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# Methods for the synthesis of vinyl sulfides

N V Zyk, E K Beloglazkina, M A Belova, N S Dubinina

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**Abstract. The published data on the methods for the synthesis of vinyl sulfides are considered and generalised. The main attention is given to methods based on electrophilic sulfenylation of unsaturated compounds. The bibliography includes 173 references.**

## I. Introduction

Vinyl sulfides play a prominent role in synthetic organic chemistry. They are extensively used as synthetic equivalents of enolate ions [1] and acyl anions.[2] In addition, vinyl sulfides are valuable intermediates in the synthesis of oxetanes,[3] spirocyclic systems [4] and other organic compounds.[5–10] Vinyl sulfides also present interest as candidate pesticides and bactericides.[11, 12]

Among numerous methods for the synthesis of vinyl sulfides that have been described in the literature, three main groups can be selected: (1) electrophilic sulfenylation of unsaturated compounds; (2) nucleophilic addition of the RS group and nucleophilic substitution at the unsaturated carbon atom; (3) synthesis *via* radical intermediates. Other methods for the synthesis of vinyl sulfides can be illustrated by only a few examples, which include addition of hydrogen halides to alkynyl sulfides, elimination of various fragments from sulfur-containing compounds, reduction of sulfoxides, the Wittig – Horner reactions of arylthio-substituted phosphonates and the Peterson reaction.

Some examples of the synthesis of vinyl sulfides can be found in reviews devoted to the synthesis of sulfides,[13] applications of sulfenyl chlorides in organic synthesis [14] and metal-catalysed formation of C–S bonds.[15] A recently published review is devoted to the synthesis of fluorine-containing alkyl(aryl)vinyl sulfides.[16] However, to the best of the authors' knowledge there are still no reviews devoted to the synthesis of vinyl sulfides. The present review is intended to bridge this gap. Here, we generalise and analyse the data on the methods for the synthesis of vinyl sulfides published in the last 15 – 20 years. Besides, we thought it expedient to mention some other methods that were developed much earlier, but are still widely used.

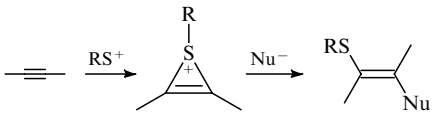
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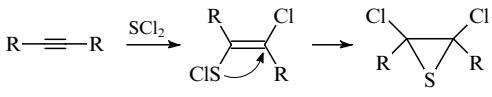
## II. Electrophilic sulfenylation of unsaturated compounds

### 1. Electrophilic sulfenylation of alkynes

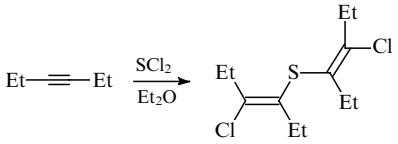
Electrophilic addition of divalent sulfur derivatives to alkynes is the most popular method for the synthesis of vinyl sulfides.




The addition of sulfur dichloride to alkenes and alkynes was studied in some detail back in the 1970's.[17–21] Reactions of alkenes [18–21] with $SCl_2$ afford chloroalkanesulfenyl chlorides which, in turn, react with the second alkene molecule to yield sulfides. It might be supposed that reactions of acetylenes with $SCl_2$ occur in a different manner and result in the formation of thiiranes, the addition products of the sulfenyl chloride group of the alkenesulfenyl chloride formed to the double bond.



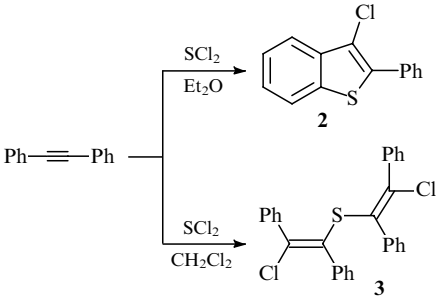

However, it was found that $SCl_2$ reacts with hex-3-yne in dry ether in the same way as with alkenes to afford divinyl sulfide **1**. The latter is formed as a result of sulfenylation of an alkyne by the alkenesulfenyl chloride formed in the first step.[17]



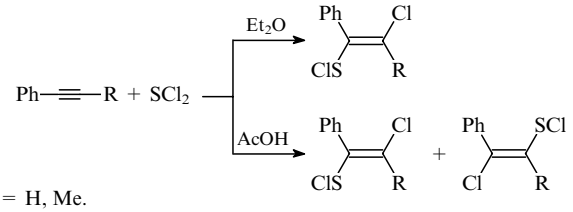

**1** (95%)

At the same time, the reaction of diphenylacetylene with sulfur dichloride in $Et_2O$ results in 3-chloro-2-phenylbenzothiophene

(**2**). The structure of the latter was established on the basis of its spectral characteristics and was confirmed by its conversion into the known 2-phenylbenzothiophene, although the reaction in dichloromethane gives divinyl sulfide **3** in high yield.[17]

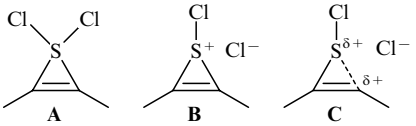


The stereo- and regioselectivity of the addition of sulfur dichloride to phenylacetylene have been studied.[17] It was found that the reaction of equimolar amounts of phenylacetylene and sulfur dichloride in $Et_2O$ yields an anti-Markownikoff adduct with a *trans*-configuration of the substituents, whereas Markownikoff and anti-Markownikoff products are formed in acetic acid. 1-Phenylpropyne reacts with $SCl_2$ in a similar way.



R = H, Me.

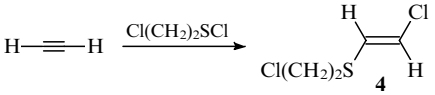
In highly polar solvents, *e.g.*, in acetic acid, the addition preferably occurs in accordance with the Markownikoff rule, while in less polar solvents, such as ethyl acetate, anti-Markownikoff adducts are preferably formed. It was thus suggested that this reaction occurs *via* one of the three intermediates **A**–**C** depending on the ion-stabilising characteristics of the solvent.



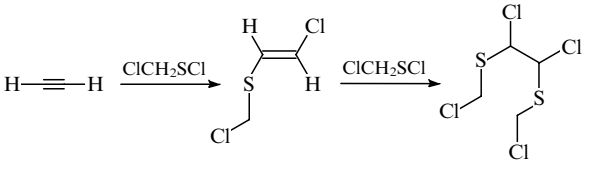
Steric factors compete successfully with the solvent effect.

Sulfenyl chlorides are one of the few sulfenic acid derivatives that add to multiple bonds without additional activation.

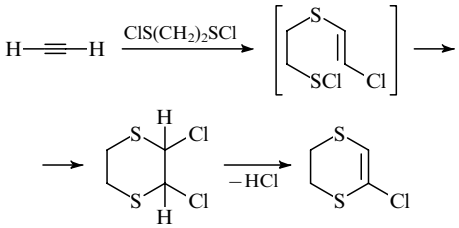
The first paper devoted to acetylene sulfenylation was published as early as 1946 within the framework of a search for methods for the synthesis of yperite and its analogues.[22] The addition of 2-chloroethanesulfenyl chloride to acetylene was studied. *trans*-Configuration was ascribed to the monoadduct **4** formed.



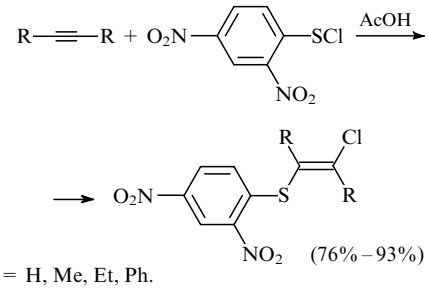
Later, it was shown[23] that the reaction of acetylene with chloromethanesulfenyl chloride yields an addition product of two sulfenyl chloride molecules to one acetylene molecule.



The reaction of acetylene with ethane-1,2-disulfenyl chloride underlies the synthesis of sulfur-containing heterocyclic compounds.[24]

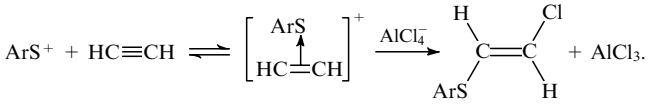


The reaction of 2,4-dinitrobenzenesulfenyl chloride with symmetrical acetylenes in glacial acetic acid yields exclusively *trans*-addition products.[24]



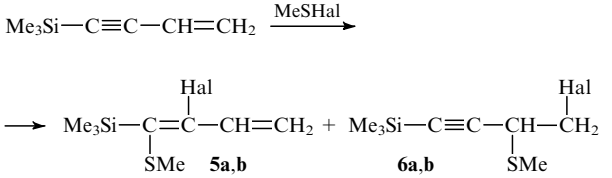
R = H, Me, Et, Ph.

It was found that sulfenyl chloride reacts with acetylene in dichloroethane only in the presence of catalytic amounts of $AlCl_3$.[25] The following reaction mechanism has been proposed:



However, in the case of higher acetylene homologues, *e.g.*, but-2-yne, hex-3-yne and diphenylacetylene, the presence of aluminium chloride is unnecessary.

As could be expected, electron-withdrawing groups deactivated the triple bond with respect to electrophilic reagents, while electron-donor groups activated it. Thus acetylenedicarboxylic acid does not react with sulfenyl chloride,[25] although methyl propiolate adds methane-, benzene- and *p*-substituted arenesulfenyl chlorides on heating.[26] Methanesulfenyl chloride adds to alkylthiovinylacetylenes exclusively at the triple bond.[27] The ratio of 1-trimethylsilylbut-3-en-1-yne adducts with methanesulfenyl halides (**5a** : **6a** and **5b** : **6b**) depends on the nature of the halogen atom in the sulfenylating reagent.[28]

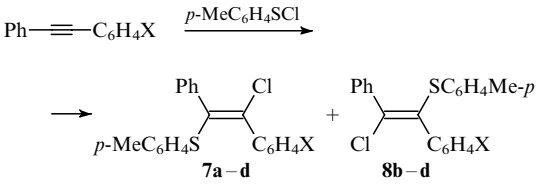


Hal = Cl (**5a**, 90%; **6a**, 10%), Br (**5b**, 75%; **6b**, 25%).

Functionalised trimethylsilylvinylacetylenes $Me_3Si-C\equiv C-CH=CRX$ (X = CN, COMe, $CO_2Et$; R = H, Me) react with methanesulfenyl chloride at the triple bond.[29] Reactions of methane-, ethane- and *p*-toluenesulfenyl chlorides with nitroenynes and their functional derivatives also involve exclusively the triple bond.[30]

The effect of substituents in the benzene ring of diarylacetylenes on the addition of sulfenyl chlorides has been studied.[31]

The reaction of *p*-toluenesulfenyl chloride with diphenylacetylene in chloroform yields the monoadduct **7a** in quantitative yield. The reaction with *p*-methoxy-substituted diphenylacetylene proceeds in a similar way. Compound **7b** is the only reaction product (no isomer **8b** was found †).



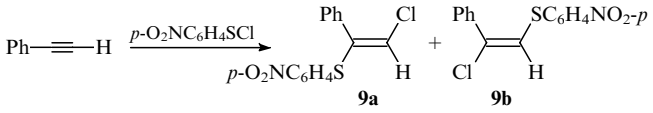
X = H (**a**), 4-MeO (**b**), 3-Cl (**c**), 4-Cl (**d**).

At the same time, the reaction of this sulfenylating agent with chloro-substituted diphenylacetylenes yields both isomers: for X = 3-Cl, the **7c** : **8c** ratio is 1 : 4, whereas for X = 4-Cl the **7d** : **8d** ratio is 3 : 2. Thus, the outcome of electrophilic addition of sulfenyl chlorides to substituted diphenylacetylenes is determined by the polar effects of the substituents.

