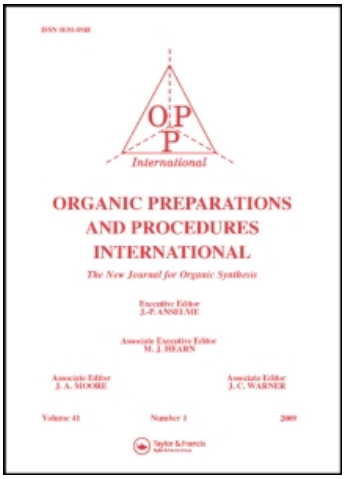

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RECENT PROGRESS IN THE USE OF SULFONYL RADICALS IN ORGANIC SYNTHESIS. A REVIEW

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INTRODUCTION

Sulfonyl radicals are versatile intermediates which can be used either as entering or leaving groups, or both simultaneously. Due to their ability to fragment, they are also employed as a source of alkyl radicals, mostly perfluoroalkyl radicals. Although their reactivity has been the subject of a few general reviews dealing with all of the sulfur-centered radicals,[1] up to now only one chapter has been devoted specifically to the structural, theoretical and chemical properties of sulfonyl radicals.[2] Over the last decade, an increasing number of publications have dealt with the synthetic potential of these short-lived intermediates. This review will focus on the properties of sulfonyl radicals and illustrate the benefits that can be derived from these properties for synthetic purpose. This survey is divided into five sections: properties; precursors and methods of formation; sulfonyl radicals as leaving groups (fragmentation of β-sulfonyl radicals); sulfonyl radical as the entering group, including addition of sulfonyl radicals to alkenes, alkynes and allenes, sulfonyl radical-mediated cyclization of dienes, enynes and enallenes and S_H2' reactions on allylic and vinylic compounds; sulfonyl radical as both the leaving and the entering groups, including rearrangement and addition of allylic sulfones and rearrangement of alkenyl tosylates; α-scission as a route to alkyl radicals and reactions with thiohydroxamates.

I. CHARACTERISTIC PROPERTIES

1. Polar Character. Addition to π Bonds

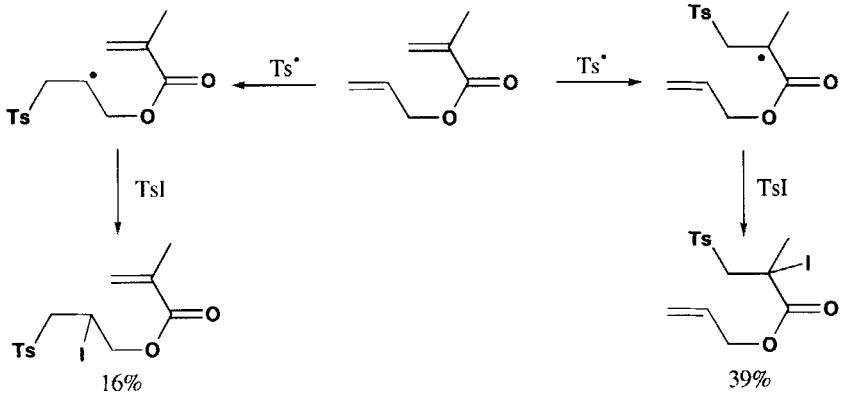
Sulfonyl radicals are reputed to be electrophilic radicals. Their polar character was deduced from the kinetics of their addition to substituted styrenes.[3a,b] The rate of addition of aryl sulfonyl radicals decreases as the electron-donating property of the *para* substituent on the aromatic ring increases. Hammett plots lead to ρ^+ values ranging from - 0.35 to - 0.88 for the addition of variously substituted benzenesulfonyl radicals. Substituted phenylacetylenes exhibit the same trend.[3c]

The following sequence of reactivity of alkenes toward benzenesulfonyl radical was established by Takahara *et al.*[3d]

CH_2=CH-C≡N (0.06) < CH_2=CH-CO_2Me (0.012) < CH_2=CH-Ph (1) < CH_2=C(Me)-Ph (3.21)

However 1-hexene and vinyl acetate did not follow this correlation. These data led to the conclusion that 1-hexene is 2.49 times more reactive than vinyl acetate towards benzenesulfonyl radical; methyl acrylate and methyl methacrylate are 1.57 times and 9.83 times more reactive respectively than vinyl acetate, which is somewhat surprising for an electrophilic radical.

Other data[3e] also indicate that the electrophilic character of tosyl radical is reliable only in a homologous series. According to competitive experiments, the rate constants for the addition of tosyl radical to allylpropyl ether and propyl acrylate are nearly identical. The addition of tosyl iodide to allyl methacrylate shows that an alkyl substituent attached to the sp^2 carbon α to the carboxylate is sufficient to reverse the selectivity with respect to predictions based on electrophilicity (Scheme 1).

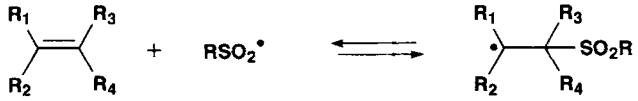


Scheme 1

It is clear that polar effects are not the only factor controlling the competitive additions of sulfonyl halides to olefins. Unfortunately, unlike many other radicals, very few absolute rate constants have been reported for sulfonyl radicals. Gozdz and Maslak[3f] have determined the relative reactivity of various alkenes and alkenylsilanes towards methanesulfonyl radical. According to this study, the rate constant for the addition of methanesulfonyl radical to 1-hexene is nearly diffusion-controlled - k_{add} = 1 x 10^9 M^{-1} s^{-1} at 0° in acetonitrile. The observed scale of reactivity correlates with the ionization potential of the olefins, which again confirms the electrophilicity; however the reversibility of the addition complicates kinetic analyses. To draw any conclusion from competitive kinetic measurements, the extent of reversibility must be estimated. Otherwise, the reversibility must be minimized by the use of precursors such as sulfonyl iodides or some bromides which serve as excellent donors in the second propagation step. Care should be taken, since sulfonyl iodide adducts are often unstable and decompose under irradiation with visible light.

2. Reversibility of the Addition to Alkenes

Addition to π systems is probably the most important reaction of sulfonyl radicals. Evidence for the reversibility of this reaction (Eq. 1) was provided in early studies by the isomerization of *cis* and *trans* 2-butenes that accompanies their copolymerization with SO_2.[4a] This reversibility is responsible for the very low temperatures above which the formation of long-chain polymers will not occur at a given monomer concentration in the alternate polymerizations of olefins with SO_2.[4a,b] The phenomenon of isomerization was also reported for the Cu(I)-mediated reaction of 2-butenes with benzenesulfonyl chloride.[4c,d]



(1)

The extent of reversibility depends on the nature of the sulfonyl radical. According to thermochemical data,[5] the enthalpy variation during the addition step would be close to zero for benzenesulfonyl radical. Conversely, the addition of methanesulfonyl radical would be exothermic (≈10 kcal per mole). This is in agreement with the assumption that the very rapid addition of $MeSO_2^•$ to *n*-alkenes proceeds through an early transition state.[3f] This property is a general feature associated with sulfur-centered radicals.[6] The rate constant for the elimination of $PhSO_2^•$ can be estimated at approximately 1 x 10^7 s^{-1} at 25° from the data of Wagner *et al.*[6a] As a consequence, benzenesulfonyl radicals are good leaving groups from β-sulfonyl radicals which, as will be shown later on, gives rise to interesting S_H2' reactions and makes allyl arylsulfones a valuable source of sulfonyl radicals.

3. α-Scission

The α-scission of most sulfonyl radicals is an unfavorable endothermic process (in fact since the electron density is shared, nearly equally, between the sulfur atom and the two oxygens, the fragmentation can also be viewed as the β-scission of oxygen-centered paramagnetic species) (Eq. 2).

$$R\text{-}SO_2^• \longrightarrow R^• + SO_2 \qquad (2)$$

Bond dissociation energies were estimated at 18 and 44 kcal. mol^{-1} respectively for R = CH_3 and R = Ph in the gas phase;[5a] lower values were found in solution.[7a] The endothermicity is reduced when the fragmentation leads to stabilized radicals such as allyl or benzyl radicals.[5a] The rate for loss of sulfur dioxide from $PhCH_2SO_2^•$ is too rapid to be measured by standard laser flash photolysis techniques, it is estimated greater to 10^8 s^{-1} at 295 K.[7b] However these reactions are of little synthetic interest. During the study of the photoaddition of $PhCH_2SO_2SePh$ to cyclohexene, Kice *et al.*[7d] observed that no adduct was formed; benzylphenylselenide was isolated in nearly quantitative yield (Eq. 3-5).

$$PhCH_2SO_2SePh \xrightarrow{h\nu} PhCH_2SO_2^• + PhSe^• \qquad (3)$$

$$PhCH_2SO_2^• \longrightarrow PhCH_2^• + SO_2 \qquad (4)$$

$$PhCH_2SO_2SePh + PhCH_2^• \longrightarrow PhCH_2SePh + PhCH_2SO_2^• \qquad (5)$$

Homolysis gives a sulfonyl radical which fragments very rapidly into benzyl radical which undergoes a transfer reaction with the selenosulfonate rather than an addition reaction to the alkene. Similarly, perfluoroalkanesulfonyl radicals fragment readily. They were shown to be convenient sources of perfluoroalkyl radicals (for synthetic applications, see section VI).[7]

II - PRECURSORS AND METHODS OF GENERATION

Synthetic planning necessitates first the choice of the best precursor and of the appropriate mode of initiating homolysis. Sulfonyl radicals can be generated *via* the addition of alkyl radicals to sulfur dioxide and this reaction is of peculiar interest as the key step of the copolymerization of alkenes and SO_2.[4b] Several different types of other precursors have been tested (Eq. 6).

$$RSO_2\text{-}X \longrightarrow RSO_2^{\bullet} + X^{\bullet} \qquad (6)$$

The most widely used source of sulfonyl radicals is probably sulfonyl halides. Due to bond dissociation energies, the S-X bond can be cleaved directly by thermolysis or photolysis when X = I or Br. The homolysis of chlorides is more difficult and the use of a radical initiator is necessary. Azobisisobutyronitrile (AIBN), phenylazotriphenylmethane (PAT) or benzoyl peroxide (BP) are frequently used. An interesting alternative route to generate sulfonyl radicals from sulfonyl chlorides uses the combination of di-*tert*-butyl peroxide and triethylsilane, since sulfonyl chlorides react very rapidly with triethylsilyl radicals; however this methodology has only been used in laser flash photolysis kinetic studies.[7b]

As exemplified later on, sulfonyl cyanides[8] (the seldom used sulfonyl thiocyanates[9] are also potential precursors) and especially selenosulfonates[10] - largely developed since the eighties - can be used instead of sulfonyl halides. Sulfonyl thiocyanates are readily available from the appropriate sodium sulfinates and thiocyanogen.[9] *Se*-phenyl areneselenosulfonates - rediscovered by Kice[10a] and Back[10b] - are readily formed by reaction of a seleninic acid with a sulfinic acid or a sulfonyl hydrazide, and are of significant interest for synthetic purpose.

