthaline (LDMAN) or 4,4′-di-*tert*-butyl-biphenyl (LDBB), each as lithium salt, gives reductive metallation yielding highly reactive carbanions [128]; Scheme 51 shows an example where the intermediate carbanion **110** undergoes ring closure to **111** and is finally intercepted by diphenyl disulfide to yield sulfide **112**.

Sometimes, a constructive way to eliminate sulfur is by way of forming a strained three-membered ring (in particular a thiirane or a thiirane *S*,*S*-dioxide) which easily eliminates sulfur or sulfur dioxide. An elegant application of the first-mentioned possibility is the Eschenmoser reaction which allows us to convert thioamides into β-aminoenones (equivalents of 1,3-dicarbonyl compounds) by way of an alkylation reaction. Thus, thiobutyrolactam **113** is alkylated with a phenacyl bromide to give a thioimidate **114** which by base-treatment easily forms an enolate **115**. This intermedi-



Scheme 51 Reductive metallation of a sulfide by lithiated 4,4′-di-*tert*-butyl-biphenyl (LDBB), ring closure and interception by diphenyl disulfide

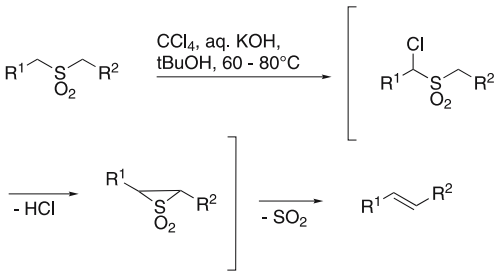
ate cyclizes to a thiirane **116** by attacking the electrophilic iminium unit. Finally, thiirane **116** is desulfurized by a phosphorus(III) reagent to give β-aminoenone **117** (Scheme 52) [129]. Additional examples are found in the recent literature [130, 131].



Scheme 52 Eschenmoser reaction of thiobutyrolactam **113** to giver a β-amino-enone **117**

Extrusion of sulfur dioxide from a thiirane *S*,*S*-dioxide intermediate is a key feature of the Ramberg–Bäcklund reaction [132, 133]. Interestingly, this reaction is sometimes addressed as a rearrangement [134–136], but a closer

look shows that no reorganization of the carbon framework takes place but formation of a C = C bond in the position of a previous sulfone unit (Scheme 53).

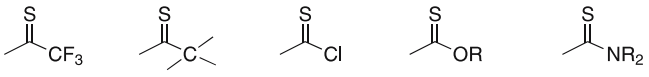


Scheme 53 The Ramberg–Bäcklund reaction

A particularly elegant way of making synthetic use of a sulfur functionality is the Mislow–Evans rearrangement which allows us to convert allyl sulfoxides into allyl alcohols (cf. "[2,3]-Sigmatropic Rearrangements of Allylic Sulfur Compounds" by M. Regglin, in this volume).

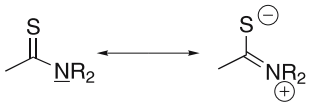
10
Carbonyl vs. Thiocarbonyl Chemistry

The carbonyl group is certainly the most important functional group as shown, for example, by the importance of aldol chemistry or of olefination reactions. So many carbonyl compounds will be among the standard repertoire of an organic laboratory. In contrast, thiocarbonyl compounds may be highly unstable, elusive species. As pointed out above, this can be explained in terms of poor overlap of orbitals in a 2p–3p π bond between carbon and sulfur. However, a closer look shows that thiocarbonyl compounds comprise a wide range of stability and reactivity depending on the substituents of the thiocarbonyl group. If thioformaldehyde is taken as a basis, substituents may lead to decreasing charge density on sulfur giving a polarization that is the inverse of the charge distribution in carbonyl compounds, or substituents may have the opposite effect. For some typical residues, the following order of increasing nucleophilicity and accordingly decreasing electrophilicity of the sulfur may be given [137] (Scheme 54):



Scheme 54 Sequence of increasing nucleophilicity (decreasing electrophilicity) of thiocarbonyl compounds