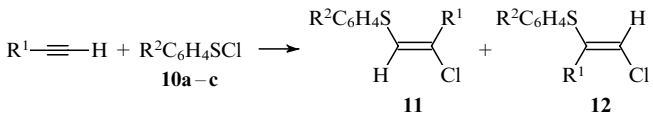
The rates of addition of sulfenyl halides to acetylenes and the structures of the reaction products depend on the nature of substituents in both the acetylene substrate and the starting sulfenyl halide. Thus the rate of addition of *para*-substituted arenesulfenyl chlorides to acetylene decreases in the following order: OMe > Me > H > Cl > $NO_2$. The methyl group and the chlorine atom in the *ortho*-position have little effect on the reaction rate, whereas the presence of a nitro group in the same position causes a 2000 — 3000-fold decrease in the reaction rate.[32]

Studies on the kinetics of the addition of 2,4-dinitrobenzenesulfenyl chloride to hex-3-yne and phenylacetylene in acetic acid have shown that both reactions are overall second order and first order with respect to each reactant; the reaction products are represented exclusively by *trans*-isomers. In the case of acetylene, the addition product is formed exclusively according to the Markownikoff rule.[33]

The effects of solvents on the ratio of Markownikoff and anti-Markownikoff addition products in reactions of sulfenyl chlorides with acetylenes have been studied.[25, 33, 34] It was shown in particular that the reaction of *p*-nitrobenzenesulfenyl chloride with phenylacetylene in ethyl acetate gives predominantly the anti-Markownikoff adduct **9a**, whereas the same reaction in acetic acid yields predominantly the adduct **9b**.[34]



The reaction product ratios of arenesulfenyl chlorides **10a**–**c** with phenylacetylene and but-1-yne in various solvents are presented in Table 1.[35]



$R^1$ = Et, Ph; $R^2$ = 4-Me (**a**), 4-$NO_2$ (**b**), 2-$NO_2$ (**c**).

All of the adducts formed are *trans*-addition products. A reaction scheme has been proposed [36] where a complex of the chloride ion with the thiirenium cation is formed in the first step. Further transformations of this ionic complex depend on the nature of the solvent and the structure of the cation; these determine the quantitative ratio of the reaction products. Thus conversions within tight ion pairs result in anti-Markownikoff adducts, while the dissociation into a chloride anion and an organic cation yields Markownikoff products.

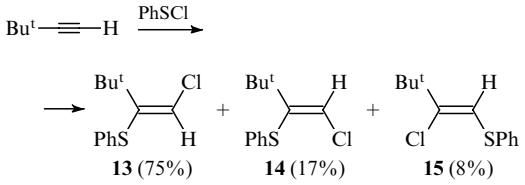
† It is worth mentioning that formation of the adduct **8b** in this reaction cannot completely be excluded. Apparently, it is present, but in insignificant amounts (< 5%).

**Table 1**. Yields of the adducts **11** and **12** prepared by sulfenylation of but-1-yne and phenylacetylene.[35]

| $R^1$ | $R^2$ | Solvent | Yield (%) | |
|---|---|---|---|---|
| | | | **11** | **12** |
| Ph | 4-Me | EtOAc | 100 | 0 |
| | 4-Me | $CHCl_3$ | 65 | 35 |
| | 4-Me | AcOH | 29 | 71 |
| | 4-$NO_2$ | EtOAc | 85 | 15 |
| | 4-$NO_2$ | $CHCl_3$ | 65 | 35 |
| | 4-$NO_2$ | AcOH | 20 | 80 |
| | 4-$NO_2$ | MeCN | 67 | 33 |
| | 2-$NO_2$ | EtOAc | 57 | 43 |
| | 2-$NO_2$ | $CHCl_3$ | 45 | 55 |
| | 2-$NO_2$ | AcOH | 11 | 89 |
| Et | 4-$NO_2$ | EtOAc | 100 | 0 |
| | 4-$NO_2$ | AcOH | 100 | 0 |
| | 2-$NO_2$ | EtOAc | 80 | 20 |
| | 2-$NO_2$ | $CHCl_3$ | 67 | 33 |
| | 2-$NO_2$ | AcOH | 58 | 42 |

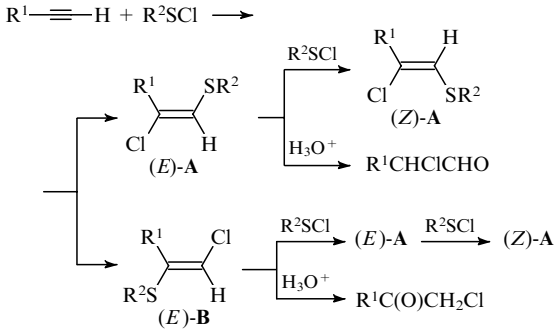
Catalytic amounts of trifluoroacetic acid and hydrogen chloride added to the reaction mixture have different effects on the structures and ratios of the reaction products of *p*-nitrobenzenesulfenyl chloride with phenylacetylene in ethyl acetate.[37] In the presence of hydrogen chloride, the ratio of Markownikoff and anti-Markownikoff *trans*-isomers changes simultaneously with the formation of *cis*-isomers. It has been found [37] that *cis*-isomers are formed as a result of isomerisation of the original *trans*-adducts. It is noteworthy that the nature of the acid influences neither the course of the reaction of but-1-yne with *p*-nitrobenzenesulfenyl chloride nor the ratio of the isomers formed.

The formation of *cis*-isomers in the chlorosulfenylation of certain alkynes has been observed earlier.[38] *cis*-Addition products have also been obtained in the reaction of benzenesulfenyl chloride with *tert*-butylacetylene.[39]



These studies have shown that compounds **13** and **14** are converted into a thermodynamically more stable isomer **15** upon heating or UV irradiation in benzene.

Later, it was found [40, 41] that reactions of sulfenyl chlorides with alkynes are *trans*-stereospecific and afford a mixture of Markownikoff [adduct (*E*)-**A**] and anti-Markownikoff products

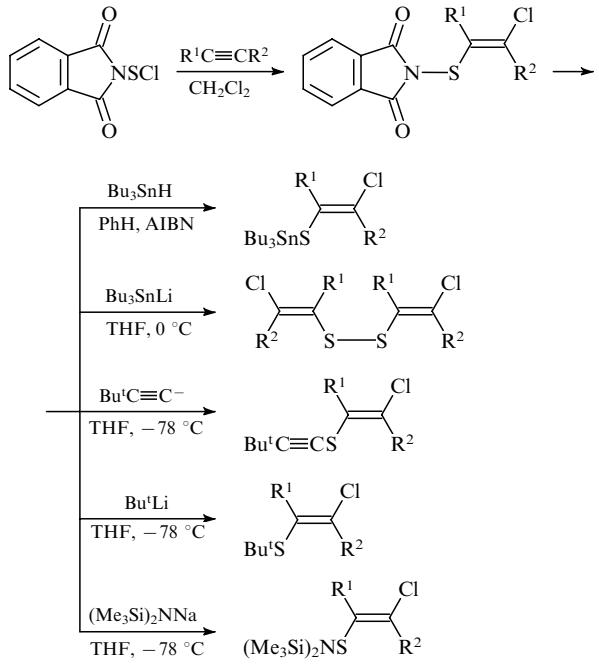


$R^1$ = $Pr^i$, $Bu^n$,$Bu^t$, Ph; $R^2$ = Me, $C_6H_4$Me-*p*, $C_6H_4$Cl-*p*.

[adduct (*E*)-**B**] which are converted into Markownikoff *cis*-isomers (*Z*)-**A** in the presence of an excess of sulfenyl chloride or catalytic amounts of trifluoroacetic acid.

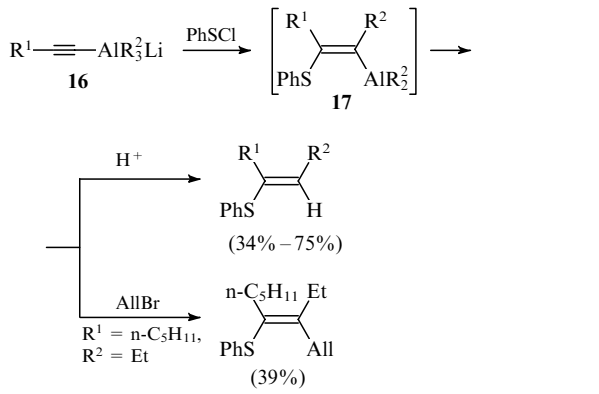
Aldehydes and ketones can in principle be prepared [40,41] from β-chlorovinyl sulfides synthesised upon acid hydrolysis.

A method for electrophilic sulfenylation of alkynes with phthalimidosulfenyl chloride, which can be regarded as a synthetic precursor of sulfenic acid derivatives, has been developed.[42] The nucleophilic substitution of the phthalimide group at the sulfur atom enables the preparation of hitherto unavailable vinyl sulfides and alkenesulfenamides. Some of them manifest pesticidal and bactericidal activities.[11]



$R^1 = R^2 = Me$, Ph; $R^1 = Bu^n$, $R^2 = H$; $R^1 = Ph$, $R^2 = H$;
AIBN is azobisisobutyronitrile.

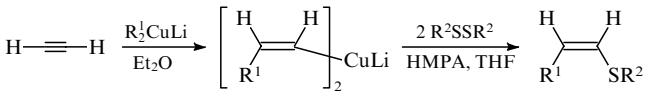
Yet another convenient approach to the synthesis of vinyl sulfides has been described.[43] Complexes **16** formed in the reaction of lithium acetylides with trialkylaluminium were used as the starting substrates. The reactions of these complexes with benzenesulfenyl chloride afford the intermediates **17** which yield vinyl sulfides upon hydrolysis or on treatment with allyl halides.



$R^1$ = n-$C_5H_{11}$: $R^2$ = Me, Et, $Bu^i$, n-$C_8H_{17}$; $R^1$ = n-$C_{10}H_{21}$, $R^2$ = Et.

The formation of side products, such as $R^1C{\equiv}CR^2$, $R^1C{\equiv}CSPh$, PhSSPh and $PhSR^2$, is a disadvantage of this reaction.

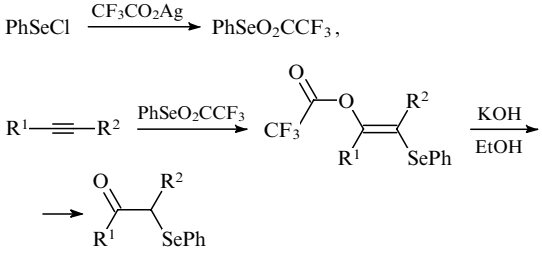
Vinyl sulfides can also be synthesised in a reaction of acetylene with alkyllithium cuprates.[44]



$R^1$ = Et, $Bu^n$, n-$C_7H_{15}$; $R^2$ = Me, $Bu^t$, Ph, Bn;
HMPA is hexamethylphosphoramide.

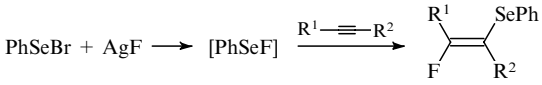
It is of note that in many studies devoted to electrophilic addition various selenium and tellurium derivatives were investigated along with sulfenyl chlorides. Thus reactions of areneselenenyl and arenesulfenyl chlorides containing 4-MeO, 4-Me, 4-Cl, 4-Br, 3-Br, 4-$NO_2$ and 3-$NO_2$ groups in the benzene ring with various unsaturated compounds have been studied.[45] It was shown [46] that the addition of sulfenyl and selenenyl halides (Hal = Cl, Br) to the triple bond of 1,4-dichlorobut-2-yne and subsequent dehydrohalogenation can be used for the synthesis of novel 1,3-disubstituted butadienes.

It was found [47] that reactions of areneselenenyl chloride and bromide with silver trifluoroacetate yield reactive complexes which are added to alkynes to give α-arylseleno-substituted esters. Hydrolysis of the latter yields α-arylseleno-substituted ketones.



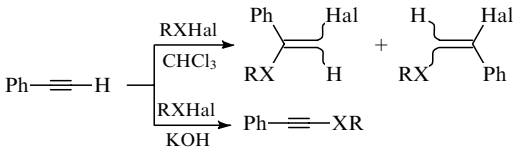
$R^1$ = Ph: $R^2$ = H, Me; $R^1 = R^2$ = Et.

Later,[48] fluoroselenenylation of a vast variety of alkyl- and dialkyl acetylenes was performed using sonication of an alkyne–phenylselenenyl bromide–silver fluoride mixture.



$R^1 = R^2$ = Et, Pr, Bu, Ph; $R^1$ = Et, $R^2$ = Ph;
$R^1$ = Pr, iso-$C_5H_{11}$, $R^2$ = Me.

The addition of sulfenyl, selenenyl and tellurenyl halides to phenylacetylene has been studied and their reactivities have been compared.[49] It was shown that the reaction rate decreases in the following order: AlkSHal > AlkSeHal > AlkTeHal. If the reaction is carried out in chloroform, a mixture of addition products is formed, whereas addition–elimination products are formed under conditions of phase-transfer catalysis (KOH–crown ether–PhMe).

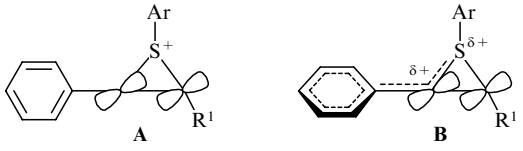


R = Me, Et, $Pr^i$, $Bu^n$; X = S, Se, Te; Hal = Cl, Br, I.