A few examples of generating sulfonyl radicals from homolytic substitution on tosylates have been reported.[11] In this particular case, the initiator can be *t*-butylperoxide associated with hexabutylditin.[11a] This protocol has only been applied to spectroscopic studies.

Though sulfonyl radicals are rather inefficient in abstracting hydrogen from hydrocarbons,[7c] they can be generated *via* the reverse process - i. e. hydrogen abstraction from sulfinic acids[12] - but as above, no synthetic applications are known at present.

Conversely, redox processes have proved to be very efficient (Eq.7). Developed early by Asscher and Vofsi,[4c,d, 13a] the Cu-mediated homolysis of sulfonyl chlorides are carried out in the presence of an amine ligand; most often, triethylamine hydrochloride is added to the reaction medium. It is noteworthy that though sulfonyl iodides undergo spontaneous homolysis by heating or by simple exposure to ambient light, their addition is best carried out under the catalytic action of cupric chloride.[13b] Copper can be replaced by another catalytic system based on Ru(II) for the cleavage of

sulfonyl chlorides.[14] Fe(II) cannot be used since it reduces sulfonyl radicals to sulfinates.[15a] Cobalt(II) is rarely used.[15b]

$$RSO_2\text{-}Cl \xrightarrow{M^{n+}} RSO_2^{\bullet} + M^{(n+1)+}Cl \qquad (7)$$

M^{n+} = Cu(I) ; Ru(II)

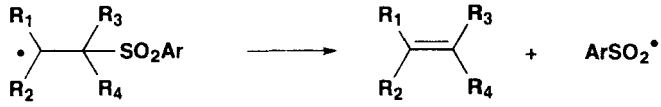
Organometallic processes with transition metals, like Pd^0, Rh(I), Ir(I) generally result in the extrusion of SO_2.[16] The palladium-catalyzed addition of alkane or arenesulfonyl chlorides to vinyl and allyl stannanes is an exception (Eq. 8).[17] The oxidation of sodium sulfinate appears very promising (Eq. 9).[18] The oxidative termination makes new kinds of adducts of sulfonyl radicals to unsaturated systems available.

$$ArSO_2Cl + RCH{=}CH\text{-}SnR'_3 \xrightarrow{Pd^0} ArSO_2\text{-}CH{=}CHR + R'_3SnCl \qquad (8)$$

$$RSO_2^- \xrightarrow{[Ox]} RSO_2^{\bullet} \qquad (9)$$

[Ox] = O_2 ; *t*-BuOOH ; Ce(IV) ; $S_2O_8^{2-}$; Cu(II)

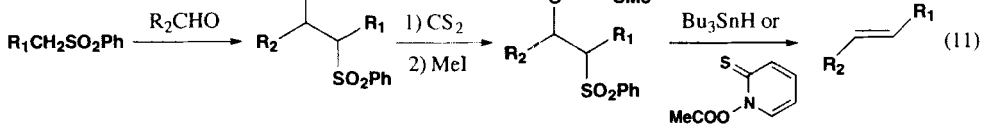
Finally, an interesting mode of formation of sulfonyl radicals relies on the fragmentation of β-sulfonyl radicals (Eq. 10).[4] Allylic sulfones have become precursors of choice for the introduction of both a sulfone group and an alkenyl chain on unsaturated systems (see section V).[19] Based on this fragmentation reaction, the chemistry of arenesulfonyl radicals as leaving groups is discussed in the following paragraph.



(10)

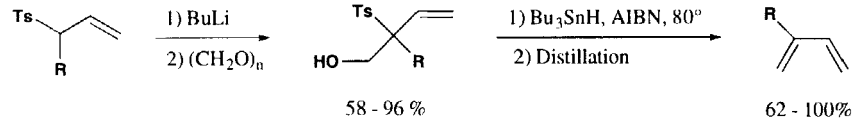
III. SULFONYL RADICAL AS THE LEAVING GROUP

The application of the Barton-Mc Combie reduction of alcohols to β-hydroxysulfones provides a substitute to Julia olefin synthesis (Eq. 11).[20] The reaction, proceeding *via* a β-sulfonyl radical, was applied to the preparation of pseudomonic acid.[20b,c,e] More recently, the pyrolysis or photolysis of acyl derivatives of N-hydroxy-2-thiopyridone has proved to be a useful alternative which avoids the use of tin hydrides (Eq. 11).[20d]



(11)

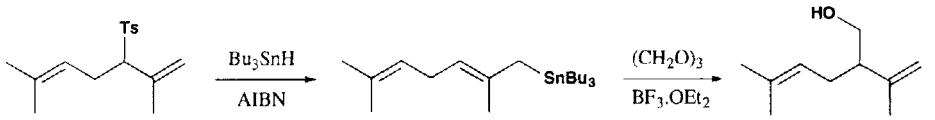
S_H2' reactions on allyl sulfones were applied to the preparation of various olefins[21a] and dienes[21b] (Eq. 12) and to the preparation of (±) lavandulol (Eq. 13).[21c] As indicated in Eq.12, refluxing of a mixture of hydroxymethyl allylsulfone (2.23 mmol), tributyl tin hydride (4.46 mmol) and AIBN (~ 10mg) in dry benzene (3 mL) for 2h followed by direct Kugelrohr distillation gives dienes in high yields.



(12)

58 - 96 %

62 - 100%

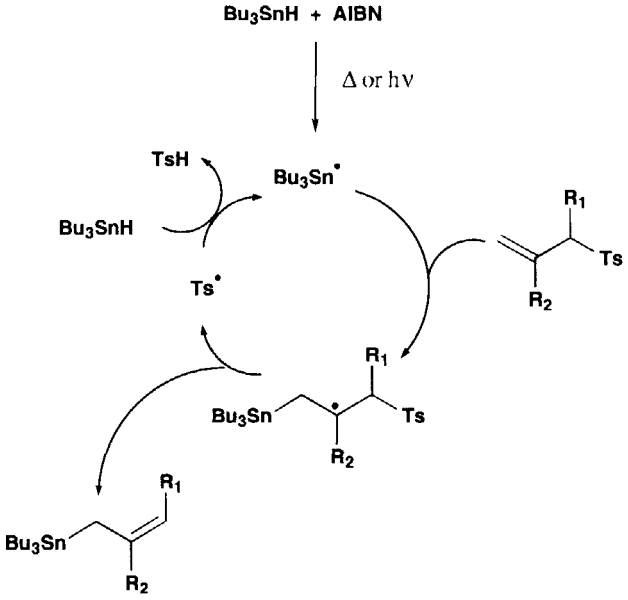


(13)

97%

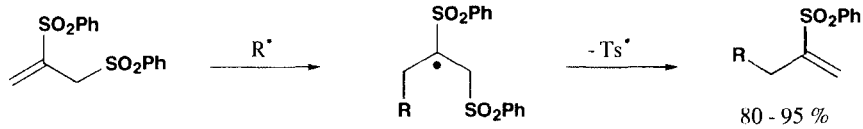
57%

In the second example, the direct addition of tinhydride to an allylsulfone leads to an allyl stannane which is condensed with formaldehyde under acid catalysis (Eq. 13). The reaction proceeds *via* a tributyltin radical addition-elimination sequence according to scheme 2.

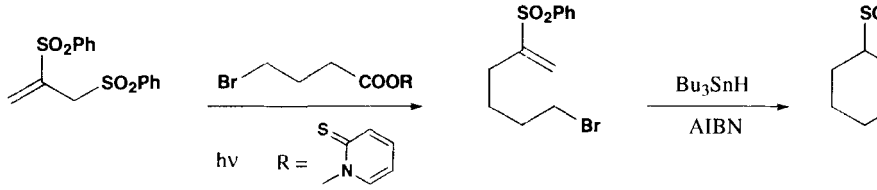


Scheme 2

The same methodology, using 2,3-bis(phenylsulfonyl)-1-propene as the substrate leads to vinylic sulfones in high yields (Eq. 14). These can further undergo a radical cyclization (Eq. 15).[22a]

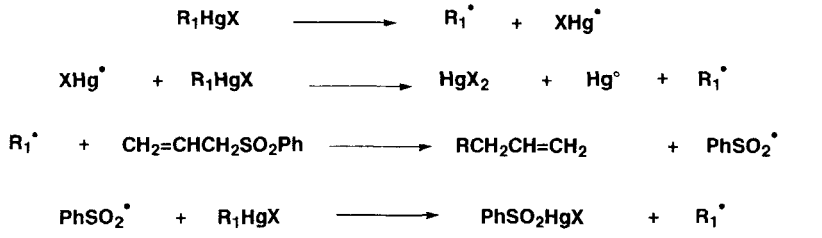


(14)



(15)

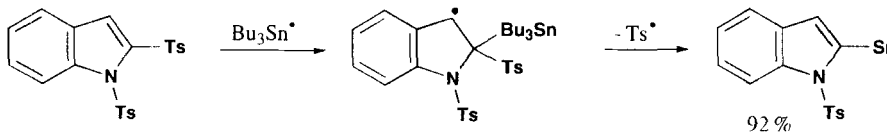
The generation of alkyl radicals *via* hydroxamic esters allows the addition of primary, secondary and tertiary radicals. In a typical procedure, a solution of bis-sulfone and a three-fold excess of thiohydroxamic ester is irradiated with a 250 W tungsten lamp during 30 min to afford substitution products in 80-95% yield. The same process is also involved in the Mn(III)-based allylation of β-keto-esters.[22c] The reaction can be performed in the presence of cupric acetate and lead dioxide using a three-fold excess of allylic sulfone with respect to the β-keto-ester.[22c] Similar radical chain processes can be carried out with alkyl mercurials and allyl sulfones.[22d] The chain reaction is summed up in Eqs. 16-19.



(16)
(17)
(18)
(19)

With α-substituted allylic derivatives, undesirable rearrangement into γ-substituted derivatives may occur. $PhSO_2^•$ can effectively add to the allylic system and therefore lead to rearranged products after elimination. The synthetic potential of these rearrangements is discussed in § V *(vide infra)*. Allenes are obtained from propargylic sulfones but yields are low - less than 10%.

