Synthesis of Thiiranes by Direct Sulfur Transfer: The Challenge of Developing Effective Sulfur Donors and Metal Catalysts

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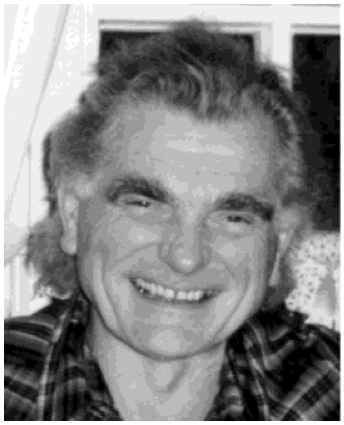
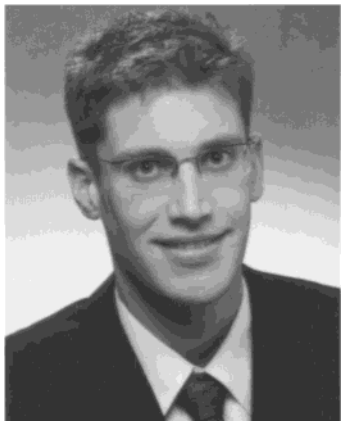
Contents



Waldemar Adam, born in 1937 in the Ukraine, was raised in Germany and received his education in the United States (Ph.D. degree in 1961 at M.I.T. under the guidance of Prof. F. D. Greene). He moved to Puerto Rico, where he started his academic career in 1961 at the University of Puerto Rico (Rio Piedras), and was promoted to Professor in 1970. From 1980 to 2002, he was appointed to the Chair of Organic Chemistry at the University of Würzburg. He was honored by numerous awards and coauthored more than 950 publications. In April 2003, he moved back to Puerto Rico (San Juan) for retirement.



Rainer M. Bargon, born 1973 in Ulm, Germany, received his chemical education at the Julius-Maximilians-University of Würzburg. In 1997, he spent 4 months with Prof. Pommelet as an undergraduate research student at the ISMRA in Caen, France, before he joined Prof. Adam's research group. He received his Master's degree in 1999 and his Ph.D. degree in 2002. His main research interests concern sulfur-transfer reactions to organic substrates.

1. Introduction

The first thiirane, a saturated three-membered-ring heterocycle with one sulfur atom, also named episulfide or thioepoxide, was synthesized by Staudinger and Pfenninger in 1916,[1] which marks the beginning of a fascinating research area in organosulfur chemistry. Like the related epoxides or oxiranes, such sulfur heterocycles constitute key intermediates in synthetic chemistry. For example, nucleophilic ring-opening of episulfides serves as a convenient access to sulfur-containing compounds, which include thiols, thioethers, cyclic sulfides, sulfoxides, sulfones, sulfinates, sulfonates, etc.[2] Moreover, episulfides have been employed in numerous commercial and industrial applications, in particular as desinfectants,[3] as precursors for synthetic polymers,[4] as stabilizers for plastics,[5] and as pharmacologically active substances.[6] *S*-Thiirane carboxylic acids,[6a] for instance, serve as selective inhibitors for cysteine protease, and thiodroles[6c] have been used in cancer therapy. In view of the practical need and synthetic utility, it is highly desirable to have available convenient methods for the preparation of episulfides directly from readily accessible alkenes, especially if costly and toxic reagents are avoided.

Numerous synthetic routes to synthesize episulfides have been developed in the past, and these have been extensively reviewed.[7] In these conventional syntheses of episulfides from alkenes, indirect methods have been used since the beginning of the last century.[7] Specifically, the alkene is first transformed into an oxygen-functionalized precursor, usually an

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epoxide, from which the thioepoxide is generated in a subsequent nucleophilic substitution step. Frequently polymerization of the thiirane occurs, an undesirable side reaction whose minimization requires optimization of the reaction conditions to be properly adjusted for each substrate.[8] Catenation and sulfur extrusion severely limit the synthetic value of these round-about methods.[9] Recently, special catalysts have been used for the transformation of oxiranes into thiiranes under mild conditions to afford thiiranes in excellent yields.[10] To overcome such preparative drawbacks, similar to the case of epoxidation, the analogous thioepoxidation offers attractive opportunities in which the thiiranes are conveniently prepared from the appropriate alkenes by direct sulfur transfer. Indeed, this challenging concept has been first realized some 40 years ago,[9] a rewarding activity that has been intensified during the last two decades. Particularly promising achievements have been made within the last handful of years, particularly through our efforts. Besides the coverage of our own work, we collect herein the scattered reports in the literature on this demanding synthetic problem. Our incentive with this comprehensive review is to stimulate more intensive research activity in sulfur chemistry in the hope that new direct episulfidation methods will be developed, especially catalytic and selective ones, and that existing ones will be perfected.

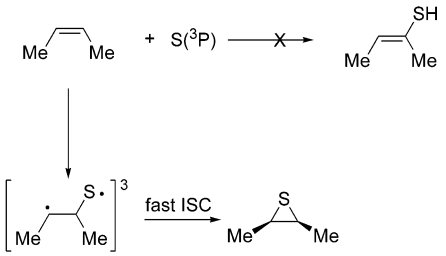
The variety of available sulfur-transferring agents for the direct episulfidation will be classified into two broad categories; namely, the *stoichiometric* and the *metal-catalyzed* modes of operation. Of these two, the most intensively investigated is the stoichiometric episulfidation, which shall be presented first with an overview of the various sulfur sources. Their potential synthetic value will be outlined, and the efficacy of the sulfur donors will be addressed; for each, the scope and limitations will be pointed out. Then will follow the recent achievements in catalytic sulfur transfer, a challenging and timely aim, in which readily available sulfur sources are activated by recyclable transition metal catalysts for effective sulfur transfer to alkenes. The emphasis will be on the synthetic aspects, but the mechanistic work on this formally classified oxidation of alkenes will also be discussed briefly.