Much attention in the majority of papers devoted to reactions of sulfenyl chlorides with alkynes is given to the nature of reaction intermediates. The reaction of 2,4-dinitrobenzenesulfenyl chloride with 1-phenyl-prop-1-yne in $CHCl_3$ yields exclusively *trans*-addition products; the reaction mixture contains 94% of the Markownikoff adduct.[50] It was found that this reaction is second order and occurs in two steps. The first, rate-determining step is the formation of a cyclic intermediate (a thiirenium ion); the second step consists of its opening. The second reaction is *trans*-stereo-

specific rather than regioselective. The predominance of one of the isomers in the reaction mixture testifies to a non-symmetry of the cyclic intermediate.

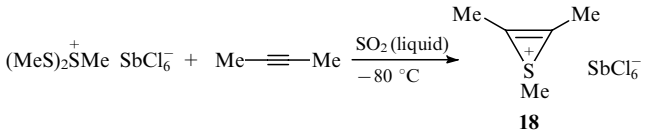
Further studies [51–54] of chlorosulfenylation of substituted acetylenes by sulfenyl chlorides in various solvents, *e.g.*, tetrachloroethane,[51,52] acetic acid [53] and $SO_2$ (see Ref. 54), revealed that the effects of the alkyl substituents at the triple bond on the rate of ArSCl addition are adequately described by the Taft correlation equation. Steric factors prevail over electronic ones only in the case of *tert*-butyl-substituted alkynes. The effects of aryl substituents at the triple bond are not so unambiguous. The data obtained [51–54] have made it possible to propose a theory for the cyclic structure of the reaction intermediate **A** and to postulate the role of the benzene ring in the delocalisation of the positive charge in the thiirenium ion (structure **B**) (see also Refs 17 and 20).




More recent studies [55] into kinetic isotope effects of the solvent in addition of 4-chlorobenzenesulfenyl chloride to alkenes and alkynes in AcOH and AcOD corroborated the earlier proposed mechanism.[50–54]

The kinetic aspects of reactions of arylacetylenes and styrenes with arenesulfenyl chlorides have been studied in detail; the rate constants and the activation barriers have been established.[56,57]

The isolation of trimethylthiirenium hexachloroantimonate (**18**) formed in a reaction of di(methylthio)methylsulfonium hexachloroantimonate with an excess of but-2-yne provided direct evidence for the role of thiirenium intermediates in the addition of sulfenyl chlorides to acetylenes.[58] This salt retained stability in liquid $SO_2$ at temperatures up to $-60$ °C.



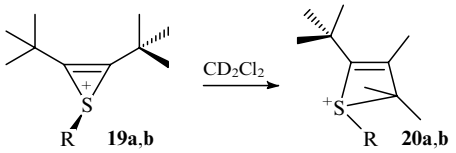

**18**

The $^1$H NMR and $^{13}$C spectra of compound **18** and the corresponding spectra of 2,3-diethyl-1-methylthiirenium ion isolated from hex-3-yne could be recorded.[58]

The use of alkynes containing bulkier substituents, *e.g.*, [di(*tert*-butyl)acetylene, 3-methyl-1-phenylbut-1-yne and 3,3-dimethyl-1-phenylbut-1-yne] increased the stabilities of thiirenium ions, and 1-methyl-2-phenyl-3-(*tert*-butyl)thiirenium and 1-methyl-2,3-di(*tert*-butyl)thiirenium hexachloroantimonates and tetrafluoroborates were isolated as white crystals at 20 °C.[59,60] The structures of 1-methyl-2,3-di(*tert*-butyl)thiirenium hexachloroantimonate, tetrafluoroborate and hexafluorophosphate were established using X-ray diffraction analysis.[61] The nucleophilic stereo- and regiospecific Markownikoff attack of the chloride ion on the sulfur atom of the thiirenium ring in the absence of stabilising non-nucleophilic anions ($SbCl_6^-$, $BF_4^-$) yields the corresponding (*E*)-chlorovinyl sulfides.[60]

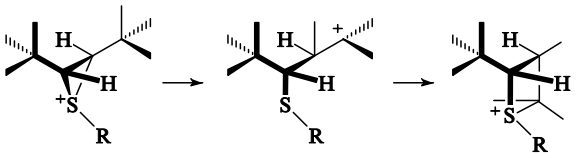
The structures, stabilities, reactivities and rearrangements of thiirenium and thiiranium ions have been studied by a group of Italian investigators.[62–66]

$^1$H NMR studies have shown [62] that compounds **19a,b** containing thiirenium rings are quantitatively isomerised in deuteriodichloromethane into thietene derivatives **20a**,**b** within several hours.

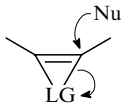



R = Me (**a**), $C_6H_4Cl$-*p* (**b**).

It is believed [63,64] that the rearrangement mechanism ($S_N2$-Vin) of thiirenium cations is similar to that of their saturated analogues, *viz.*, thiiranium ions.




The $S_N2$-Vin mechanism implies an attack of the nucleophile (Nu) lying in the plane of the molecule from the side opposite to the leaving group (LG). This results in the formation of a planar transition state which resembles that in $S_N2$.

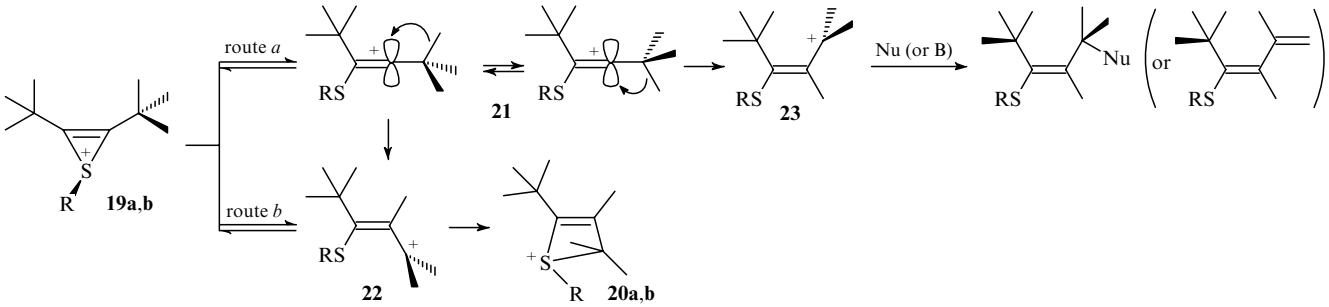



Theoretically, the rearrangements of the thiirenium ion may proceed according to two routes (Scheme 1, routes *a* and *b*). Route *a* leads to the linear intermediate **21** for which a 1,2-methyl shift is possible. This shift yields *Z*- and *E*-isomers of carbenium ions **22** and **23**. It is of note that only one of these isomers, *viz.*, the isomer **22**, can be converted into thietene derivatives **20a**,**b**, whereas the second ion (isomer **23**) reacts with a nucleophile or a base to give addition or dissociation products. Route *b* is no other than the $S_N2$-Vin mechanism, which yields exclusively compounds **20a**,**b**.

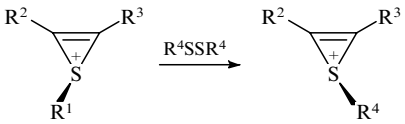
The quantitative conversion of compounds **19a**,**b** into compounds **20a**,**b** is in favour of a rearrangement according to route *b*.

Later, it was found [65] that thiirenium hexachloroantimonates react with dialkyl disulfides at 20 °C to yield substitution products.

Scheme 1

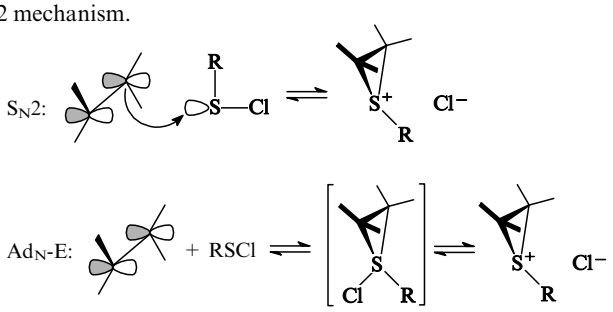



R = Me (**a**), $C_6H_4Cl$-*p* (**b**); B is a base.

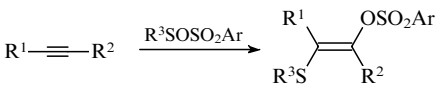


$R^1$ = Me, $C_6H_4Cl$-*p*; $R^2$, $R^3$ = Bu$^t$, Ph, Ad (Ad is adamantyl);
$R^4$ = Me, Et, Pr$^i$.

Steric hindrances created by substituents at the sulfur atom and the carbon atoms of the thiirenium ring strongly affect the reaction rate. An analysis of the kinetic data has led to a hypothesis that attack on the sulfur atom occurs in the plane of the ring parallel to the C=C bond. Such a direction corresponds to the maximum electron density of the lowest unoccupied molecular orbital (LUMO) of the thiirenium ions (*ab initio* calculations data [65, 66]). Taking into account the effects of the substituents on the reaction rate and the calculated data, Fachini *et al.*[65] put forward a hypothesis that nucleophilic substitution at the sulfur atom in thiirenium ions follows an addition–dissociation mechanism *via* a sulfurane-like intermediate rather than the $S_N2$ mechanism.



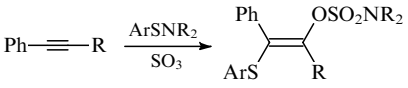
*o*-Sulfenylarene sulfonates react with unsaturated hydrocarbons like sulfenyl chlorides to give *trans*-adducts (1 : 1).[67]



$R^1$ = H, Me; $R^2$ = Ph; $R^3$ = Me, Ph, 4-$MeC_6H_4$;
Ar = 2,4,6-$(NO_2)_3C_6H_2$, 2,4-$(NO_2)_2C_6H_3$, 4-$NO_2C_6H_4$, 4-$BrC_6H_4$.

The orientation of substituents in the products of this type of reaction suggests that their mechanisms are similar to the mechanism of addition of sulfenyl halides to the triple bond.

The addition of weak electrophilic reagents to the multiple bonds requires the presence of activating reagents. A search for such agents has led to a vast variety of novel sulfenylating systems. Thus the use of readily available inorganic Lewis acids, *e.g.*, sulfuric anhydride and its complexes with pyridine,[68] thionyl and sulfuryl chlorides [69] as well as phosphorus halides and oxyhalides,[70, 71] zinc, magnesium and tin iodides,[72] as activating reagents has made it possible to perform electrophilic addition reactions with sulfenamides and sulfenates,[68–72] thio- and dithiobisamines,[69, 70, 72, 73] disulfides [74] and many other sulfur-containing compounds, which themselves cannot add to the multiple bond. This has made it possible to extend the range of reactants and to develop novel methods for one-step synthesis of substituted vinyl sulfides which cannot be prepared by other methods. The activation of arenesulfenamides by sulfuric anhydride is one of such reactions.[68, 75]

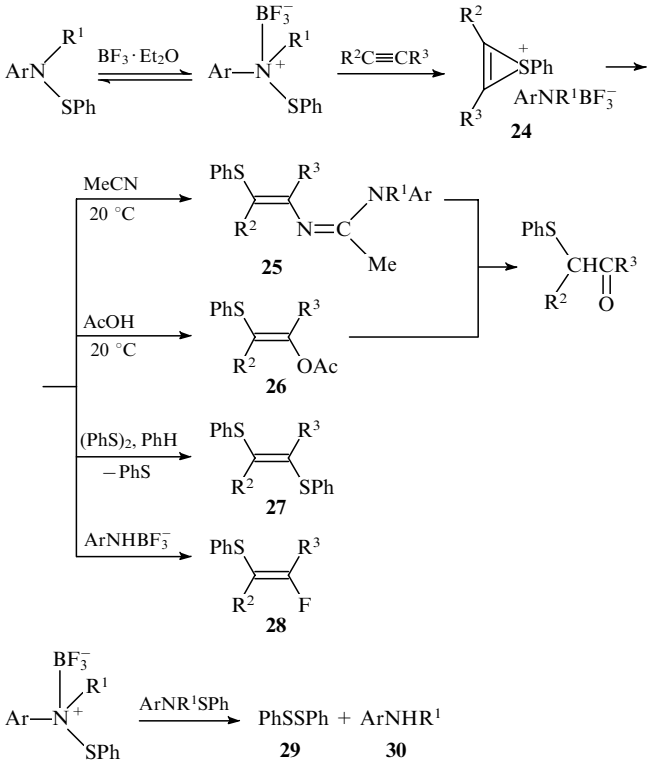


R = H (13%–15%), Ph (12%–14%).