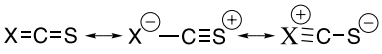
Consequently, hexafluorothioacetone is the prototype of a thiocarbonyl compound with electrophilic sulfur showing—relative to ketones—an inverse sense of addition reactions [138]. In contrast, high negative charge density is seen for the sulfur in thioamides, thionocarbamates and thioureas because of resonance interaction between the non-bonding electron pair on nitrogen and the carbon–sulfur π bond favoring resonance structure **118b** (Scheme 55):



118a **118b**

Scheme 55 Thioamide resonance

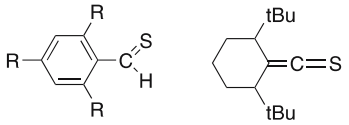
The same considerations apply to compounds with a cumulated thiocarbonyl unit. If the atom X at the other end of the cumulated system can act as an electron-donor because of available π or non-bonding electrons, resonance structure **119c** will be important giving some stability to the system whereas the reverse is true for groups X which are electron-accepting and favor resonance structure **119b** (Scheme 56).



119a **119b** **119c**

Scheme 56 Resonance in cumulated thiocarbonyl systems

So thionocarboxylic [139, 140] and thionocarbonic acid derivatives [141, 142] and also isothiocyanates (X = RN) [143] or carbon disulfide (X = S) [143, 144] are compounds with a highly nucleophilic sulfur as shown in **118b**, **119c**, but their thermal stability is quite pronounced. Even thioketenes may enjoy considerable stability if cumulated with a triphenylphosphoranylidene (X = $R_3P=C$) or an alkylidene unit (X = $R_2C=C$) [137, 145] or if the system is cumulated as in carbon subsulfide (X = S = C = C) [146]. The notorious instability of thiocarbonyl compounds is in particular seen for thioaldehydes [114, 147–150], aliphatic thioketones [114, 151–155] and thioketenes [137, 145] where an ambiphilic nature may be assigned to the C = S group giving a high tendency to dimerize, oligomerize or even polymerize. However, the thermodynamic lability of the thiocarbonyl group may be overruled by kinetic stabilization using bulky substituents. Typical examples include Okazaki's thioaldehydes **120** [156, 157] and thioketene **121** [158] (Scheme 57).



120 121

R=CH(SiMe$_3$)$_2$, tBu

Scheme 57 Examples of thiocarbonyl compounds with steric stabilization

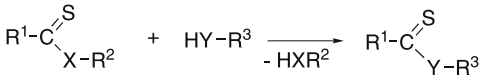
In thiocarbonyl compounds which lack electronic stabilization and which have hydrogen in the α position as in **122**, formation of the corresponding enethiol **123** is much more favored than enolization for carbonyl compounds (Scheme 58).

122 123

Scheme 58 Thione-enethiol tautomerism

So rapid formation of the enethiol is often observed on synthesizing a thioketone with α hydrogen(s).

While acylation is a standard reaction in organic chemistry, thioacylation is much more delicate. The reason is that the sulfur equivalents of the usual acylating reagents, i.e. thioacyl chlorides, thionoanhydrides or thioketenes, are unstable or even elusive species. So thioacylation chemistry is mainly based on thionoesters (**124**, X = O) or dithioesters (**124**, X = S) [140, 159] which are activated by the leaving-group efficiency of residue R^2 (Scheme 59) or by special reaction conditions [130, 160, 161].



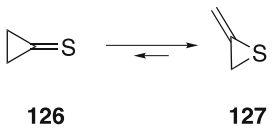
124 125

X = O, S
Y = O, S, NR^1; NNR^{4}R^5 etc.

Scheme 59 Thioacylation

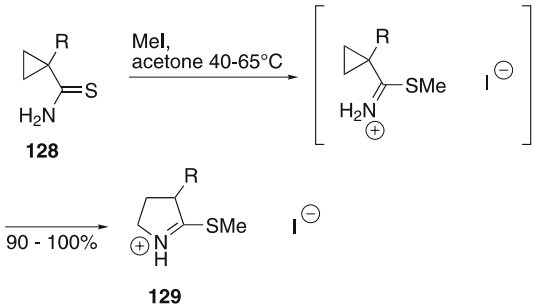
Cyclopropanethione **126** is handicapped by a non-stabilized thiocarbonyl group and by ring strain. So it is an elusive species and a formal 1,3 sig-

matropic shift will rapidly give methylenethiirane **127** [162] (Scheme 60). Similarly, ring strain probably is the main driving force in the rearrangement of cyclopropanethiocarboxamides **128** to pyrrolines **129** [163] (Scheme 61).