2. Stoichiometric Sulfur Transfer

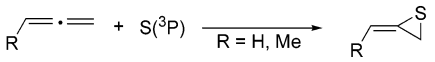
2.1. Atomic Sulfur

The chemistry of atomic sulfur has been intensively studied and reviewed by Strausz.[11] Predominantly, the atomic sulfur was obtained by vapor-phase irradiation of COS. Directly after photolysis, sulfur is in its singlet state [S(^{1}D)], whose reactivity was examined in a methane matrix.[12] With mercury[13] as a triplet sensitizer or in the presence of collisional deactivators such as CO_2[14] or noble gases,[15] the singlet sulfur atom is converted to its triplet ground state [S(^{3}P)]. Thus, the kinetics of trapping of the atomic sulfur species S(^{3}P)[16] and S(^{1}D)[17] with various alkenes was examined independently, and the differing reactivity of the two electronic states was assessed.[13]

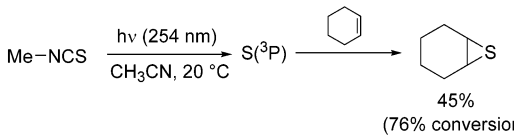
Scheme 1. Stereoselective Addition of Triplet Atomic Sulfur to *Z*-Butene



Scheme 2. Addition of Triplet Atomic Sulfur to Allenes



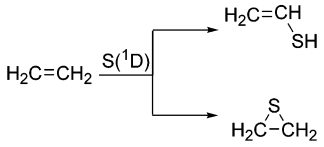
Scheme 3. Direct Episulfidation of Cyclohexene by Triplet Atomic Sulfur



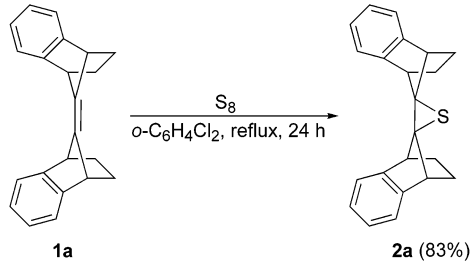
First, the reactions of triplet atomic sulfur will be discussed (Scheme 1). This radical-type atomic sulfur adds to *Z*-butene to form a diradical, which on cyclization and intersystem crossing affords the thiirane; insertion into a C−H bond to form mercaptans was not observed.[13] Due to the fast intersystem crossing (heavy atom effect of sulfur),[18] the episulfidation with S(^{3}P) occurs under retention of the alkene configuration.[19] Since the trapping of S(^{3}P) by a CC double-bond substrate is very efficient, triplet atomic sulfur is also a good candidate for the stereoselective episulfidation of allenes[20] (Scheme 2). Be this as it may, the use of triplet atomic sulfur for stoichiometric preparative episulfidation is of little interest for the following reasons: (a) the photolysis of COS is conducted at wavelengths around 254 nm, and under these reaction conditions the thiiranes do not persistent sufficiently, since the small absorption coefficient of COS requires prolonged reaction times; and (b) the catenation propensity of triplet sulfur atoms leads to S_8 formation, which may only be suppressed at low COS pressure and becomes impractical at the preparative scale.[11] A strategy to overcome these drawbacks was to conduct the reaction in the liquid phase in solvents such as aromatic hydrocarbons,[21] cyclohexene,[22,23] alcohols,[24] and acetonitrile;[24] nevertheless, the episulfide yields were usually below 20%. The use of isothiocyanates as direct precursor to triplet atomic sulfur[25] raised the yield of the episulfide up to 45% at 76% conversion of the alkene, as illustrated for cyclohexene (Scheme 3).[25a] This is remarkable because cyclohexene is quite unreactive toward direct episulfidation, as shall become apparent later on.

In striking contrast to the triplet atomic sulfur [S(^{3}P)], the singlet state [S(^{1}D)] is unsuitable for episulfidation both in the vapor phase and in solution. Already with ethylene, C−H insertion occurs to afford vinylthiol in the vapor phase (Scheme 4).[12,13] The resulting vinylthiol is responsible for complex product mixtures also in solution, in which (other

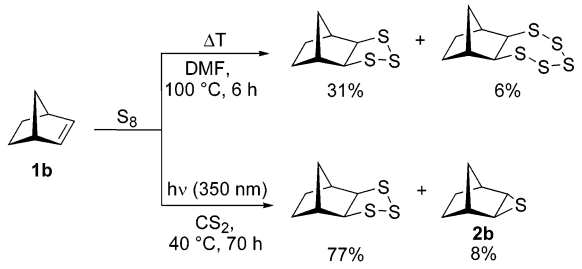
Scheme 4. C−H Insertion of Singlet Atomic Sulfur to Ethylene



Scheme 5. Stereoselective Addition of Elemental Sulfur to *syn*-Bibenzonorbornenylidene (1a)



Scheme 6. Photochemical and Thermal Reaction of Elemental Sulfur (S_8) with Norbornene (1b)

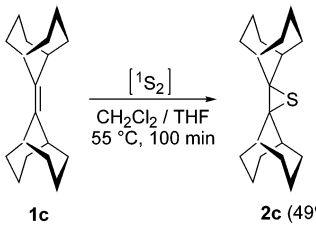


than minor amounts of episulfide) sulfides and disulfides are also formed.[26]

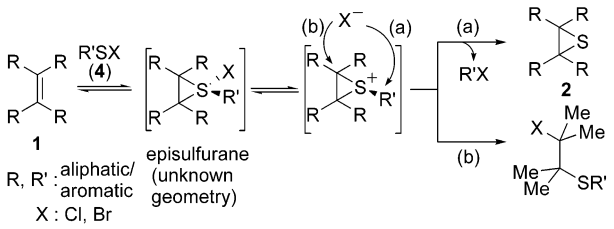
2.2. Elemental Sulfur

The cheapest direct sulfur source, elemental sulfur itself without chemical activation, was used successfully only in a few examples. When *syn*-bibenzonorbornenylidene was heated with S_8 under reflux, the respective episulfide was obtained stereoselectively in 83% yield (Scheme 5).[27] In the case of the anti isomer, the *anti*-episulfide was formed in a similar yield (72%). The retention of configuration was explained in terms of an intermediary diradical oligosulfide, which collapses to the episulfide before C−C bond rotation occurs.[27] Similarly, only in exceptional cases were episulfides obtained; for example, the thiiranes of the sesquiterpenes humulene and caryophyllene.[28] Additionally, adamantylidene adamantane[29] and norbornadiene,[30,31] were transformed in 25−58% yields to their episulfides. In other cases, the alkenes were either inactive for episulfidation or oligosulfides were formed. When norbornene was treated with thermally or photochemically activated sulfur (Scheme 6), 31% of norbornene trithiolane and 6% of norbornene pentathiepane were isolated in the thermal reaction,[30] whereas at least 8% of norbornene episulfide was observed in the photochemical reaction as a minor product together with 77% of norbornene trithiolane.[32] Nevertheless, alkene **1c** (Scheme 7) and adamantylidene adamantane were episulfidated in quite good yields.[33]

Scheme 7. Episulfidation of Alkene 1c with Diatomic Sulfur



Scheme 8. Mechanism for the Episulfidation and Ring-Opening Reaction of Alkene 1 by Sulfenyl Halides 4