It is sulfenyl sulfamate that is formed upon insertion of sulfuric anhydride at the sulfur–nitrogen bond that adds to the triple bond. However, this reaction has not gained wide acceptance for the preparative synthesis of aryl β-sulfamatovinyl sulfides because of low yields and side processes.

The studies by Italian investigators [76–83] were devoted to reactions of arenesulfenanilides with unsaturated compounds in the presence of boron trifluoride. The synthetic applications of these reactions have been investigated. It was found in particular that the reaction of *p*-nitrobenzenesulfenanilide with alkynes in the presence of boron trifluoride (20 °C) can be used for the preparative synthesis of β-substituted vinyl derivatives. It was found that $BF_3$ converts inactive arenesulfenanilides into highly reactive species (presumably into reactive $BF_3$–sulfenanilide complexes [78]) which undergo nucleophilic substitution at the sulfur atom to give thiirenium ions **24** (Scheme 2).

Scheme 2



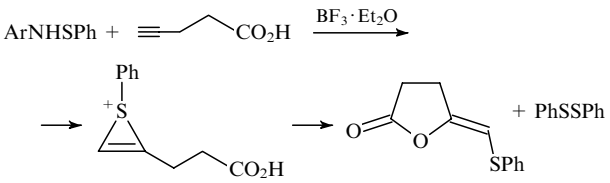
Ar = Ph, $C_6H_4Me$-*p*, $C_6H_4OMe$-*p*, $C_6H_4Cl$-*p*, $C_6H_4NO_2$-*p*;
$R^1$ = H, Me; $R^2$ = H: $R^3$ = Pr$^n$, Bu$^n$, Bu$^t$, Ph;
$R^2$ = Me: $R^3$ = Me, Pr; $R^2$ = $R^3$ = Et.

The nucleophilic opening of the thiirenium ring in the intermediate **24** is *trans*-stereospecific and highly regioselective and yields vinyl sulfides according to the Markownikoff rule. The ring opening in nucleophilic solvents, such as acetonitrile [75, 78] and acetic acid,[79] is accompanied by formation of β-amidino- (**25**) and β-acetoxyvinyl sulfides (**26**),[78, 79] respectively, in good yields. Compounds **25** and **26** are convenient starting reagents for the synthesis of β-oxosulfides.[82]

The addition of PhSSPh in non-nucleophilic solvents, such as dichloromethane and benzene, results in bissulfides **27**.[80] Alkyl-substituted acetylenes react with thiirenium cations in the presence of $ArNHBF_3^-$ to give β-fluorovinyl sulfides **28**.[80] In all cases studied, diphenyl disulfide **29** and substituted anilines **30** are formed along with the main reaction products.

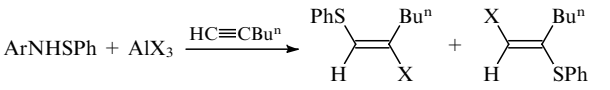
The reaction of boron trifluoride-activated *p*-nitrobenzenesulfenanilide with alkyl- and arylacetylenes in chlorobenzene (80 °C) occurs *trans*-stereospecifically and regioselectively and yields β-fluorovinyl sulfides **28**.[80]

If the sulfenamide molecule contains nucleophilic sites involved in the opening of the thiirenium ring, heterocyclic compounds are formed.[83]



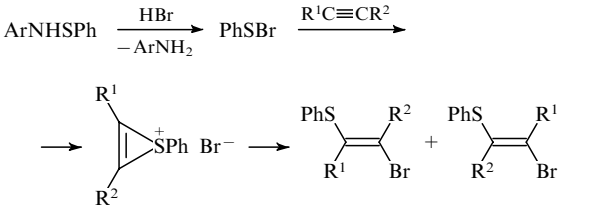
Ar = $C_6H_4NO_2$-*p*.

The activation of arenesulfenanilides by Lewis acids, such as $AlCl_3$ or $AlBr_3$, affords *E*-isomers of β-halogenovinyl sulfides.[83]



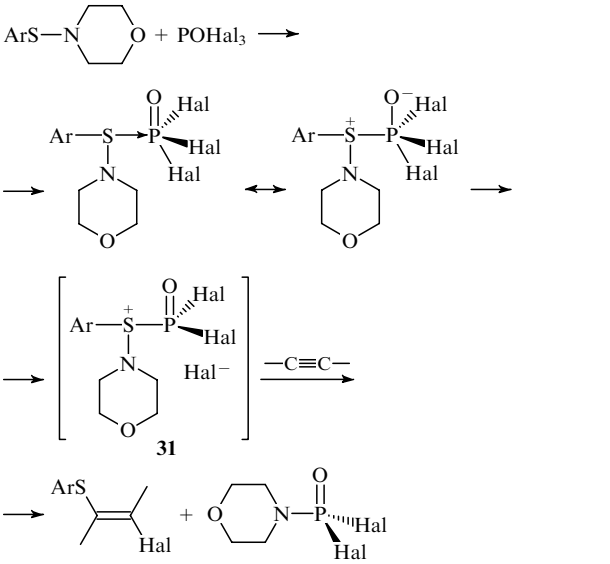
X = Cl (55%), Br (35%).

The *p*-nitrobenzenesulfenanilide–HBr system was recommended as a bromosulfenylating reagent.[83,84] The sulfenyl bromide formed adds *trans*-stereoselectively and regiospecifically to alkenes and alkynes against the Markownikoff rule. The mechanism of this reaction seems to be similar to the mechanism of addition of sulfenyl chlorides to multiple bonds.



Ar = $C_6H_4NO_2$-*p*; $R^1$ = H: $R^2$ = $Pr^n$, $Bu^n$, $Bu^t$, Ph;
$R^1$ = Me, $R^2$ = Ph; $R^1$ = Et: $R^2$ = Et, Ph.

Arenesulfenamides activated by phosphorus oxyhalides are promising sulfenylating reagents for alkynes.[85–87] It is believed that the role of reactive sulfenylating species in this reaction is played by complexes of the type **31**; the positive charge on the sulfur atoms is higher than that on the starting sulfenamide.[88]



Ar = Ph, $C_6H_4NO_2$-*p*, $C_6H_4NO_2$-*o*; Hal = Cl, Br.

The complexes **31** react with alkynes according to the electrophilic substitution mechanism. In the final addition step, the halogen atom of phosphorus oxyhalide acts as a nucleophile; this reaction yields β-halosubstituted vinyl sulfides.[71,85,87]

According to kinetic data, no sulfenyl chlorides are formed in reactions of arenesulfenamides with phosphorus oxychlorides. The data presented in Table 2 suggest that the reaction time of

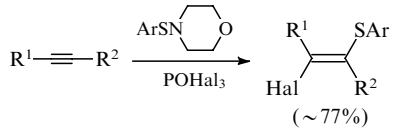
**Table 2**. Addition of sulfenyl chlorides and arenesulfenamides to unsaturated hydrocarbons.

| Alkyne or alkene | Sulfenyl chloride or arenesulfenamide | Activating reagent | Reaction time | Ref. |
|---|---|---|---|---|
| $H_2C=CH_2$ | 2,4-$(NO_2)_2C_6H_3SCl$ | – | 16 h | 89 |
| $HC\equiv CH$ | 2,4-$(NO_2)_2C_6H_3SCl$ | – | 5 days | 25 |
| $EtC\equiv CH$ | 4-$NO_2C_6H_4SCl$ | – | 12 h | 35 |
| $PhC\equiv CH$ | 2-$NO_2C_6H_4SCl$ | – | 30 days | 35 |
| $PhC\equiv CH$ | 2-$NO_2C_6H_4SN$ | $POCl_3$ | 20 h | 87 |
| $C_6H_{13}C\equiv CH$ | 4-$NO_2C_6H_4SN$ | $POCl_3$ | 1.5 h | 85, 87 |

$POCl_3$-activated *N*-(4-nitrophenylthio)morpholine with alkynes is much less than that of nonactivated sulfenyl chlorides.

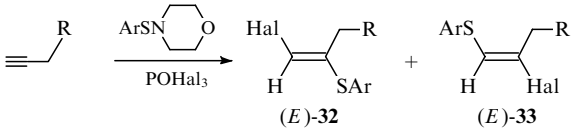
The rates of dehydration of sulfenyl bromides into disulfides often exceed the rates of their addition to multiple bonds, which decreases the yields of the final products.[22,90] At the same time, arenesulfenamides activated by phosphorus oxybromide react readily with alkenes,[71] alkynes[85,86] and dienes[88] to give high yields of bromosulfides. No new stable compounds are formed upon mixing of sulfenamides with $POCl_3$ or $POBr_3$ in dichloromethane in the absence of alkenes (TLC data).[87]

The reaction of $POHal_3$-activated arenesulfenamides with acetylene and its derivatives in dichloromethane chloride is *trans*-stereospecific.[85,87]



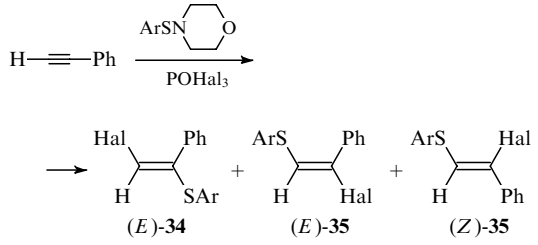
$R^1$ = $R^2$ = H, $Pr^n$; Ar = Ph, $C_6H_4NO_2$-*p*, $C_6H_4NO_2$-*o*, $C_6H_4Me$-*p*;
Hal = Cl, Br.

The addition of arenesulfenamides to terminal alkynes yields a mixture of isomeric aryl β-halogenovinyl sulfides (total yield 50%–90%), which represent addition products formed both against (**32**) and according to the Markownikoff rule (**33**).[85,87] The anti-Markownikoff product **32** prevails.



R = $Pr^n$, $Bu^n$, n-$C_5H_{11}$; Ar = $C_6H_4NO_2$-*p*, $C_6H_4NO_2$-*o*.

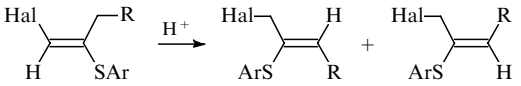
The *cis*-isomers of aryl β-halogenovinyl sulfides (*Z*)-**35** are formed in reactions of arenesulfenamides with phenylacetylene along with the *trans*-addition products (*E*)-**34** and (*E*)-**35**.[85,87]



Ar = Ph, $C_6H_4NO_2$-*p*, $C_6H_4NO_2$-*o*; Hal = Cl, Br.

2-Arylthio-1-halogenoalk-1-enes (*E*)-**32**, the products of anti-Markownikoff halogenosulfenylation of terminal alkynes,

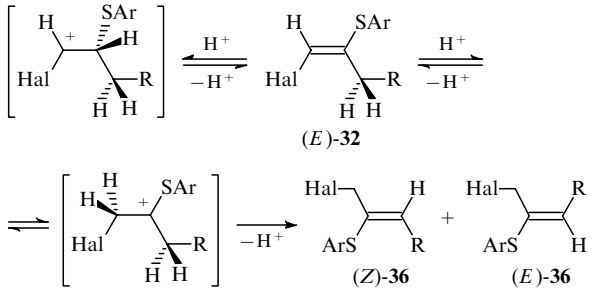
undergo isomerisation into 2-arylthio-1-halogenoalk-2-enes (*E*)-**36** and (*Z*)-**36** under the action of catalytic amounts of protic acids.[85,87]



(*E*)-**32** (*Z*)-**36** (*E*)-**36**

R = Pr$^n$, Bu$^n$, n-$C_5H_{11}$; Ar = $C_6H_4NO_2$-*p*, $C_6H_4NO_2$-*o*.

The following mechanism for the acid-catalysed isomerisation of 2-arylthio-1-halogenoalk-1-enes has been proposed:[86]



(*E*)-**32**



(*Z*)-**36** (*E*)-**36**

R = Pr$^n$, Bu$^n$, n-$C_5H_{11}$.

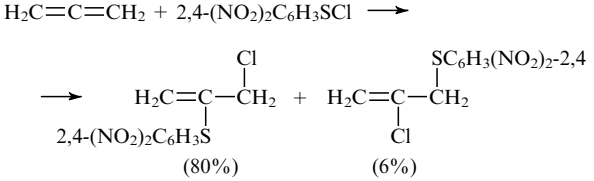
Here, the protonation of the double bond in compounds **32** and subsequent deprotonation with the formation of a mixture of isomeric alkenes is the key step. The ratio of the isomers is determined by their relative thermodynamic stabilities.