The regioselective preparation of heteroaromatic stannanes is performed *via* the displacement of tosyl radical by tributylstannyl radical (Eq. 20).[22b] The treatment of 2-tosyl-N-tosylindole with Bu_3SnH (2 equiv.) at reflux in benzene affords the corresponding stannane in high yield. This reaction is also applicable to tosyl pyrrole and tosyl pyrazole though yields are lower - 69% and 70%, respectively.



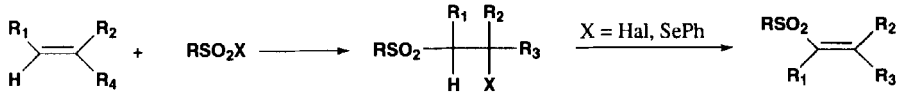
(20)

IV. SULFONYL RADICAL AS THE ENTERING GROUP

The main synthetic applications of sulfonyl radicals rely on their ability to add to carbon-carbon double and triple bonds. These reactions are properly considered among the best methods for preparing sulfones. A compilation of sulfone syntheses, covering the literature until 1985 has been published by Shank.[23a] This topic has also been treated recently by Simpkins.[23b] In addition, an extensive survey of the reactions of selenosulfonates with unsaturated systems has been reported by Metzger.[23c] The following paragraph summarizes recent work in this area. Some overlap with earlier review is unavoidable.

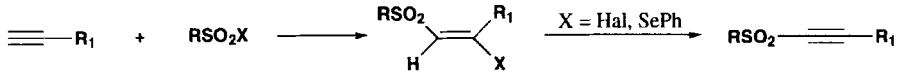
1. 1,2-Addition to Alkenes, Alkynes and Allenes

The addition of RSO_2X (X = Hal, SePh) to alkenes and alkynes leads regioselectively to β-halo- or β-selenosulfones which can undergo elimination to give vinyl and ethynyl sulfones (Eq. 21-22).[23]



(21)

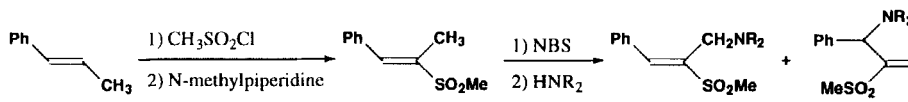
X = Hal, SePh, CN, SCN



(22)

The selenides generated (X = SePh) may be eliminated under mild conditions *via* oxidation whereas the use of a base (generally a tertiary amine) is necessary to perform the dehydrohalogenations. It has been verified that the selenide resulting from the addition of phenylselenotosylate to styrene cannot be reduced further by tin hydride to afford a saturated sulfone. Tosyl radical elimination is faster than hydrogen transfer from tin hydride and styrene is recovered.[10d] The addition of sulfonyl cyanides and thiocyanates (X = CN, SCN) proceeds similarly to yield β-cyano[8] and β-thiocyano sulfones (Eqs. 21-22).[9] While the addition to acyclic olefins is non-stereospecific, the addition to cyclic olefins [10b,d,13b,23] and to acetylenes[23,24] can be highly stereoselective (mainly with selenosulfonates) in favor of the *trans* adducts.

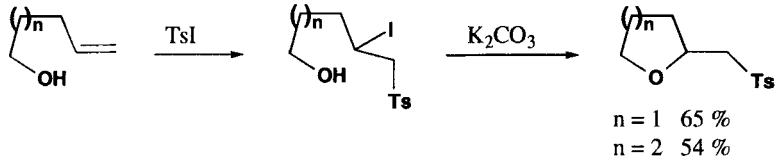
The Cu(II)-catalyzed addition of methanesulfonyl chloride to 1-phenylpropene followed by dehydrochlorination with N-methylpiperidine, subsequent allylic bromination with N-bromosuccinimide and amination, provides [2-(methylsulfonyl)allyl]amines (Eq. 23).[25a] These compounds undergo amine exchange and have been explored as models for the reactions of activated allylic substrates with ammonium groups in peptides.



(23)

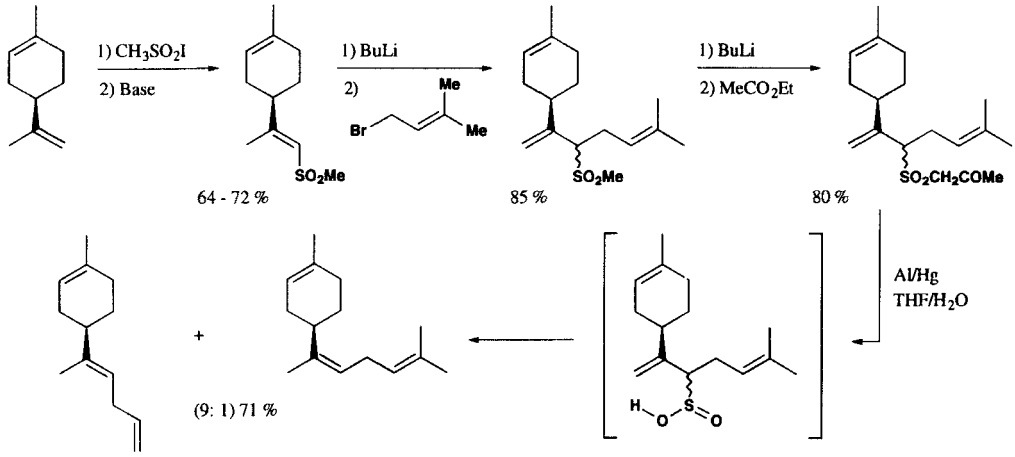
Iodosulfonation of Michael acceptors followed by dehydrohalogenation is a good route to β-sulfonyl-α,β-unsaturated carbonyl compounds.[25b]

Functionalized furans and pyrans are readily available from the addition of tosyl iodide to alkenols. The crude adduct undergoes internal substitution when treated with anhydrous carbonate in methanol at reflux (Eq. 24).[25c]



(24)

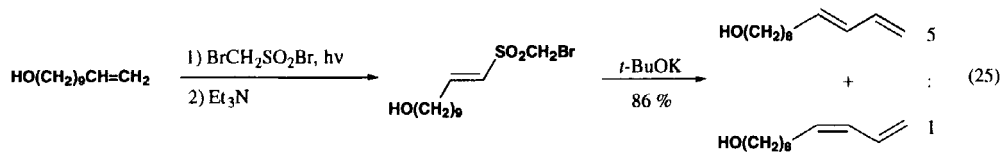
Baldwin *et al.* have designed a new method for C-C coupling of terminal alkenes *via* a sulfonylation-alkylation-desulfinylation sequence.[25d] This strategy applies to the synthesis of *E*- and *Z*-α-bisabolenes (Scheme 3).



Scheme 3

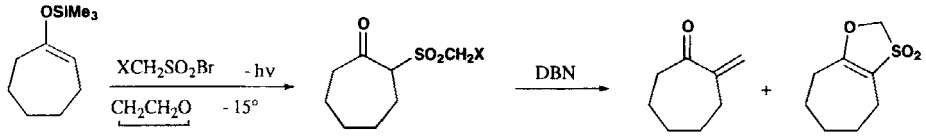
The alkene is first converted into a vinyl sulfone by radical addition of methanesulfonyl iodide and dehydroiodination. Conversion into the thermodynamic carbanion upon treatment by *n*-BuLi and alkylation with prenyl bromide is then followed by regioselective acylation at - 78°. The conversion of (+)-limonene into bisabolenes is achieved *via* the reduction of the β-ketosulfone to the corresponding allylic sulfinic acid which undergoes a regiospecific desulfinylation.

Block *et al.* devised an elegant synthesis of conjugated polyenes based on α-bromomethane-sulfonyl bromide.[25e] For example, 10-undecenol was converted to *(E,-Z)*-9,11-docadienol, the sex pheromone of the red bollworm moth, *Diparopsis castanea* (Eq. 25).



(25)

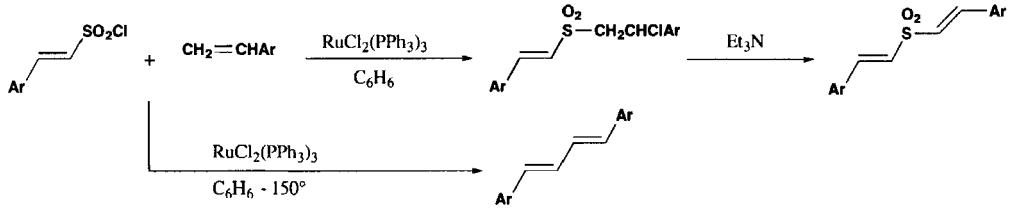
Addition of $BrCH_2SO_2Br$ and subsequent reaction with triethylamine affords the corresponding vinyl sulfone. The latter undergoes a vinylogous Ramberg-Bäcklund reaction upon treatment with potassium *tert*-butoxide thus leading to the target pheromone, as a mixture of *Z :E* isomers in a 5:1 ratio in 86% overall yield. The reaction of trimethylsilyl enol ethers as substrates, conducted in ethylene oxide as the solvent in order to prevent hydrolysis, led to 2-[(halomethyl)sulfonyl] ketones.[25e] Subsequent treatment with DBN afforded a mixture of α-methyleneketone and 1,3-oxathiole 3,3-dioxide as illustrated in Eq. 26. The latter results from an intramolecular *O*-alkylation; the chemoselectivity can be modified depending on the reaction conditions.



(26)

X = Br	CH_2Cl_2, -78°	77 %	21 %
X = Br	CH_2Cl_2, -23°	9 %	70 %
X = I	EtOH, 23°	68 %	1 %

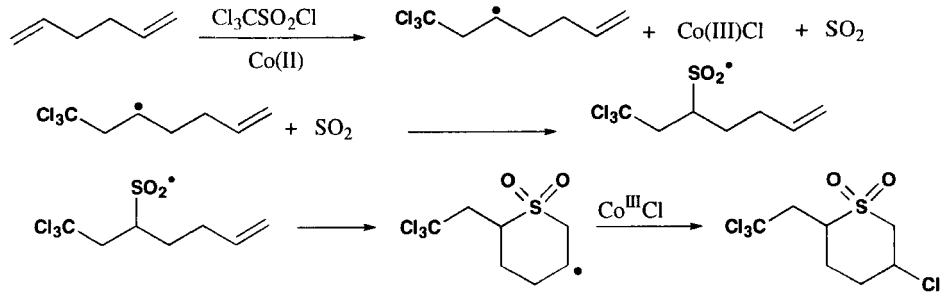
Conjugated dienes are available from the Ru(II)-catalyzed reaction of alkenesulfonyl chlorides with olefins.[14a] 1,2-Addition followed by Et_3N-promoted elimination, affords divinyl sulfones in high yields. When both the sulfonyl chloride and the alkene bear aryl groups, prolonged heating of the reaction at 150°C causes dehydrochlorination and desulfonylation, leading directly to *(E,E)*-1,4-diaryl-1,3-butadienes (Scheme 4).