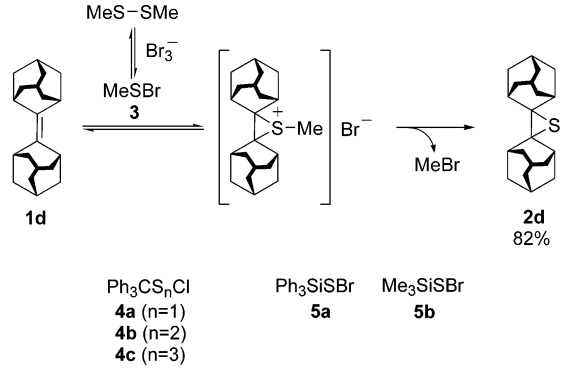
2.3. Sulfur Halides

In this section, we shall consider sulfenyl halides (RSX), namely, the sulfur chlorides SCl_2 and S_2Cl_2, as direct episulfidation sources; indeed, the chemistry of sulfenyl halides is well-documented.[34] Due to the strong electron-withdrawing effect of the halogen (X = Cl, Br), the partially positively charged sulfur atom facilitates the nucleophilic attack by an alkene molecule. For this reason, sulfenyl halides transfer a sulfur atom to an alkene at subambient temperatures (even below 0 °C), but only under special conditions may thiiranes be isolated, as will be detailed later on.

The mechanistic pathway of the reaction of sulfenyl chlorides with alkenes is given in Scheme 8, which has been substantiated by ab initio computational work at the RHF/3-21G* level.[35] An addition−elimination process was suggested in which first the episulfurane is formed and subsequently the chloride anion is lost to afford the thiiranium ion. The thiiranium ion may react with the halide ion in two ways: Either the halide attacks as a nucleophile at the exocyclic sulfonium substituent (path a) or on the carbon atom of the three-membered ring (path b). To minimize the latter possibility, which is unproductive in regard to thiirane formation, the alkene should have either bulky substituents (adamantyl) or the sulfonium sulfur substituent R′ should have a higher affinity for the halide attack than the endocyclic carbon atom of the thiiranium ring.[36] In Scheme 9, the first event is illustrated with adamantylidene adamantane (**1d**), in which methyl bromide is eliminated to afford the thiirane **2d** in 82% yield.[37] In the same sense, the sulfenyl chlorides **4** were utilized and the episulfides **2c** and **2d** were isolated in 93% yield.[38] In the case of sterically less encumbered alkenes, for instance, norbornene (**1b**), 1,2-addition through a ring opening of the intermediary thiirane by another molecule of sulfenyl chloride was observed as a side reaction.[39]

The second possibility is realized by employing silyl sulfenyl bromides **5** as episulfidizing agents. Quite

Scheme 9. Episulfidation of Adamantylidene adamantane (1d) with Methyl Sulfenyl Bromide (3)



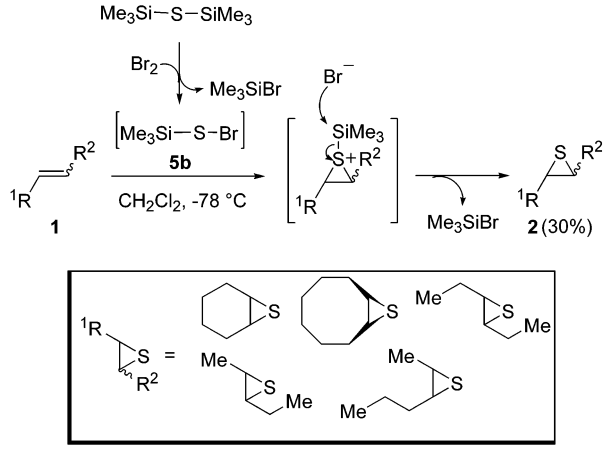
generally, sulfenyl bromides are more reactive but also more selective in addition reactions with alkenes.[34] The lower strength of the S−Br as compared to the S−Cl bond enhances the reactivity of the sulfenyl bromides, while the larger bromide ion attacks preferentially the sterically less congested substituent of the exocyclic sulfonium sulfur atom. If, in addition, a silyl group is used as the exocyclic substituent, the higher affinity of the bromide ion for silicon than for carbon completely circumvents the undesirable 1,2-addition. Thus, the reaction of sulfenyl bromide **5a** with an excess of cyclohexene gave the corresponding episulfide in 20% yield, detected by GC-MS but not isolated.[40] Furthermore, Capozzi and co-workers[41] developed an one-pot synthesis of thiiranes for trimethylsilylsulfenyl bromide (**5b**) as direct sulfur source at −78 °C (Scheme 10), the lowest reaction temperature so far utilized in episulfidations.

This episulfidation is highly selective since only 1,2-disubstituted alkenes **1** afford the corresponding episulfides **2** under preservation of the alkene configuration; however, the episulfide yield was only 30%. The reason for the low yield is the reversibility of the episulfidation, as confirmed by means of a control experiment, in which the authentic episulfides were desulfurized, when treated with trimethylsilyl bromide.[41]

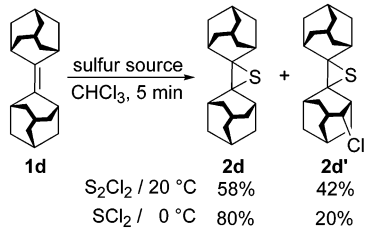
In contrast to the sulfenyl halides, the episulfidation by the sulfur chlorides S_2Cl_2[42a] and SCl_2[27,42b,43] is not stereoselective. The lack of stereoselectivity has been rationalized in terms of carbocations, formed by reversible ring opening of the intermediary thiiranium ion.[27] As further evidence for the intermediacy of carbocations, the formation of the chlorinated thiirane **2d′** in Scheme 11, obtained with sulfur monochloride (S_2Cl_2) and sulfur dichloride (SCl_2) possibly through a nonclassical carbocation, may be taken.[42]

In general, the direct episulfidation of alkenes with the sulfur chlorides suffers two main disadvantages: First, the thiirane may be desulfurized back to the alkene by the sulfur chloride. Second, SCl_2, which is also present in the S_2Cl_2 by disproportionation, dissociates into chlorine.[42a] The in situ generated chlorine may chlorinate the thiirane or add to the CC double bond of the alkene.[27,42a] To date, only adamantylidene adamantane (**1d**)[42] and substituted 7-adamantylidene norbornanes[43] have been successfully epsulfidized in good yields under precisely optimized reaction conditions.