It should be emphasised that only one of the initially formed halogenovinyl sulfides, *viz.*, the anti-Markownikoff isomer **32**, undergoes isomerisation under conditions of acid catalysis to give a mixture of *E*- and *Z*-isomers of 2-arylthio-1-halogenoalk-2-ene **36** with the predominance of the *Z*-isomer. Under these conditions, the Markownikoff adduct (*E*)-**33** is partly converted into a *Z*-isomer. Apparently, the formation of more thermodynamically stable alkenes is the driving force of the isomerisation in both cases.

## 2. Electrophilic sulfenylation of allenes

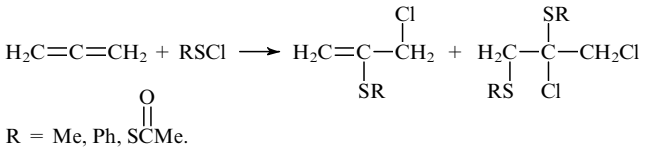
It is of note that reactions of sulfenyl halides with conjugated and non-conjugated dienes do not usually afford vinyl sulfides; therefore, electrophilic sulfenylation of these unsaturated compounds is not considered in this review. Here, only the sulfenylation of cumulated dienes, *i.e.*, allenes, will be discussed in detail.

In 1960, Jacobs and Johnson[91] established that 2,4-dinitrobenzenesulfenyl chloride reacted with allene to give 3-chloro-2-(2,4-dinitrophenylthio)prop-1-ene as an addition product (yield ~ 80%). In the authors' opinion, this reaction occurs regioselectively with the anti-Markownikoff attack by the electrophilic sulfur atom on the central atom of the allenic system. Such a regioselectivity is not unexpected, since the addition of sulfenyl chlorides to alkenes largely occurs against the Markownikoff rule. Small amount of a compound with a tentative structure of 2-chloro-3-(2,4-dinitrophenylthio)prop-1-ene could be isolated.



(80%) (6%)

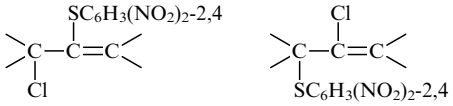
Later, it was found[92] that reactions of allenes with other sulfenyl chlorides always yield mainly anti-Markownikoff products. Bisadducts (up to 20%) are formed in small amounts along with monoadducts.



R = Me, Ph, SCMe.

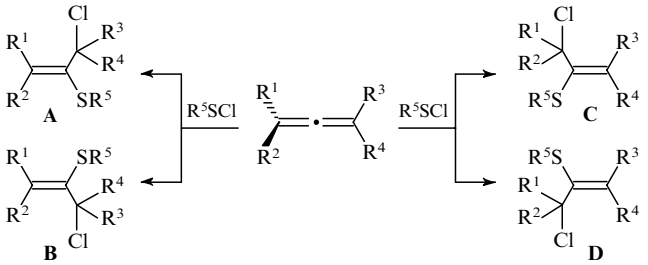
A classical mechanism including the intermediate formation of the episulfonium ion has been proposed for these reactions.[91,92]

The addition of 2,4-dinitrobenzenesulfenyl chloride to various allenes has been studied.[93] It was shown that adducts of the type **37** containing a 2,4-dinitrophenylthio group at the double bond are the main reduction products; regioisomeric compounds of the type **38** were formed in smaller amounts and with only some of the substrates studied.



**37** **38**

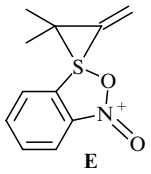
In early studies, stereochemical aspects of reactions of sulfenyl chlorides with allene derivatives have not been considered; the first paper[94] devoted to the detailed analysis of this problem appeared only in 1979. Evidently, addition of a sulfenyl chloride to a tetrasubstituted allene containing four different substituents may afford four stereoisomers **A** – **D**.



**A** **B** **C** **D**

It was shown[94] that electrophilic species always attack only the central atom of the allenic system. The stereochemistry of the addition reaction is determined by steric factors, which favour the predominant formation of (*E*)-isomers. The formation of Markownikoff products of the type **38** was explained by the rearrangement of the adducts of the type **37** formed under conditions of kinetic control.

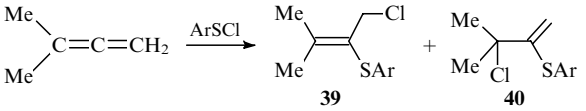
The kinetics of addition of sulfenyl chlorides to allenes and the effects of substituents in sulfenyl chlorides on the rate and stereochemistry of the reaction have been studied.[95–97] It was found that steric and electronic factors have little effect on the addition of sulfenyl chlorides to allenes.[97] It was therefore concluded that steric effects are critical only in the case of arenesulfenyl chlorides containing *ortho*-substituents in the benzene ring. It was even suggested[96] that specific intermediates **E** are formed in reactions of allenes with *o*-nitrobenzenesulfenyl chloride; however, this hypothesis has not been strictly proven.



**E**

In a more recent study,[98] using the example of the reaction of 1,1-dimethylallene with various sulfenyl chlorides it was shown that the ratios of the products **39** and **40** strongly depend on the reaction conditions and the nature of the aryl substituent in the sulfenyl chloride. Thus the adduct **39** is mainly formed in $C_2H_2Cl_4$ at 20 °C, whereas the adduct **40** is mainly formed in $CH_2Cl_2$ at −78 °C. As far as the nature of the aryl substituent in a sulfenyl

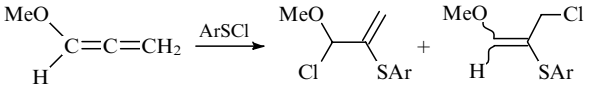
chloride is concerned, the adducts **40** are almost exclusively formed for Ar = Ph, 4-$MeC_6H_4$, while a mixture of the adducts **39** and **40** (2 : 1) is formed for Ar = 4-$ClC_6H_4$ and 2,4-$(NO_2)_2C_6H_3$, respectively.



**39** **40**

Ar = Ph, 4-$MeC_6H_4$, 4-$ClC_6H_4$, 2,4-$(NO_2)_2C_6H_3$.

Similar conclusions were made with respect to the reaction of 1-methoxyallene with arenesulfenyl chlorides.[99] Treatment of chlorosulfenylation products of 1-methoxyallene with water yields α-arylthiosubstituted aldehydes.

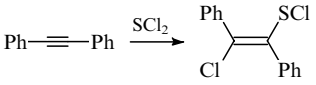


Ar = 4-$MeC_6H_4$, 4-$ClC_6H_4$, 2,4,5-$Me_3C_6H_2$.

Chloro- and bromoselenenylation reactions of allenes [100] were found to be very similar to the sulfenylation reactions.

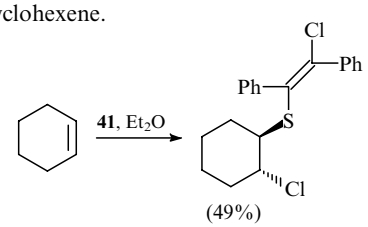
## 3. Electrophilic vinylsulfenylation of alkenes

As mentioned above, the addition of sulfur dichloride to alkynes usually results in divinyl sulfides. However, it was possible to isolate [17] an intermediate product, *viz.*, 2-chloro-1,2-diphenylethenesulfenyl chloride (**41**), upon treatment of diphenylacetylene with $SCl_2$ and to investigate its properties.



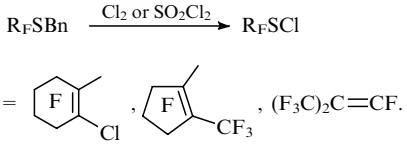
**41**

It was shown, in particular, that this compound adds to cyclohexene.

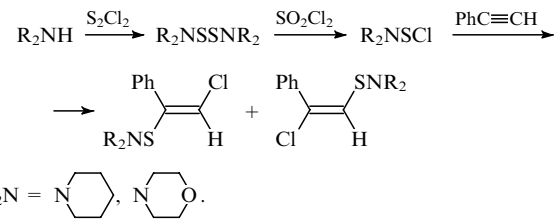


(49%)

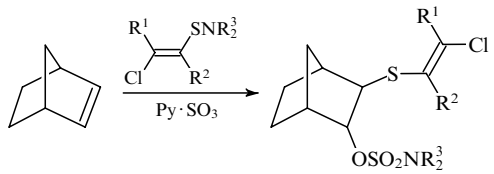
There is very little evidence on reactions of α,β-unsaturated sulfenyl chlorides, which may be attributed to their inaccessibility and low stability.[17] It is known, for example, that chlorination of some benzyl, perfluoroalkenyl and perfluorocycloalkenyl sulfides results in the chlorolysis of the C–S bond with retention of the double bond in the fluorinated substituents.[101] The perfluoroalkene- and perfluorocycloalkenesulfenyl chlorides formed are efficient sulfenylating reagents, which easily add to multiple bonds.



Later, a new method for electrophilic vinylsulfenylation of alkenes by ethenesulfenamides in the presence of activating reagents, such as sulfuric anhydride and its complexes with tertiary amines ($Py \cdot SO_3$, $Et_3N \cdot SO_3$) or ammonia, was proposed.[102, 103] Ethenesulfenamides were prepared from readily available dithiobisamines.



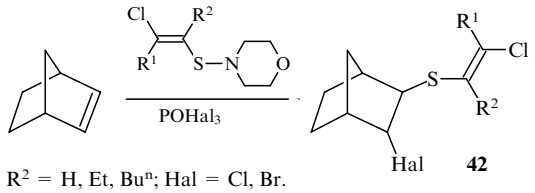
The insertion of sulfotrioxide into the S–N bond of vinylsulfenamides has enabled the sulfamatovinylsulfenylation of some cage alkenes.[102, 103]



$R^1$ = Et, $Bu^n$; $R^2$ = H, Et; $NR^3_2$ = .

An attempt to perform vinylsulfenylation of conformationally labile alkenes, such as cyclohexene and hex-1-ene, was unsuccessful, since the products formed appeared to be extremely unstable.[104]

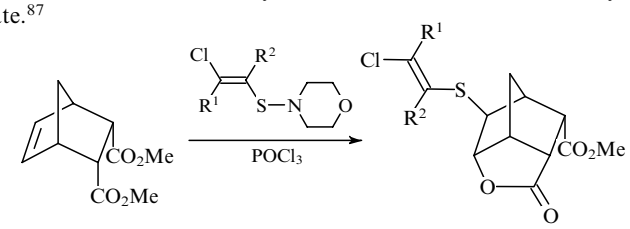
Similar results were obtained in the electrophilic vinylsulfenylation of alkenes by ethenesulfenamides activated by phosphorus oxyhalides.[87] Thus stable compounds (*e.g.*, product **42**) were obtained in reactions with cage alkenes (norbornene, norbornadiene, camphene, dimethyl 5,6-di-*endo*-norbornenedicarboxylate), while the vinylsulfenylation products of conformationally labile alkenes, *e.g.*, cyclohexene, could not be isolated because of their low stability.[87]



**42**

$R^1$, $R^2$ = H, Et, $Bu^n$; Hal = Cl, Br.

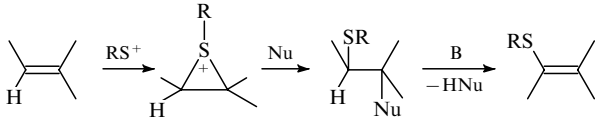
The feasibility of conjugate addition was demonstrated in the example of a reaction of phosphorus oxychloride-activated ethenesulfenamides with dimethyl 5,6-di-*endo*-norbornenedicarboxylate.[87]



$R^1$, $R^2$ = H, Et, $Bu^n$.

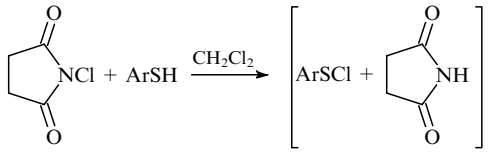
## 4. Electrophilic sulfenylation of alkenes with subsequent α,β-elimination

Electrophilic sulfenylation of alkenes with subsequent α,β-elimination is yet another convenient method for the synthesis of vinyl sulfides. Both reaction steps are carried out under mild conditions and give fairly good yields of reaction products.[105–109]

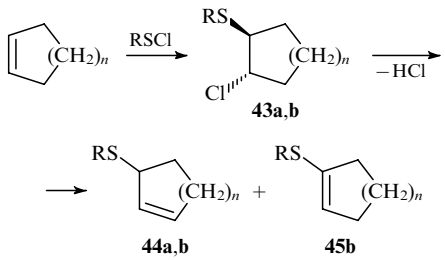


B is a base.