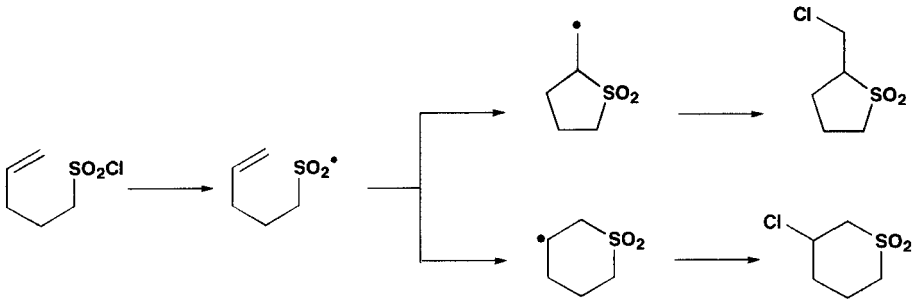
Scheme 4

Alkanesulfonyl radicals undergo cyclization *via* intramolecular addition to double bonds.[15b,26] This reaction was proposed to explain the reaction of 6-methylhept-5-en-2-ylcobaloxime with sulfur dioxide.[26a] That corroborated the reports of Ashcroft *et al.* on the Co(II)-catalyzed addition of trichloromethanesulfonyl chloride to 1,5-hexadiene (Scheme 5).[15b] The mechanism postulated involves initial rapid α-scission of trichloromethane sulfonyl radical. The result-

ing trichloromethyl radical adds to 1,5-hexadiene, thus producing an alkenyl radical which reacts with the previously evolved sulfur dioxide leading again to a sulfonyl radical. The latter cyclizes according to the 6-*endo* mode to afford a cyclic chlorosulfone after ligand transfer. The same regioselectivity was reported by Culshaw and Walton in their recent study of the cyclization of 4-alkenesulfonyl radicals (Scheme 6).[26b,c]



Scheme 5



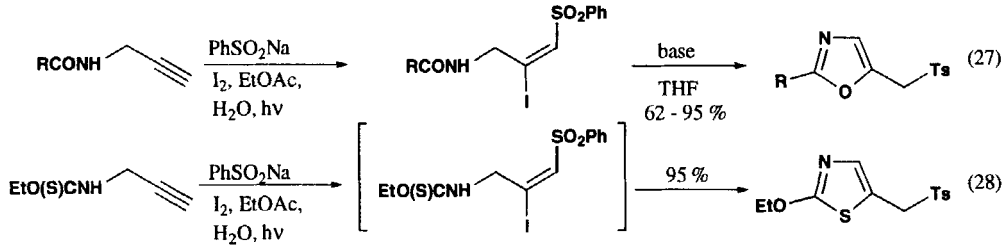
Scheme 6

Various experimental conditions were investigated, but even in the best case - i. e. $CuCl_2$-AIBN - the yields remain low. 3-Chlorothiane-1,1-dioxide resulting from the 6-*endo* ring closure is the unique product when the reaction is conducted in the presence of $CuCl_2$-AIBN at 170 ° (17% yield), however, at 75° the ratio of 6-membered ring *versus* 5-five membered ring products is 88:12 with the same initiation (yields were not determined). This regioselectivity is a typical feature for the cyclization of radicals centered on second row elements or of carbon-centered radicals that add reversibly to double bonds.[26d,e]

Long known from the pioneering works of Amiel,[27a,b] and Truce *et al.*[27c] (for related references see refs. 2, 3c and 23), the addition of sulfonyl halides to alkynes seems now to have been supplanted by the addition of selenosulfonates.[23, 24a-d] 2-Cyano vinyl sulfones are available from the addition of tosyl cyanide.[8]

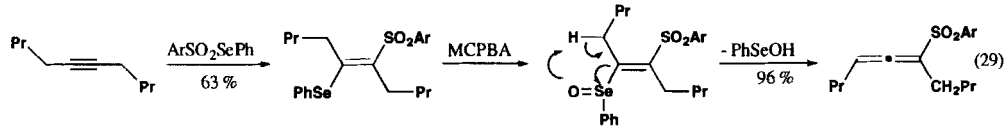
With respect to that general trend, it is noteworthy that iodosulfonylation has found a recent

application in heterocyclic synthesis (Eq. 27-28).[28a] Treatment of N-acylpropargylamines under irradiation with sodium benzenesulfinate and iodine, regioselectively converts them to *(E)*-β-iodo(vinyl)sulfones. Subsequent reaction with a base converts the amides into oxazoles. A large variety of sustituents is tolerated in this process which also applies to propargyl thiocarbamates, thus leading to thiazoles. In this particular case the cyclization appears to be spontaneous (Eq. 28).

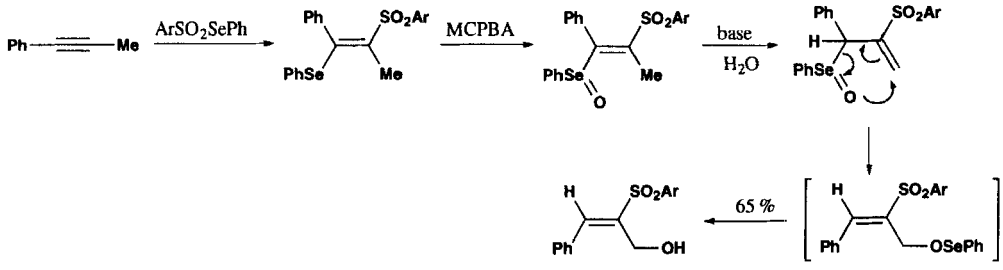


The previously mentioned addition of bromomethanesulfonyl bromide[25e] to alkynes leads to conjugated enynes in moderated yields, after base-catalyzed extrusion of sulfur dioxide.

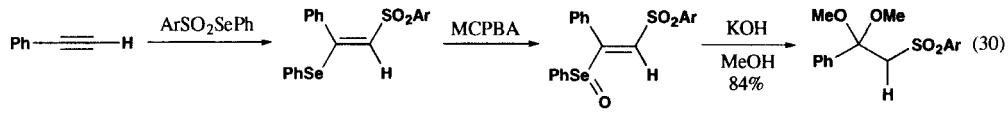
As shown in Eq. 22, the selenosulfonation of terminal alkynes leads to *trans* 1,2-adducts generally converted to acetylenic sulfones by oxidation.[24b,c] Base-catalyzed migration of the double bond, followed by asymmetric oxidation of the aryl vinyl selenides, results in the formation of chiral allenic sulfones;[24d] however, enantiomeric excess does not exceed 42%. The behavior of 1,2-adducts obtained from disubstituted acetylenes is not so clear-cut.[24c] As summed up in Eq. 29, when β-allylic protons are present, oxidative elimination easily converts the adduct to allene.



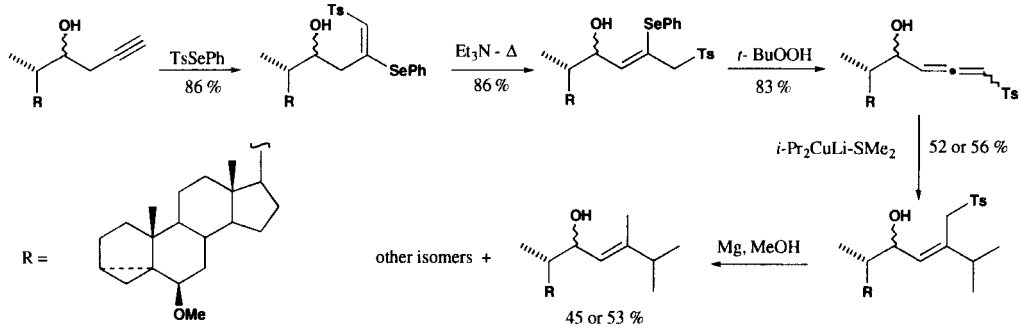
In the absence of β-hydrogens, the resulting selenoxides are stable thermally. These compounds undergo base-catalyzed fragmentation, resulting, depending on the structure, in products derived either from a rearrangement to an allylic alcohol (Scheme 7) or from a β-ketosulfone intermediate (Eq. 30).



Scheme 7

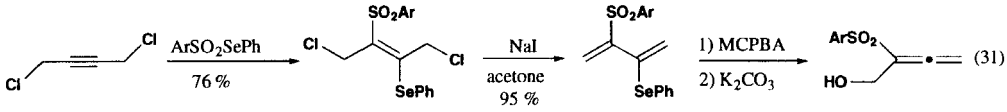


Other routes to allenes *via* the intermediacy of a selenosulfonation have been designed by Back *et al.* In the following example (Scheme 8), the epimeric homopropargylic alcohols were converted into allenyl alcohols *via* radical selenosulfonation, subsequent base-catalyzed isomerization to allylic sulfones and oxidative-elimination.[28b] The further separate transformation of each of the latter products by organocuprate addition afforded allylic sulfones, one of those is a potential precursor of a key intermediate in the synthesis of brassinolide, available by simple reductive desulfonylation.

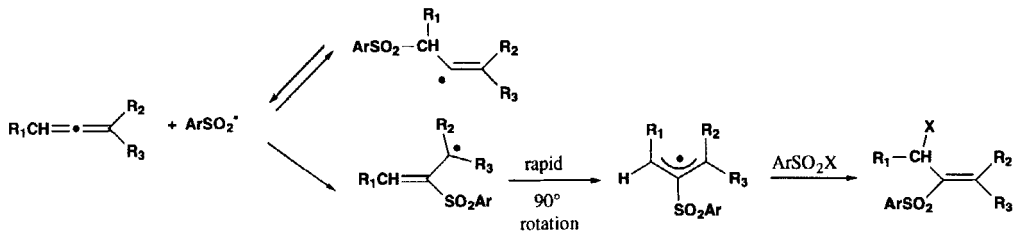


Scheme 8

Sulfonyl allenes are conveniently prepared from the adduct of phenylselenotosylate to 1,4-dichloro-2-butyne. Reductive elimination leads to a conjugated diene which undergoes [2,3] sigmatropic rearrangement to allene upon oxidation with *m*-chloroperbenzoic acid (Eq. 31).[28c] This allenic synthon is a potent precursor of various 3-substituted 2-tosyl-1,3-dienes.[28c]

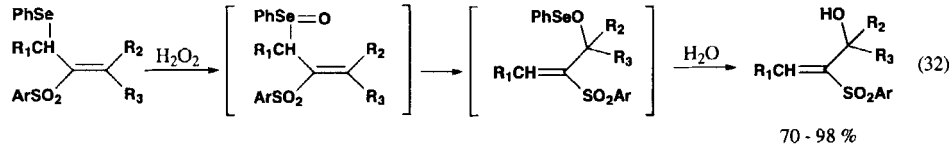


Halo- and selenosulfonations of allenes have been reviewed by Chatgilialoglu.[2] It must be remembered that excepts for propadiene,[29a] the addition of either sulfonyl iodides or selenosulfonates is totally regioselective.[29] Tosyl bromide behaves similarly.[30] The sulfonyl radical attack on the central carbon atom is probably less reversible if at all, than the addition to the terminal carbon, because it leads to a stabilized allyl radical. The ensuing atom or group transfer occurs at the less substituted end of that radical and therefore, the reaction leads to 1,2-addition to the less substituted double bond (Scheme 9). This appears to be the general behavior towards allenes of radical species that add reversibly to double bonds ($Me_3Sn^{\bullet}$, $RS^{\bullet}$, $Br^{\bullet}$). As expected, in many instances the regioselectivity depends on the rate of the atom transfer from the radical precursor (see ref. 29b and refs. therein).