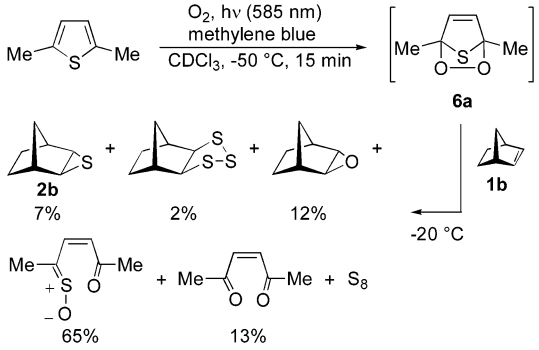
Scheme 10. Stereoselective Episulfidation of Alkenes 1 with Trimethylsilylsulfenyl Bromide (5b)



Scheme 11. Episulfidation of Adamantylidene adamantane (1d) with Sulfur Chlorides



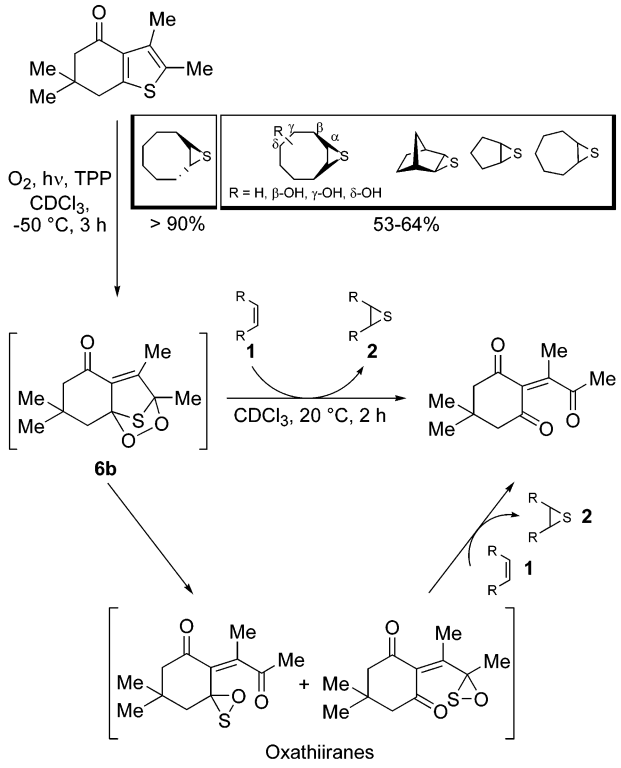
Scheme 12. Sulfur and Oxygen Transfer to Norbornene (1b) in the Decomposition of the Thiophene Endoperoxide 6a



2.4. Oxathiiranes and Thiophene Endoperoxides

An alternative preparation of thiiranes directly from alkenes of synthetic potential was reported in a communication by Matturro and co-workers.[44] On warming up the thiophene endoperoxide **6a**, which was obtained on photooxygenation of the corresponding thiophene, in the presence of norbornene, the episulfide **2b** was observed in a low (ca. 7%) yield (Scheme 12). This mechanistic study motivated our group[45] to exploit this direct episulfidation for preparative purposes by optimizing the structure of the thiophene endoperoxide **6** as well as the reaction conditions to obtain better yields of episulfide. The thermolysis of the thiophene endoperoxide **6b** was carried out in the presence of more reactive olefinic

Scheme 13. Episulfidation of Cycloalkenes by Thiophene Endoperoxide 6b

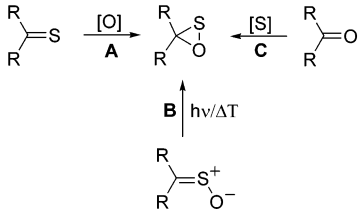


substrates as sulfur acceptors, as displayed in Scheme 13. The yields of episulfide were excellent (>90%) for *E*-cyclooctene and fairly good (53−64%) for *Z*-cyclooctene, cyclooctenols, norbornene, cyclopentene, and cycloheptene. In all cases, the initial configuration of the alkene was conserved in the resulting episulfide.[45]

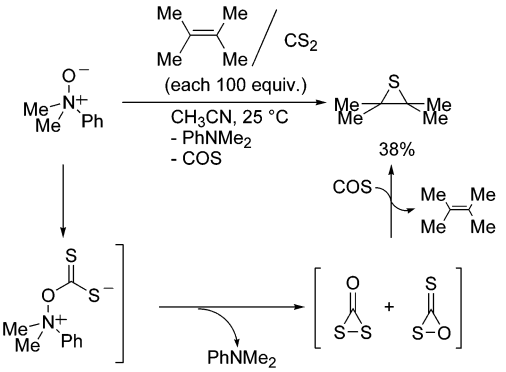
The mechanism of the reaction was proposed to involve the two possible oxathiiranes as intermediates. A comparative kinetic study of the epoxidation by dimethyldioxirane (DMD) showed that the reactivity of the alkenes as well as the diastereoselectivity of the epoxidation parallel those of the episulfidation by the thiophene endoperoxide **6b**.[46] Analogous to the results reported by Shea and Kim[47] for the epoxidation with *m*CPBA, we have observed a similar influence of ring strain on the reactivity of the cyclic alkenes in this episulfidation.[46] In view of the same reactivity and diastereoselectivity trends, it was suggested that in the epoxidation by DMD and in the episulfidation by the endoperoxide **6b** similar species are involved, namely, that the sulfur-transferring intermediate should possess an oxathiirane structure analogous to the dioxirane.[46]

Oxathiiranes have also been invoked as intermediates in some other synthetic transformations (Scheme 14), namely, in the oxidation of a thiocarbonyl compound (path A), in the electrocyclic ring-closure of thioketone *S*-oxides (path B), and in the thionation of the α-triketone of ninhydrin (path C). All three synthetic methods shall now be briefly outlined: As an example for path A, oxathiiranone and dithiiranone have been postulated as possible sulfur donors in the reaction of *N*,*N*-dimethylaniline *N*-oxide and carbon disulfide (Scheme 15).[48] In the presence of the

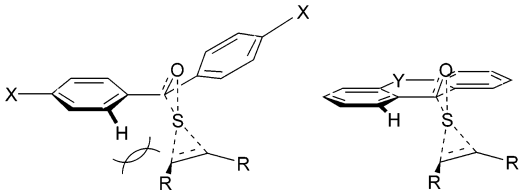
Scheme 14. Different Preparative Routes for the In Situ Synthesis of Oxathiiranes



Scheme 15. Oxidation of Carbon Disulfide and Sulfur Transfer to Tetramethylethylene



Scheme 16. Transition States of the Episulfidation by Oxathiiranes



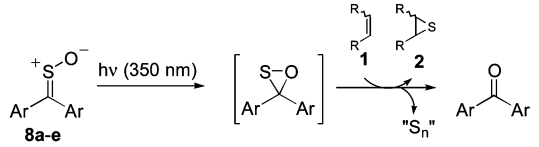
electron-rich tetramethylethylene, this oxidative desulfuration of carbon disulfide afforded as much as 38% of the corresponding thiirane. The preparative use of this unusual reaction is limited because of the 100-fold excess of the alkene and carbon disulfide.