Sulfenyl halides are usually precursors of reactive species $RS^+$. Dehydrohalogenation is carried out with different bases, *e.g.*, sodium methoxide, potassium *tert*-butoxide (in diethyl ether, DMSO or THF),[105] triethylamine,[106,107] sodium carbonate,[108] potassium fluoride (in DMSO or THF)[109] and silver trifluoroacetate.[109] A convenient method for the *in situ* synthesis of starting arenesulfenyl chlorides, which excludes isolation and purification of sulfenyl chlorides, has been described.[108]



There are two possible directions of elimination, which yield allylic or vinylic sulfides. In many cases, the formation of allylic rather than vinylic sulfides is more preferable. Thus it has been shown[105] that 1-alkylthio-2-chlorocyclohexanes **43a** undergo elimination with great difficulty and give exclusively 3-alkylthiocyclohexenes **44a**. The formation of alkenes containing an allylic RS group proves that *anti*-elimination is more preferable for cyclohexane systems with a diaxial arrangement of the hydrogen atom [at C(3)] and the leaving group (the chlorine atom). The proton at C(1) is in a *gauche*-position relative to the chlorine atom in any conformation of cyclohexane **43a** which is unfavourable for the elimination.[105]



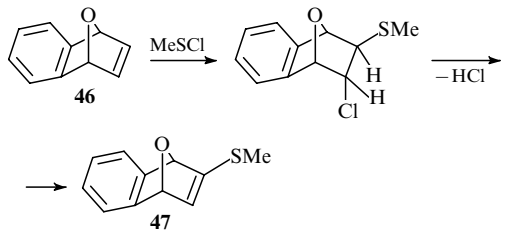
**43a**,**b**

**44a**,**b** **45b**

$n$ = 2 (**a**), 1 (**b**); R = Me, Et.

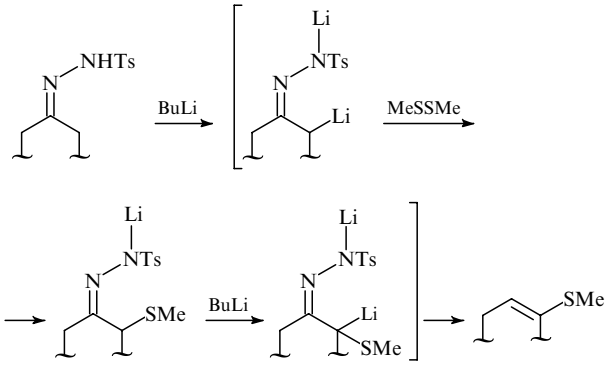
On the other hand, the dehydrohalogenation of sulfenylation products of cyclopentene **43b** occurs more smoothly and yields a mixture of 3-alkylthio- (**44b**) and 1-alkylthiocyclopentenes (**45b**) (1 : 1). The equal probability of formation of allylic and vinylic thioethers suggests that *syn*-elimination is the most probable route for this system.

*syn*-Elimination is the only route for the chlorosulfenylation products of the cage alkene **46**, which gives a quantitative yield of vinyl sulfide **47**.



**46** **47**

Dialkyl disulfides can also be used as electrophilic sulfenylating species. Their reactions with *C*,*N*-lithiated tosylhydrazones and subsequent α,β-elimination lead regioselectively to vinyl sulfides; the yields of the latter depend on the nature of substituents in the starting tosylhydrazones.[110]

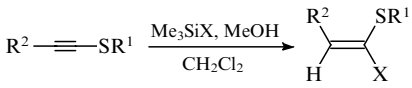


## III. Synthesis of α-halogenovinyl sulfides by electrophilic hydrohalogenation of alkynyl sulfides

Regioselective addition of hydrogen halides (HCl, HBr, HI) to alkynyl sulfides is also related to the class of electrophilic reactions. However, it can be placed in a separate group, because it is not accompanied by the formation of a new C–S bond. This reaction is the simplest and most efficient approach to the synthesis of α-halogenovinyl sulfides (see Ref. 111 and references cited therein).

Reactions of aqueous hydrohalic acids (37% HCl, 48% HBr, 51% HI) or saturated hydrogen halides in benzene with alkynyl sulfides are regioselective and yield mixtures of *Z*- and *E*-isomers that are difficult to separate.

The recently developed procedure for the synthesis of α-halogen-substituted vinyl sulfides and vinyl ethers by addition of a hydrogen halide generated *in situ* from a trimethylsilyl halide in dry methanol at low temperature is devoid of this defect.[112] This reaction is highly regioselective and affords nearly quantitative yields of vinyl sulfides.[113]

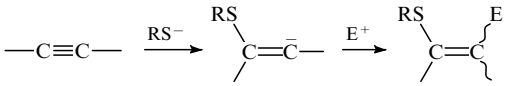


$R^1$ = Me, Ph; $R^2$ = $Bu^n$, n-$C_7H_{15}$, cyclo-$C_6H_{11}$, $BnCH_2$; X = Cl, Br, I.

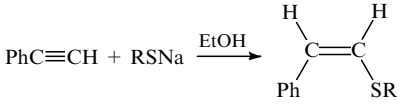
## IV. Methods for the synthesis of vinyl sulfides based on nucleophilic reactions

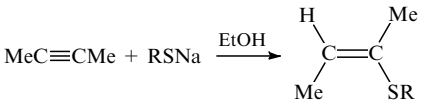
### 1. Nucleophilic thiolation of alkynes

Nucleophilic thiolation of alkynes is one of the oldest, but nevertheless valuable methods for the synthesis of nonsymmetrical unsaturated sulfides. On the whole, this reaction can be described by the following scheme:



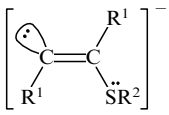
Thiols and alkali metal thiolates are most commonly used as thiolating reagents[114–116] with proton as the electrophile. The use of thiolates enables the synthesis of stereochemically pure products. Thus reactions of phenylacetylene and but-2-yne with various thiolates occur exclusively as *trans*-addition.[116]





R = Me, $C_6H_4Me$-*p*.

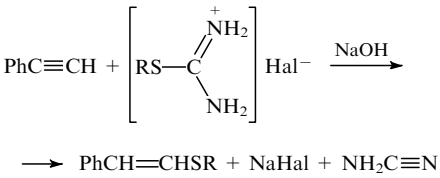
Such a stereoselectivity can be attributed to the fact that this reaction proceeds *via* a carbanion in which the negative charge on the carbon atom (the free electron pair) and the lone electron pairs on the sulfur atom tend to be arranged as far as possible from one another.



$R^1$ = H, Me, Ph; $R^2$ = Me, $C_6H_4Me$-*p*.

Thiols add to non-symmetrical alkynes in a non-stereoselective manner.[117]

A reaction described by Trofimov and co-workers [118] can also be regarded as a convenient method for the synthesis of alkyl (β-substituted vinyl) sulfides. It was found that thiolation of phenylacetylene by thiolate anions generated from *S*-alkylisothiouronium salts under the action of alkali occurs smoothly under mild conditions in both protic (ethanol) and aprotic (DMSO, DMF, *N*-methylpyrrolidone) solvents. The yields of alkyl styryl sulfides in dimethyl sulfoxide reached 98%.

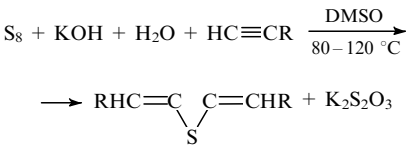


R = Me, $Pr^n$, All; Hal = Br, I.

The *in situ* generation of thiolate anions from *S*-alkylisothiouronium salts in the presence of alkali excludes the use of free thiols and, as a consequence, the occurrence of competing free-radical reactions.[118]

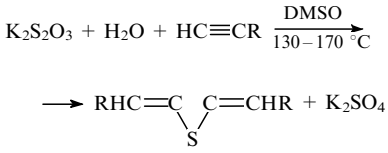
Alternative methods for the *in situ* generation of thiols include decomposition of xanthates and dithiocarbonates [119] and alkylthioimidinium salts.[120] Electrochemical generation of thiolate anions is carried out in the absence of alkali. It is possible to synthesise sulfides by this method in up to 97% yields.[121]

The salient advantages of alkyne thiolation by elemental sulfur in the presence of potassium hydroxide and catalytic amounts of water required for the proton transfer are simplicity of the procedure, availability of reactants and high yields of divinyl sulfides.[122]



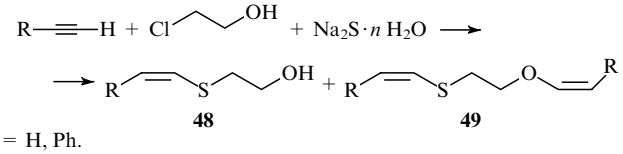
R = H, Ph.

The reaction is carried out at 80–120 °C exclusively in aprotic dipolar solvents (DMSO, HMPA), which are rather stable on heating in the presence of strong bases. In other solvents (*e.g.*, dioxane), the reaction does not occur or proceeds with low efficiency. It was shown [122] that at higher temperatures (130–170 °C) the potassium thiosulfate formed can also react with acetylene thereby increasing the yield of the final product.



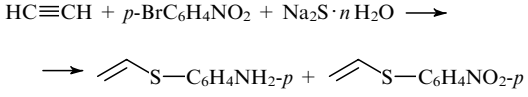
R = H, Ph.

The reactions of acetylene and its derivatives with ethylene chlorohydrin and aqueous sodium sulfide afford 2-hydroxyethyl vinyl sulfides **48** and 2-vinyloxyethyl vinyl sulfides **49**.[123]



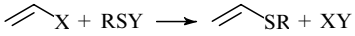
R = H, Ph.

If the reaction in DMSO is carried out in a flow reactor, it can be stopped at the stage of formation of sulfide **48**. Taking into account the accessibility of the starting reagents, this synthetic procedure can sometimes be rather convenient despite low (5%–20%) yields of the reaction products. This approach was used in the synthesis of *p*-nitrophenyl and *p*-aminophenyl vinyl sulfides.[123]



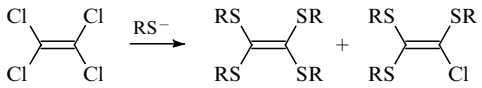
## 2. Nucleophilic substitution at the unsaturated carbon atom

Nucleophilic substitution at the unsaturated carbon atom is yet another popular synthetic procedure.



Vinyl halides (X = Cl, Br, I) are most commonly used as substrates, while thiols [124] and alkali metal,[125–127] copper [128] and magnesium [6] thiolates serve as a source of thiolating species.

Thus tetrachloroethylene reacts exothermally with sodium thiolates as suspensions in aprotic solvents (*e.g.*, DMF, DMSO, HMPA) at atmospheric pressure to afford tetra[alkyl(aryl)thio]-ethylenes in 60%–80% yields. Tri[alkyl(aryl)thio] derivatives are formed as side products.[123]



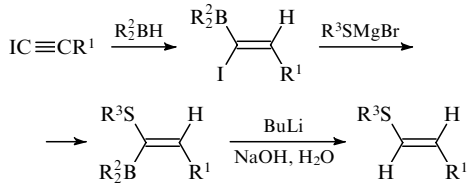
R = Et, $Pr^n$, $Pr^i$, $C_6H_{13}$, $C_8H_{17}$, $(CH_2)_2OH$, Ph.

Substitution at the double bond occurs more easily in the presence of catalysts, such as Ni (see Ref. 126) and Pd complexes.[127] Nonpolar aprotic solvents (benzene, toluene, dimethoxyethane) are used in catalytic reactions, whereas alcohols are usually used in the absence of catalysts.

Reactive thiolating species can also be generated *in situ*, if the reaction is carried out in alkaline media. Alkali metal hydroxides (NaOH, KOH) [129] or potassium carbonate in acetone [124] are most often used as deprotonating reagents.

Similar reactions were used in the synthesis of vinyl selenides.[126] High (70%–80%) yields of vinyl sulfides and vinyl selenides is a salient advantage of this method.

A highly stereospecific method for the synthesis of vinyl sulfides from alkynes, boranes and magnesium thiolates has been developed.[6] This approach can be used for the synthesis of a broad range of vinyl sulfides.



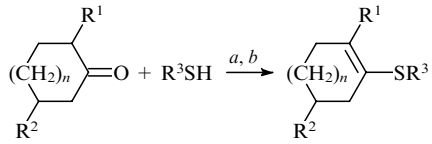
$R^1$ = $Bu^n$, n-$C_6H_{11}$; $R^2$ = $Me_2CHCHMe$; $R^3$ = $Bu^n$, $Bu^t$, Ph, Bn.