Scheme 9

It should be noted that conjugated dienes are not available from selenosulfonation of allenes. Subsequent oxidation of the adduct gives rise to a new class of allylic alcohols since the [2,3]-sigmatropic rearrangement of selenoxide is much faster than the elimination of PhSeOH in all cases (Eq. 32).[29c,d]



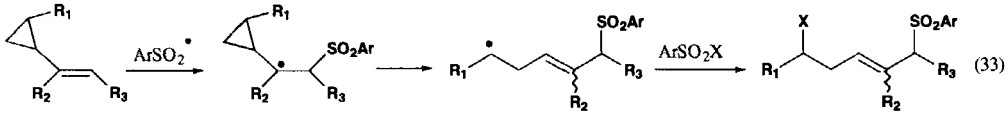
(32)

70 - 98 %

Separate discussions will be devoted to sulfonyl radical additions leading to intermediate radicals that rearrange or fragment rapidly. This is the case for the addition to vinyl cyclopropanes and their acetylenic analogs as well as for the addition to 1,6-dienes, 1,6-enynes and 1,4-enallenes. $S_H'2$ reactions are observed with alkenyl stannanes and other organometallic species.

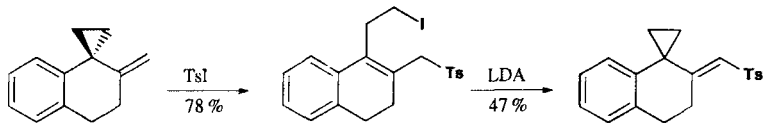
2. Addition to Vinyl and Ethynylcyclopropanes

The reaction of benzenesulfonyl chloride,[31a] tosyl iodide[31b] and phenylselenosulfonates[31c] with vinylcyclopropanes results in 1,5-adducts (Eq. 33). For kinetic purpose, dicyclopropylethene was used as a standard olefin to which methanesulfonyl radical adds irreversibly (the reaction with methanesulfonyl bromide results in the formation of approximately equimolecular amounts of the two isomeric adducts).[3f] Though sulfonyl iodide and selenosulfonates are known to be very efficient chain-transfer agents, the intermediate cyclopropylcarbinyl radicals undergo ring-opening much faster than they undergo chain-transfer.

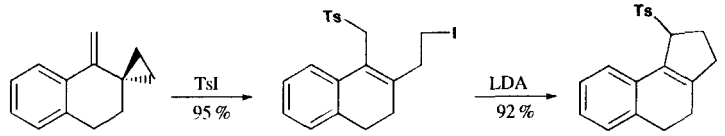


(33)

The addition of tosyl iodide offers a route to functionalized homoallylic iodides which can undergo further carbanionic cyclization when treated with bases, as illustrated below in Eqs. 34-35.[31b]

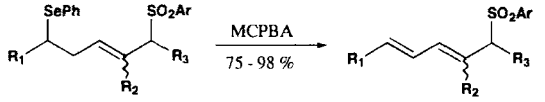


(34)



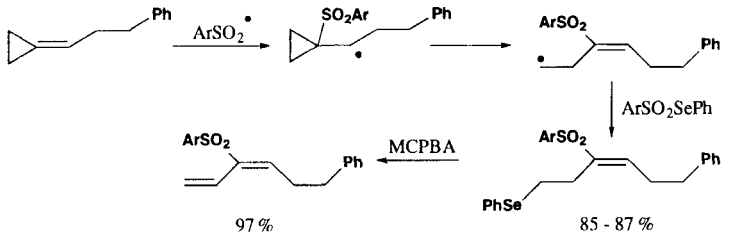
(35)

Oxidation of the selenosulfonate adducts produces allylic dienyl sulfones in high yields (Eq. 36).

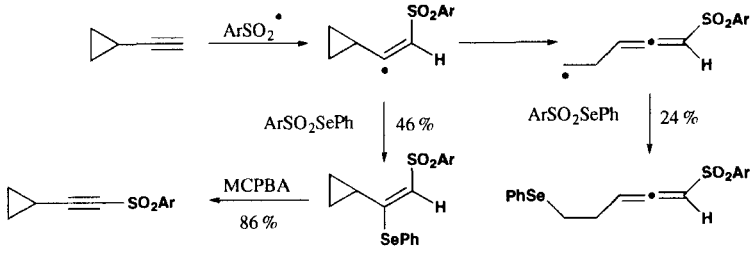


(36)

It should be mentioned that cyclopropylidene derivatives follow a similar pathway to 1,3-adducts (Scheme 10),[31c] the oxidation of which furnishes dienyl sulfones in nearly quantitative yields. In contrast, cyclopropylacetylene gives predominantly the 1,2-adduct (Scheme 11).[31c] The isolation of the 1,5-adduct as the minor product reveals that the bimolecular chain-transfer competes with the ring-opening of the intermediate vinyl radical. Improved yields of 1,2-adduct were obtained when an excess of selenosulfonate was used. On the basis of these results, it can be concluded that selenonosulfonates react substantially faster with the vinyl radical than with the primary alkyl radical.

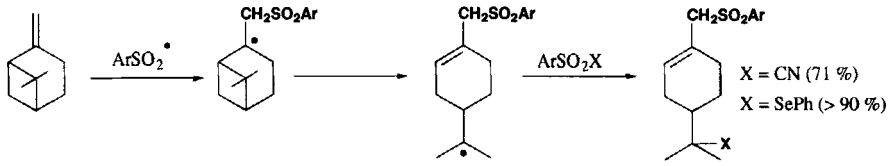


Scheme 10



Scheme 11

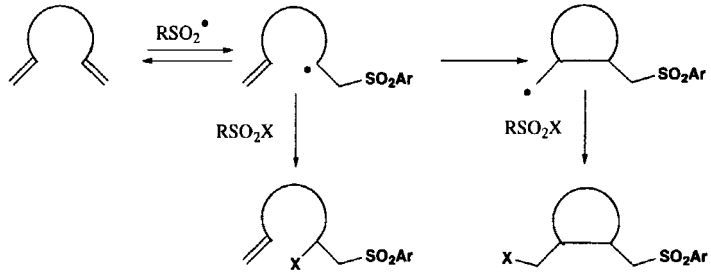
Similarly, during the radical addition of selenosulfonates,[7d] tosyl iodide[31b] or tosylcyanide[8b-d] to β-pinene, ring-opening of the strained four-membered ring occurred and led to adducts possessing the menthane skeleton; a competitive ionic addition could not be suppressed when tosyl iodide was employed.



(37)

3. Addition to 1,6-Dienes, 1,6-Enynes and 1,4-Enallenes

Carbon-carbon bond formation *via* intramolecular addition of alkyl radicals has become one of the best methods for the construction of cyclic framework.[32] Radical sulfonation of non-conjugated dienes is attractive since it allows stereoselective ring closure in one simple step and the introduction of two different useful functionalities (Scheme 12).

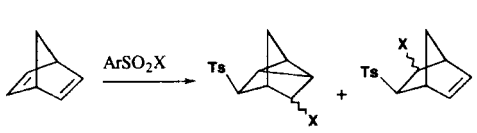


Scheme 12

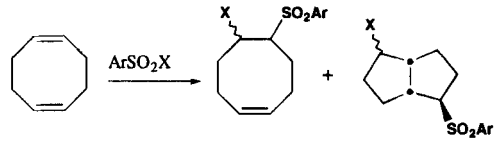
The only requirement to achieve such a reaction is the judicious selection of the right precursor and of the concentrations of both reactants. It is of prime importance to control the competition between the bimolecular chain-transfer step and the monomolecular radical rearrangement in order to avoid the formation of 1,2-adducts. In contrast to cyclopropylcarbinyl radicals that are among the fastest radical clocks ($k \approx 10^8\ s^{-1}$), the rate of cyclization of most alkenyl radicals ranges between 10^4 to $10^7\ s^{-1}$.[33]

Functionalization of norbornadiene[8b,e,10b,c,25e,34] and 1,5-cyclooctadiene[8b,10b, 25e,35a] has received much attention. The former leads to nortricyclanes and the latter to diquinanes (Scheme 13). Though the concentrations in reactants are not always directly comparable, it can be deduced from these results that selenosulfonates rank between sulfonyl iodides and sulfonyl bromides , the sulfonyl chlorides and the cyanides being the least efficient chain-transfer agents in the series. Care should be taken that in the copper salt-mediated addition of sulfonyl chlorides, the final propagation step is no longer a chlorine atom transfer but a ligand transfer with $CuCl_2$, which is much faster.

$$ArSO_2I > ArSO_2SePh \geq ArSO_2Br >> ArSO_2Cl \approx ArSO_2CN$$



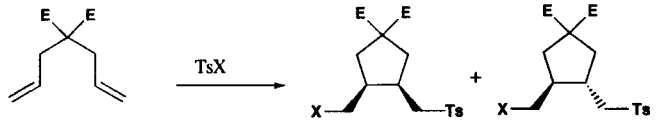
$PhSO_2Cl$[34] (11 %)	93	:	7
$PhSO_2Br$[34] (93 %)	87	:	13
$PhSO_2I$[34] (72 %)	27	:	73
$BrCH_2SO_2Br$[25c] (96 %)	50	:	50
$TolSO_2SePh$[10b] (75 %)	90	:	10
$TolSO_2CN$[8c] (83 %)	94	:	6



			exo - endo
$TolSO_2Cl$[35a]	-	:	42 - 7 %
$TolSO_2Br$[35a]	44 %	:	13 - 3 %
		:	
$BrCH_2SO_2Br$[25c]	35 %	:	-
$TolSO_2SePh$[10b]	39 %	:	34
$TolSO_2CN$[8b]	-	:	78 - 5 %