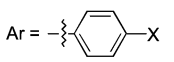
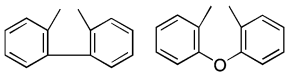
A more expedient source of oxathiiranes as sulfur donors to alkenes (path B) constitutes the photolysis of aromatic thioketone *S*-oxides **8**;[49] the latter photoreaction has been known for some time,[50] but not employed for the synthesis of episulfides. As depicted in Table 1, we have used norbornene (**1b**) and the two *E*- and *Z*-cyclooctenes **1e** for this purpose. Indeed, the photolysis of the sulfines **8a**−**e** in the presence of an excess of *E*-**1e** yielded the corresponding thiiranes in >90% yield; however, the episulfidation of norbornene (**1b**) and *Z*-cyclooctene (*Z*-**1e**) was realized in only low yields. The sulfines **8d**,**e** perform somewhat better than **8a**−**c**, which has been attributed to the lower steric interactions between the alkene acceptor and the oxathiirane donor in the postulated spiro transition state (Scheme 16).[49]

These promising results obtained with in situ prepared oxathiiranes led our group to develop a further and more general access (path C) to the reactive oxathiiranes (Scheme 17). An excess of potassium *p*-thiotosylate on indanetrione (ninhydrin) in the presence of an excess of *E*-cyclooctene afforded the related episulfide in 18% yield.[51]

When the strained acetylene cyclooctyne was employed as sulfur acceptor, the thermolysis of the

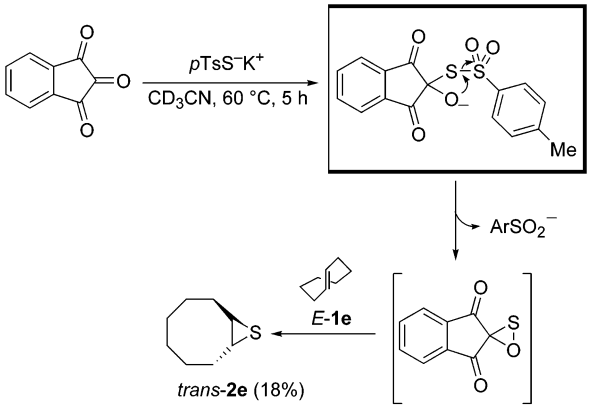
Table 1. Photochemically Induced Sulfur Transfer from the Sulfines 8 to the Alkenes 1[a]



	episulfide **2** [%]		
	norbornene	cyclooctene	
thioketone-*S*-oxide		*Z*	*E*
Ar =  **8a** (X=H) **8b** (X=Cl) **8c** (X=OMe)	12-13	< 5	80-92
Ar,Ar =  **8d** **8e**	17-18	11-13	79-94

[a] Yield of episulfide **2** is based on the initial amount of thioketone *S*-oxide **8**.

Scheme 17. Generation of an Oxathiirane in the Reaction of Potassium Thiotosylate with Ninhydrin and the Episulfidation of *E*-Cyclooctene (*E*-1e)



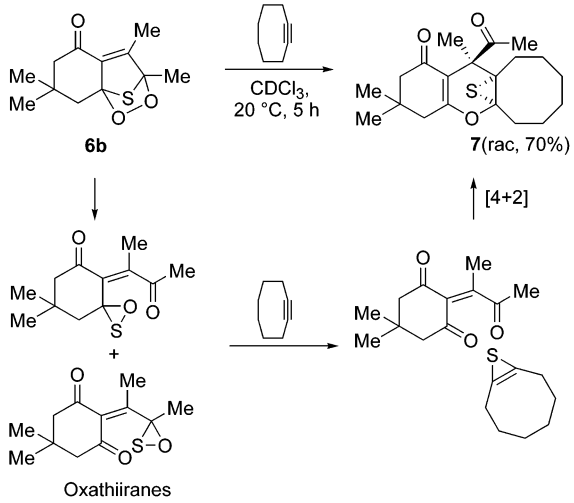
thiophene endoperoxide **6b** led to the episulfide **7** in good yield.[52] Presumably, the labile thiirene is released, which on in situ [4+2] cycloaddition with the ene dione generated in the thermolysis of **6b** leads to the episulfide **7** (Scheme 18).[52]

2.5. Cyclic Thiosulfonates and Sultenes

In the preceding section, we described that oxathiiranes, which may be obtained either thermally or photochemically from thioketone *S*-oxides **8**, may serve as potential sulfur donors to alkenes. While oxathiiranes are presumably involved not only in the photolysis but also in the thermolysis of the sulfine derivatives **8a**−**c**, some aromatic thioketone *S*-oxides such as **8d** or **8e**, and especially thioaldehyde *S*-oxides, generate the alkene on thermolysis by sulfur extrusion rather than afford the corresponding ketone through its oxathiirane (Scheme 19).[53] Clearly, this alternative reaction pathway reflects a different thermal reactivity of the sulfines toward alkenes: Whereas **8a**−**c** persist on heating in chloroform solution up to 60 °C,[49] the more reactive thioketone *S*-oxides **8d**,**e** effect sulfur transfer to norbornene (**1b**) and *Z*-cyclooctene (*Z*-**1e**).[54]

As for alkene formation (Scheme 19), it has been suggested that a [3+2] cycloaddition between two

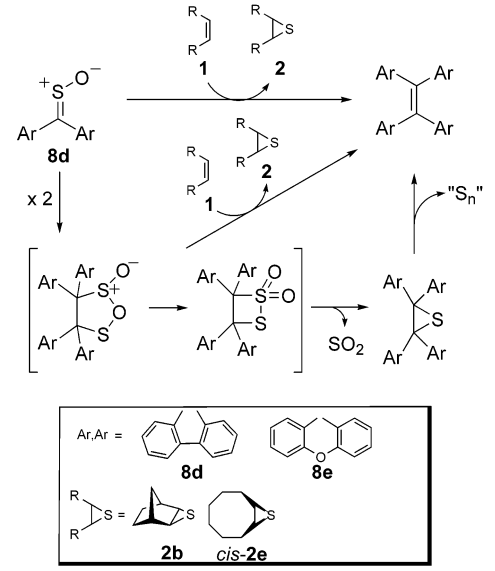
Scheme 18. Episulfidation of Cyclooctyne by Thiophene Endoperoxide 6b