All reagents used in this reaction are readily available and relatively inexpensive; moreover, all reactions can be carried out in a one-pot procedure.

## 3. Addition of thiols to the C = O bond of carbonyl compounds

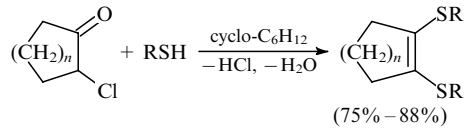
In recent years, the method based on addition of thiols to ketones under conditions of acid catalysis followed by dehydration of the hemiketals formed has been widely used for the synthesis of vinyl sulfides. Both protic [130] and Lewis acids [$AlCl_3$,[131] $P_2O_5$ (see Refs 131 and 132), *etc*.] are used as catalysts.

Thus heating of a mixture of a cyclic ketone, a thiol and a catalyst in benzene afforded the corresponding vinyl sulfides in up to 80% yields.[132]

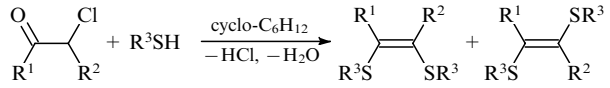


$R^1$, $R^2$ = H, Me, $Pr^i$; $R^3$ = Et, $Pr^n$; $n$ = 1, 2, 3;
(*a*) PhH, $AlCl_3$, Δ, 15 min; (*b*) PhH, $P_2O_5$, Δ, 1 h

This approach [133] was used for the synthesis of di(alkylthio)alkenes from a series of cyclic and acyclic α-chloro ketones; the former are starting compounds in [4 + 2]-cycloaddition reactions used for the synthesis of novel acetylene compounds.[134]



$n$ = 1, 2; R = Et, Pr, Bu.

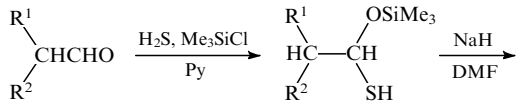


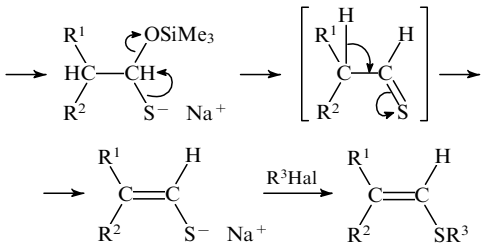
$R^1$ = Me, Et, $Pr^n$, $Bu^n$, $Bu^t$, Ph; $R^2$ = H, Me, Et, $Pr^n$; $R^3$ = Et, Pr, Bu.

The Michael addition of thiols to cyclic α,β-unsaturated carbonyl compounds, such as 3-oxo-2,3-dihydrothiophene 1,1-dioxides, with subsequent opening of the ring also affords vinyl sulfides (see Section VI).

## 4. Nucleophilic vinylthiolation

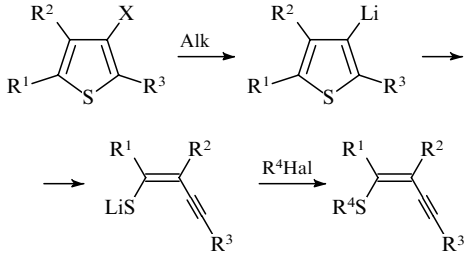
Much attention has recently been given to methods based on nucleophilic vinylthiolation. In many reactions, nucleophilic species are generated *in situ*, *e.g*., upon treatment of aldehydes with $Me_3SiCl$ and $H_2S$ in pyridine.[135]

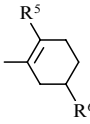




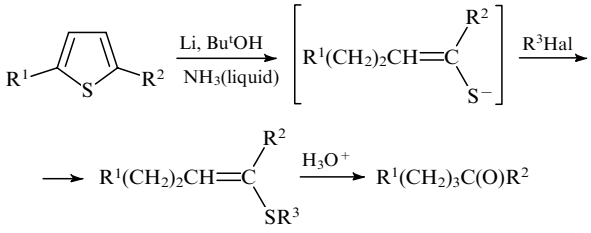
$R^1$ = H: $R^2$ = Me, Et, $Pr^i$; $R^1 - R^2$ = $(CH_2)_5$;
$R^3$ = $Ph(CH_2)_2$, Bn, cyclo-$C_6H_{11}$, $Pr^n$, $Bu^n$; Hal = Cl, Br, I.

The vinylthiolating species can easily be generated through the opening of the thiophene ring under the action of organolithium compounds [136, 137] or metals (Li, Na) in liquid ammonia in the presence of alcohols.[138]



X = Br, I; $R^1$ = H, Me, Et, $Bu^t$, Ph; $R^2$ = H, Me; $R^3$ = H, Me, Et,
$Bu^t$, Ph,  ($R^5$ = Me, $R^6$ = H; $R^5$ = $Pr^i$, $R^6$ = Me);
Alk = Et, Bu; $R^4$ = Et, Bu, $CO_2Et$, $CH_2CO_2Me$, Bn; Hal = Cl, Br.

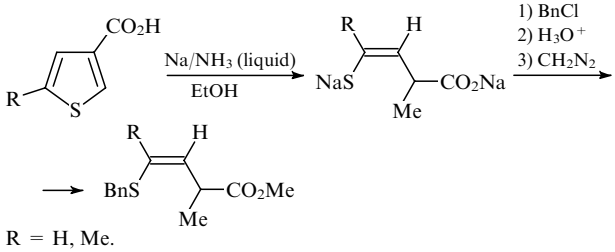
The cleavage of the thiophene ring takes place under the action of solvated electrons; subsequent alkylation of the thiolate formed gives rise to various unsaturated sulfides which are further converted into the corresponding ketones.[138, 139]



$R^1$ = H, Me; $R^2$ = Me, Et, $C_9H_{19}$, $(CH_2)_2NEt_2$, $(CH_2)_4NEt_2$, $(CH_2)_6NEt_2$; $R^3$ = Me, Et, $Bu^n$, $(CH_2)_4CO_2Et$, $CH_2COPh$, $CH_2CH(Me)OH$, $CHCH_2OH$, $CH_2\overline{CHCH_2O}$; Hal = Cl, Br, I.

In the last step, epoxides can be used as alkylating reagents.[139]

The opening of the thiophene ring in thiophene-3-carboxylic acids [140] results in enolthiolate; its benzylation and subsequent esterification give high yields of alkyl (*Z*)-4-benzylthio-2-methylalk-3-enoates.



R = H, Me.

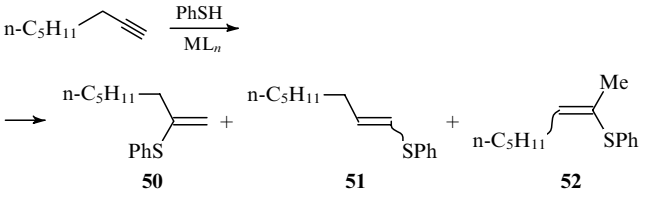
## V. Methods for the synthesis of vinyl sulfides based on reactions occurring *via* radical intermediates

### 1. Addition of thiols to alkynes

The addition of thiyl radicals to multiple carbon – carbon bonds is a well-known reaction, which has found wide acceptance in organic synthesis. Normally, thiyl radicals are generated from thiols or disulfides by thermolysis, photolysis [141] or treatment with radical initiators.[142, 143] The radical addition of thiols to alkynes occurs regioselectively against the Markownikoff rule and yields a mixture of stereoisomers.

Reactions of thiols with acetylenes are catalysed by nickel,[15, 144] platinum,[144–146] palladium,[144, 146] rhodium [144, 147, 148] and ruthenium complexes.[148]

The addition of benzenethiol to various alkynes has been studied in detail.[144, 147] The effects of the structure of the starting substrate, the nature of the catalyst and the solvent on the yields of reaction products have been investigated. Using the reaction of oct-1-yne with benzenethiol as an example, it was demonstrated [147] that the addition follows the Markownikoff rule in the presence of palladium(II) acetate and yields compound **50**. However, reactions catalysed by other divalent palladium complexes, *e.g.*, $PdCl_2(PhCN)_2$ or $PdCl_2(MeCN)_2$, afford the anti-Markownikoff product **51** and the double-bond-migration product **52**.

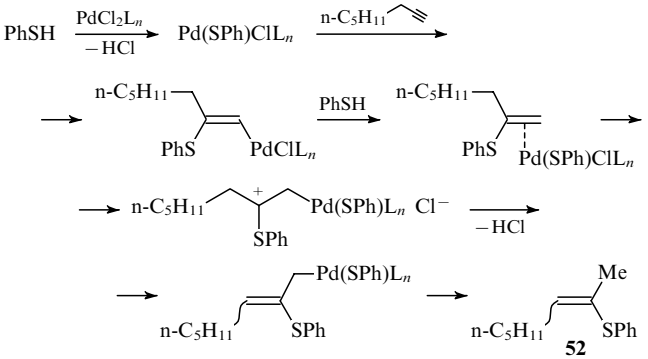



**50** **51** **52**

$ML_n$ = $Pd(OAc)_2$, $PdCl_2(PhCN)_2$, $PdCl_2(MeCN)_2$, $Pd(PPh_3)_4$, $Pt(PPh_3)_2(CH_2=CH_2)$, $RhH(CO)(PPh_3)_3$, $RhCl(PPh_3)_3$.

Both Markownikoff and anti-Markownikoff adducts are formed in the presence of $RhH(CO)(PPh_3)_3$ and the Wilkinson complex $RhCl(PPh_3)_3$. However, in-depth studies of the addition of benzenethiol to oct-1-yne in the presence of $RhCl(PPh_3)_3$ have shown that in ethanol only the *E*-isomer of the anti-Markownikoff product is formed. Thus different regioisomers can be prepared from the same starting compounds (alkyne and thiol) by varying the solvent and the catalyst.

It was also found that the double bond in addition products of thiols to alkynes migrates in the presence of metal complex catalysts. Thus the Markownikoff adducts (*e.g.*, compound **50**) formed in reactions of alkynes containing propargyl hydrogen atoms with benzenethiol in the presence of $PdCl_2(PhCN)_2$ are further isomerised under the action of the catalyst to give alkenes of the type **52** containing a non-terminal double bond. The following reaction scheme has been proposed:




**52**

L = PhCN, $n$ = 2.

It was also shown that isomerisation does not take place if alkynes contain no propargyl hydrogen atoms. Moreover, the presence of an amino group in the alkyne molecule prevents the migration of the double bond.

The addition of various thiols to substituted acetylenes in the presence of a ruthenium complex catalyst has been studied.[149] This reaction yielded a mixture of *cis*- and *trans*-alkenes; their ratio varied depending on the nature of substituents in the starting alkyne.

### 2. Substitution at the unsaturated carbon atom

The replacement of the halogen at the double bond by an arylthio or an alkylthio group yields vinyl sulfides and may occur as both nucleophilic substitution and *via* radical intermediates. These reactions are usually carried out in the presence of initiators (*e.g.*, benzoyl peroxide [146, 150, 151]) or upon UV irradiation.[152, 153] In this case, the formation of side products (diaryl disulfides) is insignificant.

For the first time, radical chlorovinylation of benzenethiol and 4-toluenethiol with trichloroethylene in the presence of benzoyl peroxide (BP) was used for the synthesis of aryl β,β-dichlorovinyl sulfides in 1966.[154]

$$ArSH + ClCH{=}CCl_2 \xrightarrow[-HCl]{BP} ArSCH{=}CCl_2$$

Ar = Ph, $C_6H_4Me$-*p*.

It has been shown [151] that aryl β,β-dichlorovinyl sulfides are formed as the main products in reactions of trichloroethylene with arenethiols irrespective of the nature of the substituent in the benzene ring.[151] Diaryl disulfides are formed as side products, but their content is not very high. Saturated sulfides of the type $ArS(Cl)CHCHCl_2$ are not formed at all.

$$XC_6H_4SH + ClCH{=}CCl_2 \xrightarrow[-HCl]{BP} XC_6H_4SCH{=}CCl_2 + XC_6H_4SSC_6H_4X$$

X = H, 4-MeO, 4-Me, 3-Me, 4-Cl.

Free-radical chlorovinylation of aliphatic thiols by trichloroethylene also results in β,β-dichlorovinyl sulfides.[151] UV irradiation of reaction mixtures is optimum for thermolysis; the trichloroethylene : thiol ratio varies from 3 : 1 to 4 : 1.