Scheme 13

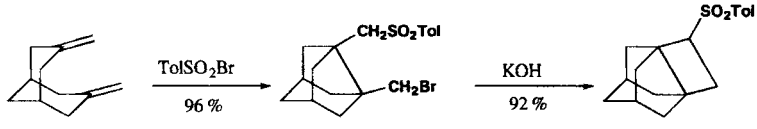
The sulfonyl radical-mediated cyclization of 1,6-dienes has recently stimulated the interest of several research groups.[3e,35-39] The intermediate 5-hexenyl radical undergoes 5-*exo* ring closure affording cyclopentane derivatives. The yields and the stereoselectivity are specially high with diallyl malonates, due to the Thorpe-Ingold effect and to unfavorable steric interactions in the transition state leading to the *trans* isomer (Scheme 14). This methodology has been applied to the synthesis of oxa- and aza-heterocyclic compounds.[35-38]



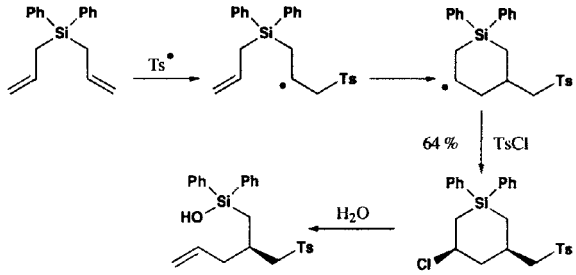
$E = CO_2R$	$X = Br$[35a]	90 %	93	:	7
	$X = Cl$[37a]	85 %	85	:	15
	$X = SePh$[38]	96 %	not reported		

Scheme 14

Because of the special behavior of 3-sila-5-hexenyl radicals, diphenyl diallylsilane leads to a silacyclohexane (Scheme 15).[35a] The resulting β-chlorosilane is readily hydrolyzed, and the yields are increased up to 64% if purification by chromatography on silica gel is avoided. Because of the slower cyclization rate, in this case it is preferable to use a sulfonyl chloride as the precursor of the sulfonyl radical. This is confirmed by the exclusive formation of *bis*-1,2-adducts from dimethyl diallylsilane and bromomethanesulfonyl bromide.[25e] An interesting application of 1,6-diene halosulfonation to the synthesis of [3.3.2]propellanes was reported by Russian co-workers (Eq. 38).[39]

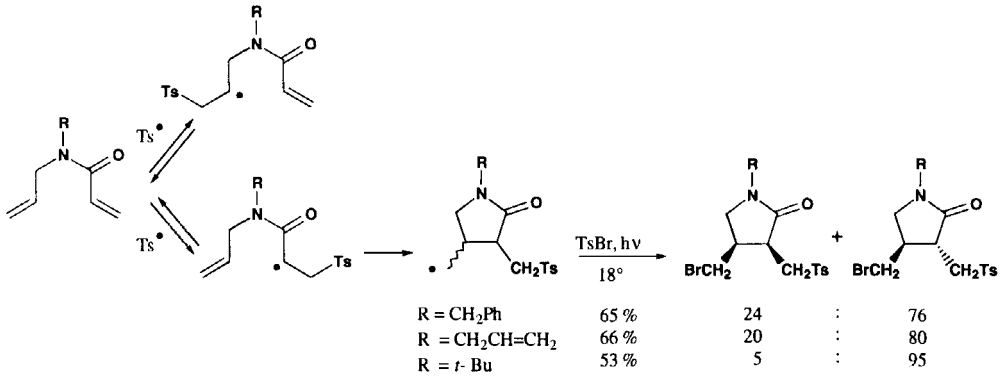


(38)



Scheme 15

The reversible addition of sulfonyl radical is of great interest in the chemoselective cyclization of unsymmetrical dienes.[3d,35c,d,36c,37a-e, 38] As an example, N-allyl acrylamides lead to γ-lactams (Scheme 16).[35d,37a,b] Only the adducts resulting from the addition to the conjugated double bond are obtained (a small amount of 1,2-adduct to the conjugated double bond was isolated as by-product when R = CH_2Ph).[35d] They are not the products expected on the basis of the electrophilic character of sulfonyl radicals. Their formation is rather the consequence of the reversible initial addition that favors the intermediate radical which cyclizes faster than it returns to the substrate (the rate of the reverse step should be significantly slowed down when the intermediate radical is resonance-stabilized). It is noteworthy that the cyclization of α-carbamoyl radicals exhibits an atypical stereoselectivity, leading predominantly to *trans* stereoisomers.[35d] The stereoselectivity is improved when the substituent on nitrogen is bulky.

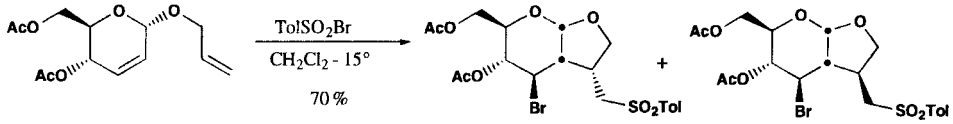


R = CH_2Ph	65 %	24	:	76
R = $CH_2CH{=}CH_2$	66 %	20	:	80
R = *t*-Bu	53 %	5	:	95

Scheme 16

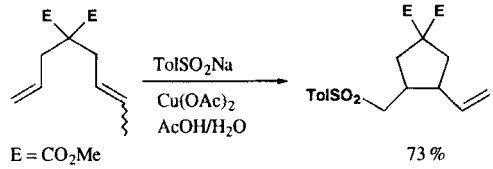
The chemoselectivity applies to other unsymmetrical dienes but lactone ring closure from allyl acrylates failed by this strategy.[3e,38] As shown below (Eq. 39), cyclization on sugar templates offers an interesting route to C-branched sugars.[35c,f] Due to the exclusive *cis* ring junction and the exclusive *exo* transfer of bromine atom, the reaction allows the total control of two of the stereogenic centers. As regard to the third one, stereoselectivity is somewhat lower than in acyclic series due to the exclusion of sterically hindered chair-like transition states for the cyclization step. The cyclization

proceeds *via* epimeric boat-like transition states, which are energetically less different one from the other than are chair-like conformations.[35de] This explanation holds for gluco derivatives where the *O*-allyl side chain is bonded to C-1. When the side-chain is attached to C-4 (*vide infra* Eq. 59), the stereoselectivity is higher; in that case, no steric strain precludes the involvement of chair conformers for the cyclization transition state.



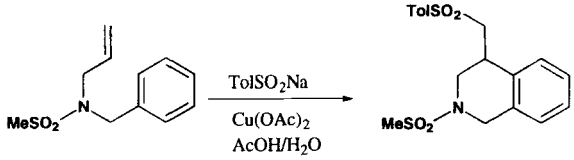
(39)

As mentioned earlier, oxidative termination offers a route to new kinds of adducts.[7d,e,18] The generation of tosyl radical from sodium tosylate and $Cu(OAc)_2$ in the presence of diallyl malonates led to unsaturated adducts (Eq. 40).[37b] The final step in that case is an oxidative elimination, 10-40 equivalents of TsNa and 2-8 equivalents of copper salt being required depending on the substrate.



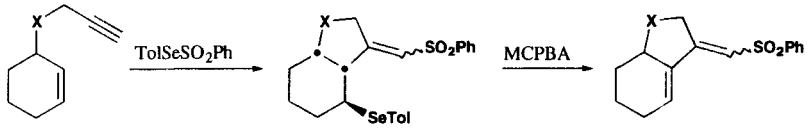
(40)

In the following example, the oxidative cyclization of the intermediate radical onto an aromatic ring results in tetralin derivatives (Eq. 41).[37b]



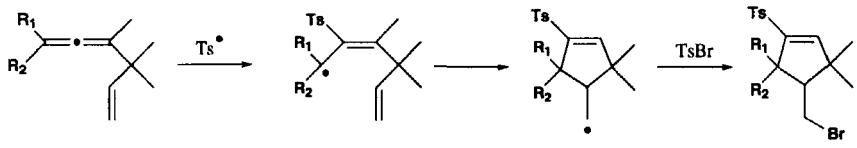
(41)

Simpkins[38] reported the chemo- and stereoselective additions of selenosulfonates to 1,6-enynes (Eq. 42).



(42)

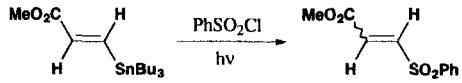
When tosyl bromide is added to 1,4-enallenes, cyclopentenyl sulfones are obtained. Again the reaction is totally chemoselective; only the cyclo-adducts resulting from the addition of tosyl radical to the central carbon of the cumulene are formed (Eq. 43).[30]



(43)

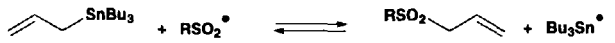
4. Addition to Allyl Sulfides and Selenides to Allyl, Propargyl and Vinyl Stannanes and to Other Organometallic Species

The ruthenium(II)-catalyzed addition of arenesulfonyl chlorides to allyl sulfides and selenides results in allylic sulfones *via* a S_H2' reaction (the isomerization of 1-butenyl compounds and 2-butenyl compounds is a complicating factor).[40] The same mechanism applies to the reaction of sulfonyl chloride with vinyl and allyl stannnanes (Eq. 44-45).[41a,b] This reaction is the reverse of the aforementioned S_H2' reaction of tin hydride with allyl sulfones.[22] The equilibrium is driven either to the left by the reaction of sulfonyl radical with tributyltin hydride or to the right by the reaction of tributyl stannyl radical with the sulfonyl chloride. Propargyl stannanes behave similarly and lead to allenyl sulfones (Eq. 46).[41a]

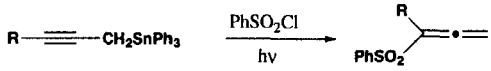


(44)

68 % E/Z > 50

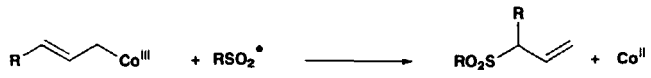


(45)



(46)

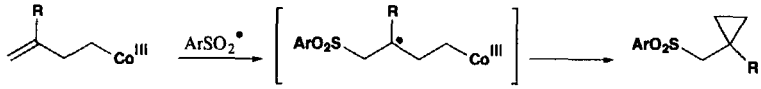
This typical behavior is also encountered with cobaloximes (Eq. 47).[42a]



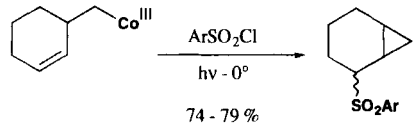
(47)

Co = Co(dmgH)$_2$Py

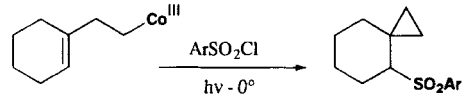
The reaction of sulfonyl chlorides with homoallylic cobaloximes affords an original route to a variety of methyl cyclopropyl sulfones (Eq. 48).[42b] The mechanism of ring closure may be either concerted or stepwise. Fused and spiro bicyclic cyclopropyl derivatives are available in good yields by this strategy (Eq. 49-50). Those reactions are best carried out under irradiation at 0° - thermal reactions give poor yields and side-products.