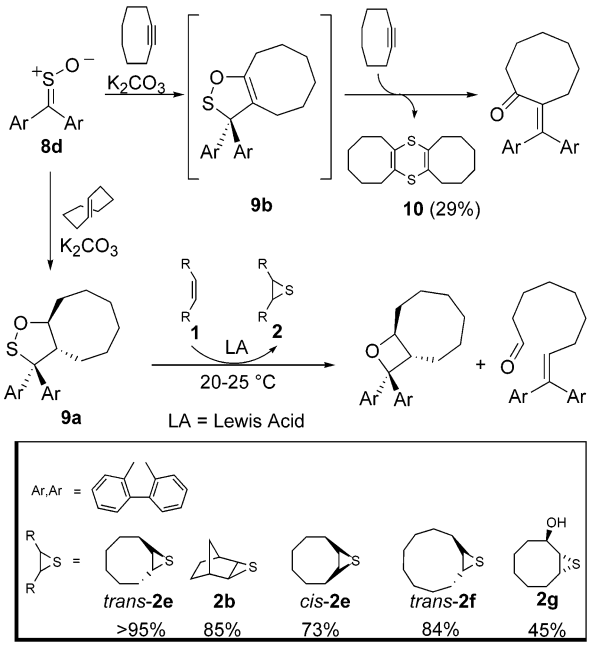
sulfine molecules leads to the initial cycloadduct, which subsequently rearranges to a cyclic thiosulfonate; subsequent loss of sulfur dioxide and elemental sulfur yields the alkene. The primary [3+2] cycloadduct or the resulting thiosulfonate may act as sulfur donor to norbornene (**1b**) and *Z*-cyclooctene (*Z*-**1e**), but control experiments have shown that it is not the extruded sulfur.[54] A similar intramolecular sulfur transfer of an unsaturated thioaldehyde *S*-oxide appears to follow also the mechanism illustrated in Scheme 19.[55]

When *E*-cyclooctene (*E*-**1e**) is employed in the thermolysis of the sulfine **8d**, an oxetane and an aldehyde are obtained (Scheme 20).[54] In this reaction, carried out in the presence of potassium carbonate to scavenge traces of acid (hydrochloric acid is unavoidable in chlorinated solvents), the thermally labile bicyclic sulfenate, namely, the sultene **9a**, was isolated and demonstrated to serve as a sulfur donor to alkenes in its acid-catalyzed thermolysis.[54] Thus, with trifluoroacetic acid as catalyst, the sultene **9a** afforded the corresponding episulfides in excellent yields (90−95%) with norbornene (**1b**) and cyclooctenes (**1e**).[54] Especially when mild Lewis acids (e.g.,

Scheme 19. Sulfur Transfer by Sulfines 8d and 8e to *Z*-Cyclooctene (*Z*-1e) and Norbornene (1b)



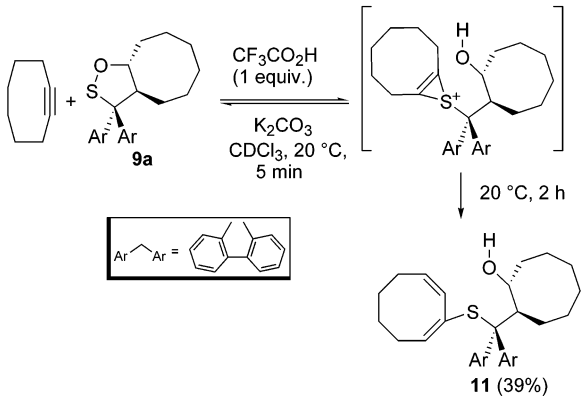
Scheme 20. Sulfur Transfer by Sultene 9a and Sultine 9b



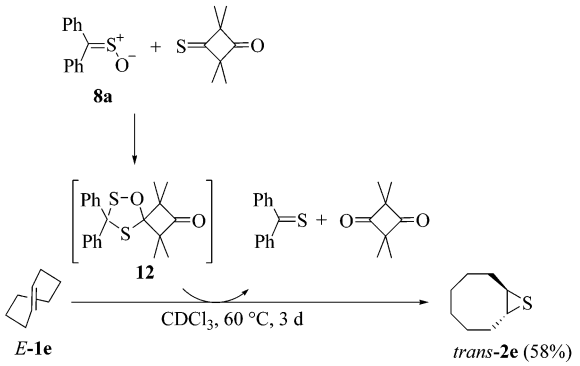
main group metal halides), Jacobsen's catalyst, and tin porphyrins are used, the sulfur transfer takes place readily at room temperature.[56] Despite the pronounced reactivity of this sultene, the sulfur transfer occurs only in special cases in good yield with norbornene (**1b**), the *E*/*Z*-cyclooctenes (**1e**), *E*-cyclododecene (**1f**), and α-cyclooctenol (**1g**) under Lewis acid catalysis.[56] Although most of the yields have been determined by means of NMR spectroscopy, in some cases the thiirane product was isolated and obtained in good yields (>70%). Tetramethylethylene, cyclopropylidenes, and cycloheptene are not episulfidated by the sultene **9a**.[57] Presumably, steric inhibition by the bulky fluorenyl substituent is responsible for the critical choice of the alkene as reaction partner with the sultene **9a**.

An attempt failed to isolate the sultine **9b** from the reaction of fluorenyl sulfine (**8d**) with cyclooctyne, in

Scheme 21. Sulfur Transfer to Cyclooctyne by Sultene 9a



Scheme 22. Episulfidation of *E*-Cyclooctene (*E*-1e) in the Thermolysis of the In Situ Generated 1,2,4-Oxadithiolane 12



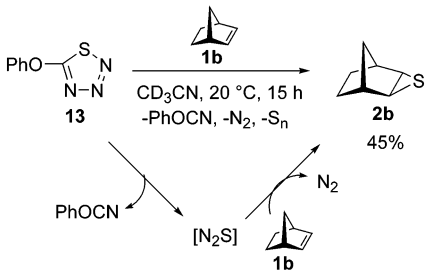
an analogous manner as proved successful for the sultene **9a**. Instead of the desired sultine, the dithiine **10** was obtained, presumably by sulfur transfer to cyclooctyne and subsequent dimerization of the in situ generated thiirene.[58]

Under trifluoroacetic acid catalysis, the sultene **9a** also reacted with cyclooctyne, but a thiirenium ion was formed (Scheme 21) that persisted in solution for several hours after exchange of the trifluoroacetate against the perchlorate anion. Remarkable and unprecedented is the fact that the thiirenium ion reverses back to the starting materials when K_2CO_3 is added. In contrast, the thiirenium chloride decomposed as depicted in Scheme 21 to the vinyl sulfide **11**, which was isolated in 39% yield.[52] The involvement of a thiiranium (thiirenium) ion favors a concerted, monocentered, polar reaction pathway for alkenes (alkynes), which parallels the mechanism proposed for the reaction of sulfenyl halides with alkenes (cf. Scheme 8 in section 2.3).