126 **127**

Scheme 60 Rearrangement of cyclopropanethione



128 **129**

R = Me, CF_3, COOBu, NHBz, OBn, Ph

Scheme 61 Formal 1,3-sigmatropic shift in cyclopropanethiocarboxamides

A special feature of thiocarbonyl compounds is the relatively small energy for a n,π^* transition making thioaldehydes, thioketones, thioketenes and thioquinones colored. A rich photochemistry has been reported also involving the π,π^* transition [164, 165] which quite often leads to different photoreactions.

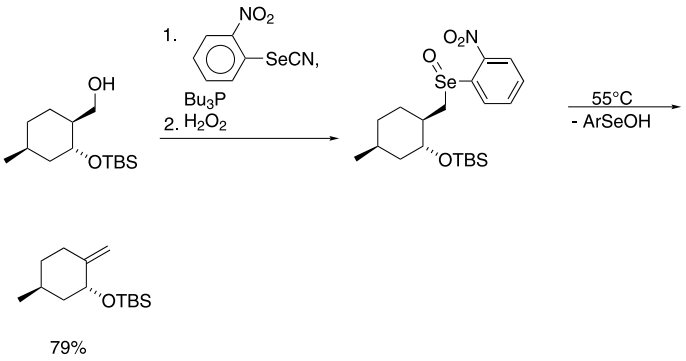
Furthermore, the relatively weak C = S π-bond makes thiocarbonyl compounds useful in cycloaddition chemistry, where the thiocarbonyl compounds normally enter as 2π systems, but 4π reactivity of α,β-unsaturated thiocarbonyl compounds is also seen [130, 160]. In particular, thiones are "superdipolarophiles" in [2 + 3] cycloaddition reactions, for example with diphenyldiazomethane [166], and have also been named "superdienophiles" in Diels–Alder reactions [167].

The inefficient p_π–p_π C = S bond is the basis for the thione-thiol (Newman–Kwart) rearrangement (see "Thione-thiol Rearrangement: Newman–Kwart Rearrangement and Others" by C. Zonta, O. de Lucci, R. Volpicelli and L. Cotarca, in this volume) and is an interesting feature in the efficiency of [3.3] sigmatropic rearrangements of allyl vinyl sulfide-type compounds (see

"Sulfur Participation in [3,3]-Sigmatropic Rearrangements" by R. Fernandez, de la Pradilla, M. Tortosa and A. Viso, in this volume).

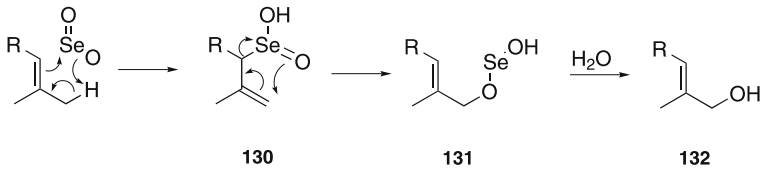
11 And Selenium?

When sulfur is so beneficial in many organic transformations, the question may be raised whether selenium isn't even more useful. In fact, some reactions of organosulfur chemistry proceed with greater ease or under milder conditions if the corresponding selenium compound is employed [168–170]. A prominent example is the alkene-forming elimination of selenoxides; Scheme 62 shows an illustrative example from a natural product synthesis [171].



Scheme 62 C = C Bond formation by thermolysis of a selenoxide

Selenium dioxide has been used for specific oxidation reactions. An important application is the hydroxylation of allylic C – H bonds [172]. The reaction proceeds with complete stereocontrol indicating a sequence of ene reaction and [2, 3]-sigmatropic rearrangement of intermediate **131** (Scheme 63).



Scheme 63 Allylic oxidation using selenium dioxide

However, concerns about the toxicity of organoselenium compounds [173] apparently hamper the broad use of these materials as reagents and as synthetic intermediates.

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