(48)



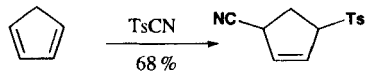
(49)



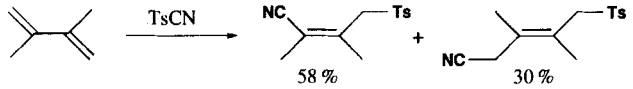
(50)

5. Addition to Conjugated Dienes and Enynes

The addition of the various sulfonyl radicals precursors to conjugated dienes results in 1,4-addition.[4c-d,8,9b,10d,25e,23a] Among some of the most recent relevant data, the thermal addition of tosyl cyanide to cyclopentadiene may be mentioned which affords a single adduct in 68% yield (Eq. 51).[8] The reaction with 2,3-dimethyl-1,3-butadiene leads to an approximately 2:1 mixture of isomers in 88% yield (Eq. 52).[8]

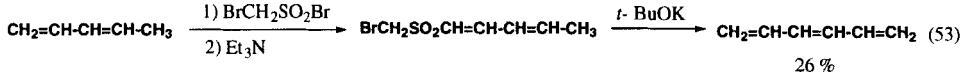


(51)



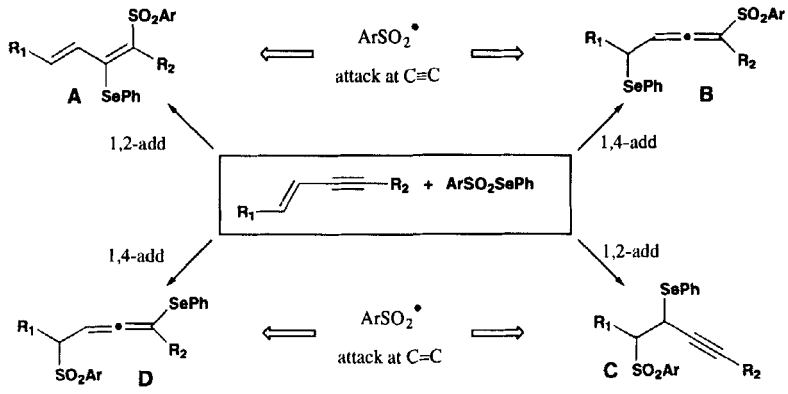
(52)

The light induced addition of bromomethanesulfonyl bromide to conjugated dienes, followed by treatment with triethylamine and subsequent reaction with potassium *tert*-butoxide, allows a three-step synthesis of conjugated trienes (Eq. 53).[25e] Therefore, *(E)*-1,3,5-hexatriene may be prepared stereoselectively in 26% overall yield, from *(E)*-1,3-pentadiene (less than 1% of the *Z* isomer was detected). This strategy has been applied to the synthesis of various trienic targets.[25e] Since trienes fail to give adducts, it is not possible to convert conjugated trienes to conjugated tetraenes by this method.



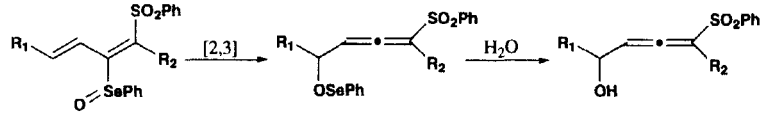
(53)

The long known addition of sulfonyl radicals to 1,3-enynes[15a, 43] is less regioselective than their addition to 1,3-dienes. A mixture of allenic adducts and acetylenic adducts is obtained from vinyl acetylenic ethers.[43b] A recent report described the influence of structural parameters on the regioselectivity of the selenosulfonation of 1,3-enynes (Scheme 17).[28d]



Scheme 17

Addition to the triple bond occurs preferentially with enynes having a terminal acetylene to afford more or less selectively, 1,2- and 1,4-adducts. Conversely, enynes having a terminal olefin and disubstituted acetylenes give 1,2- and 1,4-adducts to the double bond, albeit in lower yields. A stereospecific [2,3] rearrangement of the resulting selenoxides (**A**) can be performed, provided that excess oxidant is used and the reaction is worked up promptly (Eq. 54).[28d]

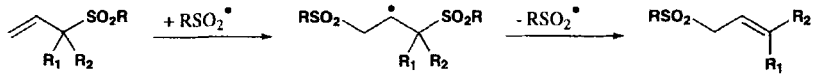


(54)

V. SULFONYL RADICAL BOTH AS THE LEAVING AND ENTERING GROUPS

1. Rearrangement and Addition of Allylsulfones

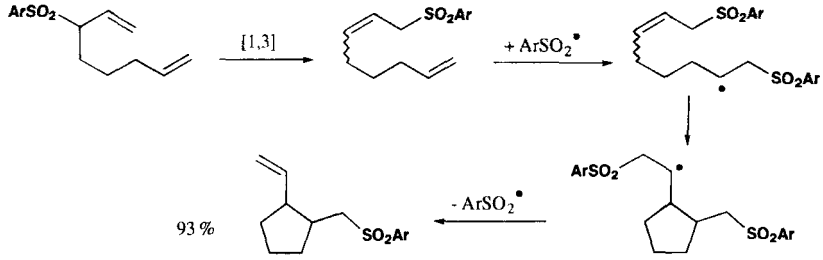
Whitham *et al.* were the first to systematically investigate the radical-induced rearrangement of allylic sulfones.[19] When treated with catalytic amounts (5 mol %) of benzoyl peroxyde in refluxing carbon tetrachloride, acyclic allylic sulfones undergo complete rearrangement after 18 hrs. During the course of those studies, the authors discovered that the same reaction could be promoted by heating the allylic sulfones in AcOH - H_2O (6:4) in the presence of $ArSO_2Na$ (Eq. 55).[19a,d]



(55)

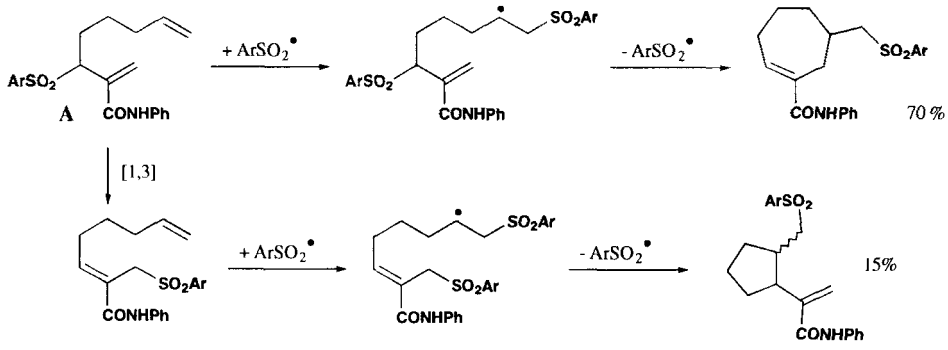
This 1,3-rearrangement clearly demonstrates that allylic sulfones can play the role of a radical acceptor and the role of a radical donor at the same time. The process relies on the reversibility of the addition of sulfonyl radicals to double bonds. Based on this key feature, an elegant chemistry of allylic sulfones has been developed. Under these experimental conditions, radical cyclization of allylic sulfones of appropriate structures can be promoted.[19c,f,g] For example, cyclopentane derivatives are available from 3-sulfonyl-1,7-octadienes, easily prepared by alkylation of metalated allylic sulfones

with bromopentene (Scheme 18).[19c] The cyclization occurs *via* an internal $S_H'2$ process that follows the initial 1,3-rearrangement and the subsequent chemoselective addition of sulfonyl radical to the less substituted double-bond.



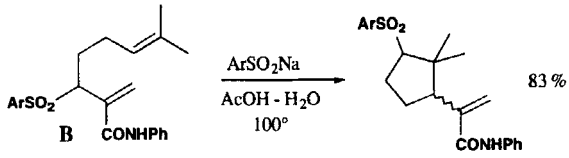
Scheme 18

Radical-induced tandem rearrangement-cyclization of allylic sulfones bearing an amide group β to the sulfone affords five-, six- or seven-membered rings depending on the structure of the starting sulfone (Scheme 19).[19f] Heating sulfone **A** with TsNa in aqueous acetic acid at 100°C leads to a mixture of rearranged five- and seven-membered rings products in 15% and 70% yields respectively (Scheme 19). The predominance of the cycloheptene derivative over the cyclopentane derivative indicates that 1,3-rearrangement, involving the addition of the electrophilic sulfonyl radical to the activated double bond, is slow compared to the rapid cyclization of the nucleophilic radical resulting from the addition of sulfonyl radical to the other double bond.

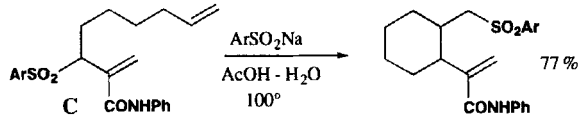


Scheme 19

In contrast to the foregoing example, in the case of sulfone **B**, 1,3-rearrangement precedes 5-*exo* cyclization; the alternative 7-*endo* cyclization mode is no longer competitive (Eq. 56). Sulfone **C** illustrates the facile formation of six-membered rings (Eq. 57). The fate of the substrate depends on the relative rate of 1,3-rearrangement *versus* the primary available cyclization pathway. With this sulfone, the 8-*endo* cyclization is too slow to compete with the allylic rearrangement.