2.6. 1,2,4-Oxadithiolanes

In light of the promising results obtained with the sultene as episulfidation agent, we anticipated that such direct sulfur-transfer methodology should be extendable to other sulfur heterocycles. The related 1,2,4-oxadithiolane **12** contains the reactive sulfenate functionality and may be generated in situ from the sulfine **8a** and a reactive thioketone (Scheme 22). Indeed, when conducted in the presence of *E*-cyclooctene, besides the thermolysis products (namely,

Scheme 23. Sulfur Transfer to Norbornene (1b) by Thiatriazole 12



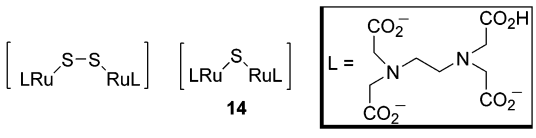
thiobenzophenone and the dione), the episulfide *trans*-**2e** was isolated in 58% yield.[59]

2.7. 1-Thia-2,3,4-triazoles

In section 2.1, we have reported that the photolysis of several sulfur-containing compounds generates atomic sulfur, which is trapped by alkenes in the form of episulfides. Also 1,2,3,4-thiatriazoles serve this purpose, when photolyzed in liquid cyclohexene;[22] however, in the thermolysis of 1,2,3,4-thiatriazoles **13**, dinitrogen sulfide was observed as a sulfur donor.[60] Indeed, in the presence of norbornene (**1b**) and *E*-cyclooctene (*E*-**1e**), the corresponding episulfides were obtained. Thus, the parent episulfides were isolated in 45% and 80% yields, when 5-phenyloxy-1,2,3,4-thiatriazole (**13**) was thermolyzed at room temperature (Scheme 23).[61] In a recent theoretical study, it was shown that the liberated N_2S transfers its sulfur atom not in an addition−elimination mechanism through a thiiranium ion (like sulfur halides **3**−**5**,[35] sultene **9a**,[54] and presumably thiosulfonates[54,55]) but through a concerted S_N2 reaction pathway (like DMD[62] and oxathiiranes[49]).[63]

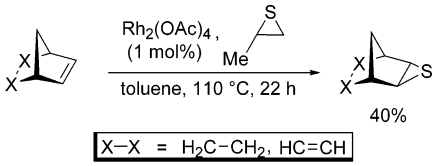
3. Metal-Catalyzed Sulfur Transfer

In 1991, the first metal-catalyzed sulfur transfer to cyclohexene was claimed by Taqui Khan and Siddiqui,[64] in which a persulfidoruthenium(IV) complex was used as the active sulfur-transferring agent and elemental sulfur as the sulfur source. When two equivalents of cyclohexene were treated with the disulfur complex in a protic medium (ethanol/water), the cyclohexene episulfide was supposedly observed, but no yield was given. In the proposed catalytic cycle, the [RuL] complex activates first the elemental sulfur (S_8) in form of the $\mu-\eta^1$-disulfide complex, the latter is converted to a $\mu-\eta^1$-sulfide complex **14**,



which subsequently transfers a sulfur atom to cyclohexene to regenerate the initial [RuL] complex to sustain the catalysis. Unfortunately, our attempt to reproduce this report failed, since not even traces of the cyclohexene episulfide were detected by GC analysis. Even when the stoichiometric mode of this ruthenium catalysis was tested by using directly the preformed sulfur-activated ruthenium complex **14**, no thiirane was observed.

Scheme 24. Rhodium-Catalyzed Sulfur Transfer to Norbornene and Norbornadiene

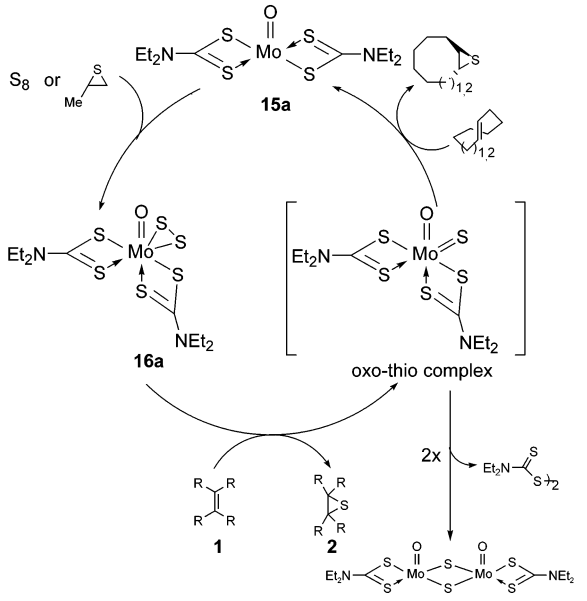


Later, Kendall and Simpkins[65] reported the rhodium-catalyzed sulfur transfer to norbornene and norbornadiene as sulfur acceptors and methylthiirane as sulfur donor (Scheme 24). This attractive metathesis reaction offers a direct and effective method of episulfidation. The norbornene and norbornadiene episulfides were isolated both in 40% yield by simply heating together the alkene substrate, 1 mol % of rhodium acetate and a 2.3-fold excess of methylthiirane at 110 °C for 22 h. The scope of this promising metathesis reaction has yet not been explored, nor its mechanism elucidated.

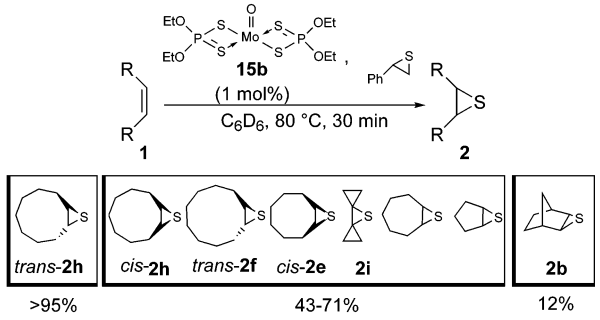
The advantages of a metal-catalyzed sulfur-transfer process for the direct episulfidation of alkenes over the so far presented stoichiometric reactions are manifold: (i) In view of the metal activation, a cheap and easily accessible sulfur source may be employed (e.g., elemental sulfur). (ii) Product selectivities may be controlled by the proper design of the activating metal catalyst. (iii) The active sulfur-transferring species may be generated in situ in low concentrations by using little metal catalyst, which may favor sulfur transfer over extrusion of elemental sulfur by adjusting the amount of the alkene substrate. (iv) The metal catalyst may be recycled and the amount of toxic waste material minimized.