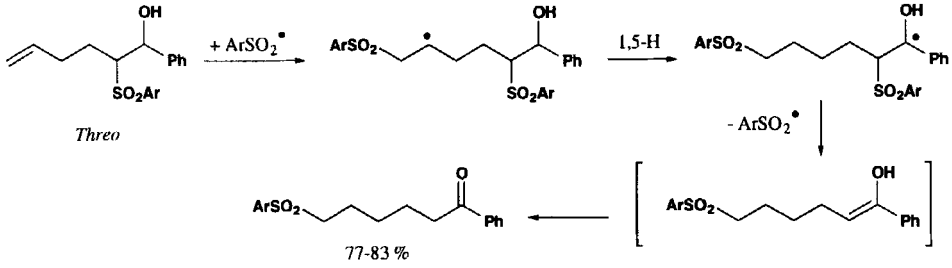


(56)



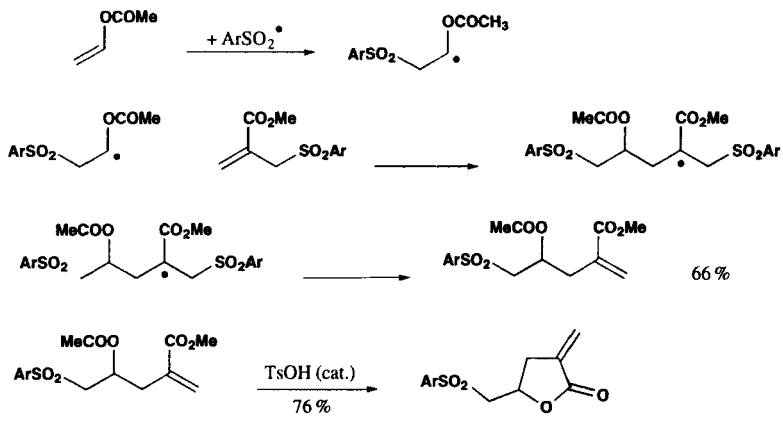
(57)

The cascade combination of radical addition, 1,5-hydrogen transfer and β-fragmentation allows the rearrangement of other unsaturated sulfones.[19e] This reaction may be of practical interest when 1,5-hydrogen transfer is activated by a hydroxyl group (Scheme 20). It is noteworthy that only the *threo* diastereoisomer undergoes transposition efficiently. Unfavorable conformational strain hinders the rearrangement of the *erythro* compound.



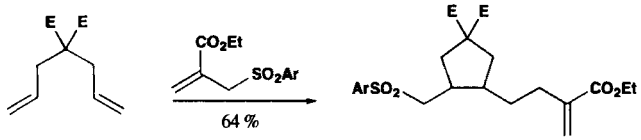
Scheme 20

Intermolecular carbon-carbon bond forming reactions involving allylic sulfones have also been developed. The addition of allylic sulfones can be efficient provided some benefit is derived from polar effects which are well known to influence the free-radical reactions. The best conditions are obtained when the alkene bears an electron-donating substituent while the allylic sulfone bears an electron-withdrawing group.[19b] Such sulfones are readily available from the addition of arenesulfonyl iodide to activated alkenes followed by base induced dehydrohalogenation. As shown in Scheme 21, the electrophilic sulfonyl radical adds readily to the electron-rich double bond and the resulting nucleophilic radical adds to the electron-poor allylic sulfone. The adduct is converted to α-methylene lactone under acid catalysis.



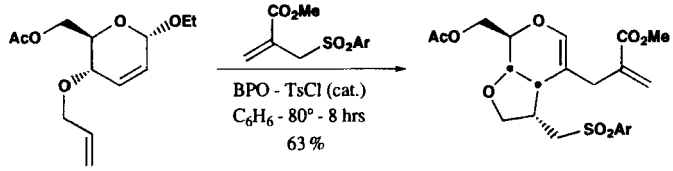
Scheme 21

The cyclization of 1,6-dienes (cf p. 275) can also be achieved by addition of allylic sulfones. Cyclopentane derivatives are thus obtained in good yields from a variety of dienes (Eq. 58).[44]



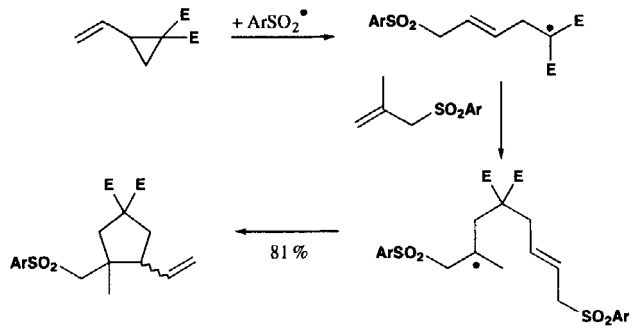
(58)

When the reaction is conducted with 2-methyl-1-sulfonyl-2-propene, in the presence of benzoyl peroxide and a tetrahalomethane, the reaction leads to the adducts previously obtained *via* the addition of sulfonyl halides.[44b] The halogen atom abstraction proceeds more rapidly than the addition to the allylic sulfone. The chain process is continued *via* the addition of the trihalomethyl radical to the sulfone double bond. This methodology has been applied to the cyclizations on sugar templates[35f] and allows the stereoselective simultaneous branching of sugar with two alkyl chains. The acidic reaction medium explains the obtention of a 1,2-deoxy sugar, possibly assisted by the ester group (Eq. 59).



(59)

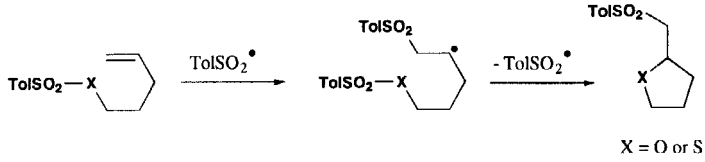
It must be added that the addition of allylic sulfones to vinyl cyclopropanes affords another route to cyclopentane derivatives,[44b] according to Scheme 22.



Scheme 22

2. Rearrangement of Alkenyl Sulfonates

A recent report by Correa *et al.* illustrates the availability of heterocyclic sulfones *via* a radical chain intramolecular displacement on the oxygen of alkenyl tosylates (Eq. 60).[11b] Substituted thiolanes are also obtained in quantitative yields similarly from thiotosylate, even in the absence of initiation.

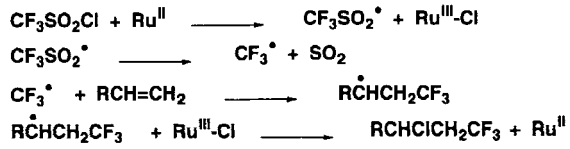


(60)

X = O or S

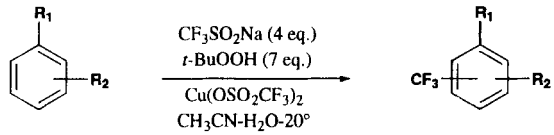
VI. α-SCISSION AS A ROUTE TO PERFLUOROALKYL RADICALS

Recent developments in the chemistry of perfluoroalkanesulfonyl halides have shown that they can be used as fluoroalkylating agents to introduce a R_F group by addition to olefinic linkages.[7e, 45] Ru(II)-catalyzed homolysis of trifluoromethane sulfonyl chloride leads to trifluoromethyl radical after rapid extrusion of sulfur dioxide (Scheme 23). The reaction with various alkenes results in the formal addition of CF_3Cl, the adducts being readily converted into the corresponding alkenes by base promoted dehydrochloration.[45] Perfluoroalkanesulfonyl bromides react spontaneously with alkenes and alkynes.[7e]



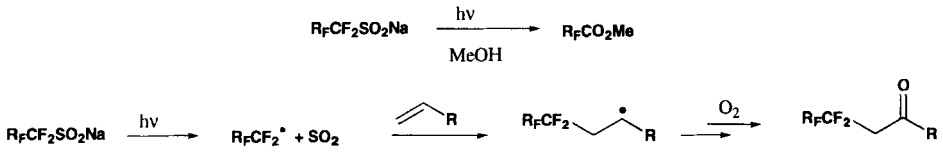
Scheme 23

An alternative protocol involves the oxidative generation of perfluoroalkane sulfonyl radicals from the corresponding sodium sulfinates.[18] This reaction was used as a convenient method for the trifluoromethylation of aromatics (Eq. 61).[18b]



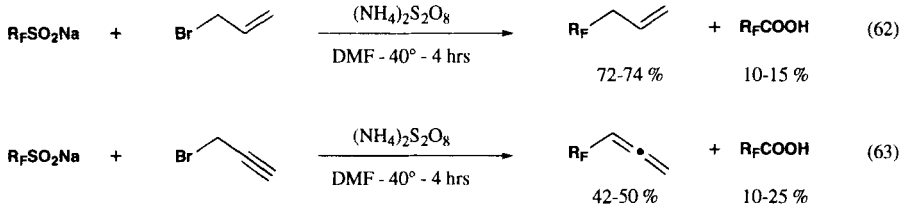
(61)

The photooxidation of perfluoroalkane sulfinates in the presence of olefins in water or methanol, gives rise to oxidatively terminated adducts. These reactions probably involve electron-transfer processes;[18a,c-e] such a process is yet to be applied to other types of sulfinates (Scheme 24).



Scheme 24

The reaction of perfluoroakane sulfinates with allyl bromide and propargyl bromide results in perfluoroolefins and perfluoroallenes respectively *via* a radical addition-elimination mechanism (Eqs. 62 and 63).[18c]

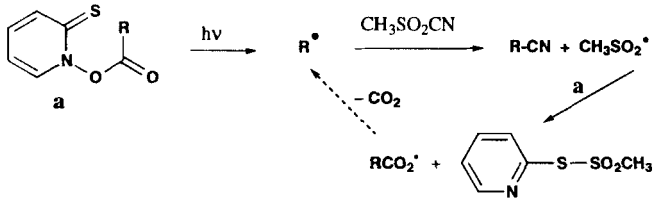


(62)

(63)

VII. REACTION WITH THIOHYDROXAMATES

Sulfonyl radicals may be efficient chain carriers in the decomposition of thiohydroxamates.[22a, 46a] Sulfonyl cyanides are efficient chain transfer agents for the synthesis of nitriles.[46b] This reaction cannot be classified in any of the preceding sections. Alkyl radicals generated photochemically by the Barton method,[46] react with the sulfonylcyanide to give the corresponding nitrile. The sulfonyl radical acts as the chain carrier and adds to the thiocarbonyl function. An alkyl radical is generated again by this step and continues the radical chain process (Scheme 25). Yields are nearly quantitative when six equivalents of sulfonyl cyanide are used. Methanesulfonyl cyanide is a better radical trap than tosyl cyanide.



Scheme 25

VII. CONCLUSION

In conclusion, sulfonyl radicals available from many precursors, are versatile intermediates which can participate in a large variety of radical chain reactions. Acting as the entering group, the sulfonyl radical allows the chemo-, regio- and stereoselective introduction of a sulfone group, leading to a major development of these sulfone syntheses over the last few years. There is no doubt that these advances are related to the attractive and powerful chemistry of sulfone group. Further exploration of sulfonyl radical reactivity will certainly broaden the scope of their synthetic utility. Although we attempted to cover all pertinent references, it is possible that a few valuable contributions might have been omitted.

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