In view of these advantages of the catalytic versus the stoichiometric episulfidation process and the limited activity in this challenging and promising field of sulfur chemistry, our group set out to develop a viable sulfur-transfer system based on metal catalysis. For this purpose, we employed the known molybdenum disulfur complex **16a**[66] (Scheme 25), accessible by treating the known molybdenum oxo complex **15a**[67] with S_8 or propene sulfide as sulfur sources.[68] First, the feasibility of the disulfur complex **16a** as sulfur-transferring agent had to be demonstrated under stoichiometric conditions. The oxo complex **15a** was allowed to react with elemental sulfur to form in situ the disulfur complex **16a**, and subsequently the alkene was added. Under these stoichiometric conditions, the substrates cyclopentene, cycloheptene, norbornene, *Z*-cyclooctene, dicyclopentadiene and bicyclopropylidene are all transformed in moderate yields to their episulfides by the disulfur complex **16a**. Under catalytic conditions, with the less reactive alkenes (e.g., Z-cyclooctene), the intermediary oxo-thio complex decomposes faster into a dimer,[69] which is inactive for sulfur transfer, than transfers a sulfur atom to the alkene.[70] When, however, the reactive substrates *E*-cyclooctene or *E*-cyclononene are used, the catalytic cycle in Scheme 24 is sustained, and their episulfides have been isolated in 69% and 87% yields with 8 mol % of the

Scheme 25. Catalytic Cycle for the Molybdenum-Catalyzed Sulfur Transfer to Alkenes



Scheme 26. Episulfidation of Alkenes, Mediated by the Molybdenum Oxo Complex 15b

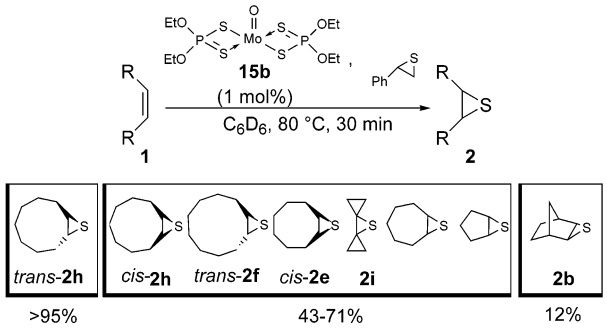


catalyst **15a**.[71] Similarly, also isonitriles may be used as sulfur acceptors, which afford the corresponding isothiocyanates in high to excellent yields.[72]

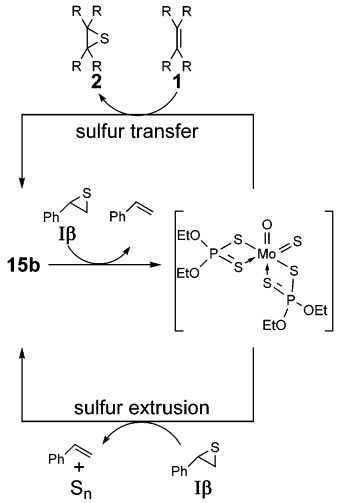
To develop a more efficient and general catalytic episulfidation method, a metal catalyst screening was carried out,[70] which revealed that the molybdenum oxo complex **15b**, in combination with styrene sulfide as sulfur source, is so far the most reactive catalyst system for the episulfidation of alkenes (Scheme 26).[70] Heating of the alkenes with complex **15b** (1 mol %) in the presence of an excess

(1.1−1.5 equiv) of phenylthiirane in toluene at 80 °C for 30 min afforded the episulfide of *E*-cyclononene (*E*-**1h**) quantitatively; those of *Z*-cyclononene (*Z*-**1h**), *E*-cyclodecene (*E*-**1f**), and *Z*-cyclooctene (*Z*-**1e**) in good yields; those of bicyclopropylidene (**1i**), cycloheptene, and cyclopentene in moderate yields; but the episulfide of norbornene (**1b**) in low yield.[70] The low yield of the norbornene episulfide is attributed to the high steric demand of the catalyst **15b**.[70] Of particular note is the dispirocyclic thiirane **2i**, which is now readily accessible through our novel synthetic methodology. Furthermore, for the first time the thermally persistent methylenethiiranes have been prepared from a variety of allenes by this catalytic episulfidation process (Scheme 27).[70] All attempts to isolate the active form of the catalyst **15b**

Scheme 27. Molybdenum-Catalyzed Episulfidation of Allenes



Scheme 28. Sulfur Transfer and Extrusion of Sulfur, Mediated by the Molybdenum Oxo Complex 15b with Phenylthiirane (I*β*) as Sulfur Source



have failed so far, but on the basis of ^{31}P NMR spectra, we suggest an oxo-thio complex as intermediate (Scheme 28). The latter either transfers sulfur to an alkene or extrudes elemental sulfur on reaction with a sulfur donor molecule (phenylthiirane).[70]

4. Future Perspectives

The current review makes evident that the direct thioepoxidation of alkenes, contrary to the nowadays intensively explored, mechanistically well-understood, and preparatively established epoxidation,[73] still represents a formidable challenge in sulfur chemistry.[73a] More than 20 alternatives to realize direct sulfur transfer to alkenes have been presented herein, most of these of the stoichiometric type, as well as a few catalytic ones; but none of these to date offers the desired broad preparative scope. For instance, none of the so far available preparative methods may be used to episulfidate even a tetrasubstituted and quite reactive acyclic alkenes such as tetramethylethylene. Several reasons may be proposed to account for the difficulties in realizing sulfur transfer in a general manner versus the well-established oxygen transfer: A most significant feature of sulfur versus oxygen is its much lower electronegativity, which limits severely the electrophilic character of the sulfur donor; thus, the unreactive sulfur source must either be activated (a good

example is the sulfur transfer by the sultene **9a** in the presence of acid catalysts), or a reactive sulfur donor must be generated in situ (e.g., the formation of oxathiiranes in the photolysis of sulfines). Another disadvantage of sulfur versus oxygen for transfer processes is the persistence of the S−S bond as compared to the labile nature of the O−O bond, which provides sulfur the propensity to catenate; consequently, instead of sulfur transfer, the reactive sulfur donor prefers to extrude elemental sulfur (in oligomeric or polymeric form).[74] This may be particularly problematic in metal-catalyzed sulfur-transfer processes.[70] Furthermore, unlike oxygen, sulfur may exist in higher oxidation states (+IV or +VI), which implies that the divalent sulfur donor necessary for the sulfur transfer may be readily oxidized, especially under the conditions of oxidative activation.

Despite these problems, substantial progress has been achieved in the development of more effective sulfur donors, as should have become evident from our efforts during the last handful of years. Nonetheless, much work will still be necessary to design more reactive and selective sulfur-transferring systems. Little if anything is as yet known on chemoselectivity, regioselectivity, diastereoselectivity, and enantioselectivity. In this context, catalysis by transition metals should be definitely an advantage since the ligand sphere as well as the activating metal may be properly tuned to achieve reactivity and selectivity through the template effect.[75] In this spirit, we hope that our timely review will stimulate chemists to become active in this fascinating and challenging research field of sulfur chemistry.

5. Acknowledgment

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