Reactions of 1,2-dichloroethylene with thiols upon UV irradiation yield β-chlorovinyl sulfides $RSCH=CHCl$ and disulfides $RSCH=CHSR$ in addition to saturated products.[151]

A similar UV-induced reaction of tribromoethylene with benzenethiol yields β,β-dibromovinyl phenyl sulfide.[153] A general scheme for the substitution of the thiol group for the halogen atom in trichloro- and tribromoethylenes has been proposed:[151, 153]

Initiation

$$RSH \longrightarrow RS^{\bullet} + H^{\bullet};$$

Chain growth

$$RS^{\bullet} + HalCH{=}CHal_2 \longrightarrow RS{-}C(Hal)H{-}\dot{C}Hal_2,$$

$$RS{-}C(Hal)H{-}\dot{C}Hal_2 \longrightarrow Hal^{\bullet} + RSCH{=}CHal_2,$$

$$RSH + Hal^{\bullet} \longrightarrow HHal + RS^{\bullet};$$

Chain termination

$$RS^{\bullet} + RS^{\bullet} \longrightarrow RSSR,$$

$$H^{\bullet} + H^{\bullet} \longrightarrow H_2,$$

$$Hal^{\bullet} + Hal^{\bullet} \longrightarrow Hal_2.$$

It should be noted that some reactions of thiols with tribromoethylene yield aryl monobromovinyl sulfides as side products,[153] similar reactions with trichloroethylene do not give aryl monochlorovinyl sulfides.[151]

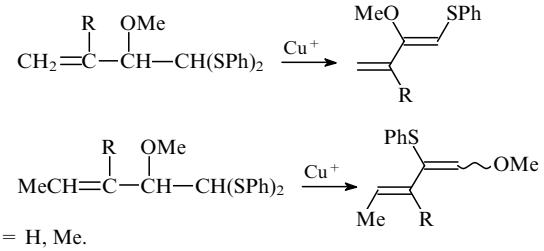
# VI. Miscellaneous methods for the synthesis of α,β-unsaturated sulfides

## 1. Elimination from sulfur-containing compounds

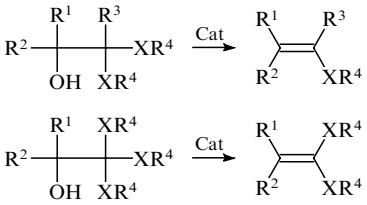
### a. α,β-Elimination from dithioacetals and dithioketals

The method for the synthesis of vinyl sulfides based on α,β-elimination of thiols from dithioacetals and dithioketals has found wide acceptance owing to the ease of preparation of the starting compounds. Usually, thiols are eliminated from dithio compounds by treatment with Simmons–Smith reagent,[155] phosphorus iodides,[156] mono- or divalent copper salts [157, 158] or mercury trifluoroacetate.[132] The main disadvantage of these reactions is their nonstereoselectivity.

Phosphorus iodides, copper salts and thionyl chloride are widely used for α,β-elimination of thiols from acetals, α-hydroxy-, α-alkoxythio(seleno) ketals and orthothioesters.[159, 160]

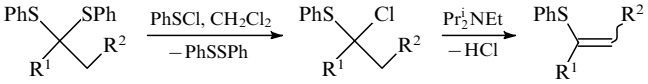


R = H, Me.



X = S, Se; $R^1$ = n-$C_5H_{11}$, n-$C_7H_{15}$, cyclo-$C_3H_5$, Ph; $R^2$ = H, Me; $R^3$ = H; $R^4$ = Me, Ph; Cat = $P_2I_4$, $PI_3$, CuY, $CuY_2$, $SOCl_2$.

Yet another approach to the conversion of dithioketals into vinyl sulfides has been proposed.[1] It consists of treatment of thioacetals and thioketals with benzenesulfenyl chloride and subsequent elimination of HCl from the α-chloro sulfide formed.



$R^1$ = H: $R^2$ = H (63%), Me (64%); $R^1$ = Me: $R^2$ = $CH_2CO_2Et$ (97%), $CH(CO_2Et)CH_2CH=CH_2$ (71%), $CH(CO_2Et)CH_2C\equiv CH$ (73%); $R^1-R^2$ = $-(CH_2)_4-$ (91%).

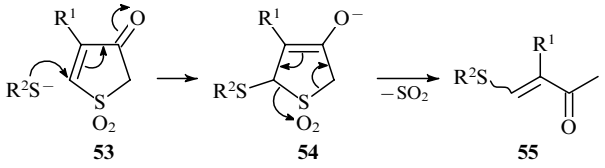
High yields and applicability of this method for a broad range of substrates make it extremely promising.

### b. Elimination of sulfur dioxide from the Michael adducts of thiols to 3-oxo-2,3-dihydrothiophene 1,1-dioxides

Boiling of 3-oxo-2,3-dihydroxythiophene 1,1-dioxide **53** ($R^1$ = H) with benzenethiol in toluene in the presence of catalytic amounts of pyridine results in the elimination of $SO_2$ and the formation of a 5:1 mixture of *Z*- and *E*-isomers of 4-phenylthiobut-3-en-2-one.[161] In THF, this reaction occurs in the absence of a base.[162] The reaction of substituted 3-oxo-2,3-dihydroxythiophene 1,1-dioxides with aliphatic thiols proceeds in a similar way.[162]

Although the mechanism of this reaction has not been strictly proven, it is believed [162] that it occurs as a cheleotropic disrotatory conversion **53** → **54** (Scheme 3), although a two-step mechanism with the initial formation of the sulfinate anion and a subsequent loss of $SO_2$ is not excluded. Exclusive formation of the *E*-isomer of compound **55** ($R^1$ = H, $R^2$ = Ph) upon heating of the intermediate **54** in ethanol is the supporting evidence in favour of a concerted mechanism. The *Z*-isomers **55** are formed in subsequent conversions of *E*-isomers.

Scheme 3

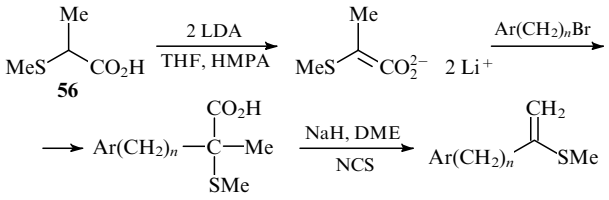


**53** **54** **55**

$R^1$ = H, Me; $R^2$ = Ph, Bu, $(CH_2)_2CO_2Me$.

### c. Decarboxylation of α-methylthiocarboxylic acid salts

Regioselective syntheses of terminal vinyl sulfides can be implemented using mild decarboxylation of (α-methyl)(α-methylthio)alkanoic acids **56** with *N*-chlorosuccinimide (NCS) and sodium hydride in dimethoxyethane (DME).[163]

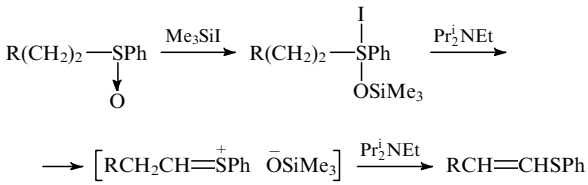


LDA is lithium diisopropylamide; Ar = Ph, 3-$MeOC_6H_4$, 3,4-$(CH_2O_2)C_6H_3$; *n* = 2–5.

No regioisomer with a non-terminal double bond was found in this reaction. However, it was concluded [163] that reactions in protic solvents, *e.g.*, Bu$^t$OH, lead to the reduction of the oxidative potential of *N*-chlorosuccinimide and the establishment of a rapid equilibrium between the regioisomers, as a result of which the regioselectivity of the reaction decreases.

## 2. Reduction of sulfoxides with subsequent α,β-elimination

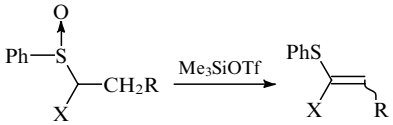
Reduction of sulfoxides to sulfides usually occurs under mild conditions and with good yields and does not require any complex equipment. Trimethylsilyl iodide in combination with bis(trimethylsilyl)amine or sterically hindered tertiary amines is one of the most efficient reagents for the reduction and subsequent α,β-elimination of sulfoxides.[164]



R = n-$C_6H_{13}$.

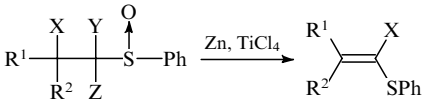
Treatment of α-chloroalkyl sulfoxides with trifluoroacetic anhydride and sodium iodide in acetone at low temperatures affords vinyl sulfides in high yields.[2]

Trimethylsilyl trifluoromethanesulfonate ($Me_3SiOTf$) can be used in the synthesis of α-cyano- and α-alkoxycarbonyl-substituted vinyl sulfides.[5]



R = H, Et, Pr$^n$, cyclo-$C_6H_{11}$; X = CN, $CO_2R$.

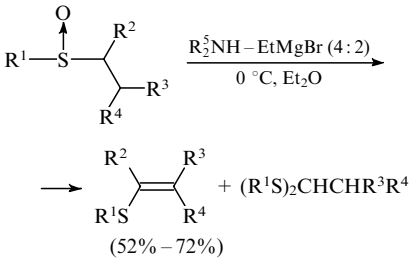
Sulfoxides containing a halogen or a hydroxy group in the α- and β-positions easily undergo reductive elimination in diethyl ether under the action of Zn and $TiCl_4$.[165]




(60% – 85%)

$R^1$, $R^2$ = H, Alk, Ar; X = H, OH; Y = H, Cl, Br; Z = H, Cl.

A method for the reduction of sulfoxides containing hydrogen atoms in α- and β-positions was developed in 1995,[166] which involves their treatment with *in situ* generated magnesium amide $Mg(NH_2)_2$.



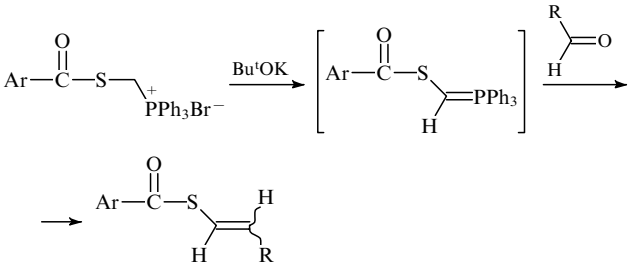

(52% – 72%)

$R^1$ = $Bu^n$, Ph, 4-$MeC_6H_4$; $R^2$ = H, Me, Ph; $R^3$ = H, Me, Et, Ph; $R^4$ = H, Me; $R^5_2NH$ = 2,2,6,6-$Me_4C_5H_6NH$, $Pr^i_2NH$.

## 3. Methods for the synthesis of vinyl sulfides based on the Wittig – Horner and Peterson reactions

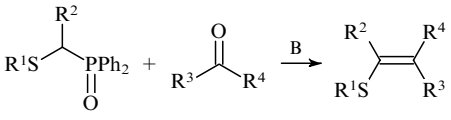
### a. Synthesis of vinyl sulfides using the Wittig – Horner reaction

The Wittig reaction using sulfur-containing reagents can be used for the synthesis of vinyl sulfides.[167]



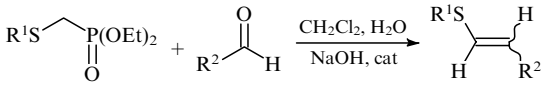

Ar = Ph, 4-$MeC_6H_4$, 4-$MeOC_6H_4$;
R = Me, Et, Ph, 4-$NO_2C_6H_4$, PhC≡C, 2-$NO_2C_6H_4$CH=CH.

However, the Wittig – Horner reactions where phosphonates are used instead of phosphonium salts have found wider application in the synthesis of α,β-unsaturated sulfides.[3, 168, 169] This reaction is carried out in the presence of strong bases, such as NaH (see Ref. 3) or $Bu^nLi$.[168, 169]




$R^1$ = Me, Ph; $R^2$ = H, Et, $Pr^i$, Bn; $R^3$ = H: $R^4$ = Ph, n-$C_6H_{13}$, 4-$MeOC_6H_4$, PhCH=CH, 3,4-$(CH_2O_2)C_6H_3$; $R^3$ = Me, $R^4$ = 4-$MeOC_6H_4CH_2$; $R^3$ = $R^4$ = Ph, Bn; $R^3$ – $R^4$ = $-(CH_2)_4-$, $-(CH_2)_2CHBu^t(CH_2)_2-$,  .

Sometimes, these reactions require $BF_3$ for their completion.[169] They can also be carried out under conditions of phase-transfer catalysis.[170]

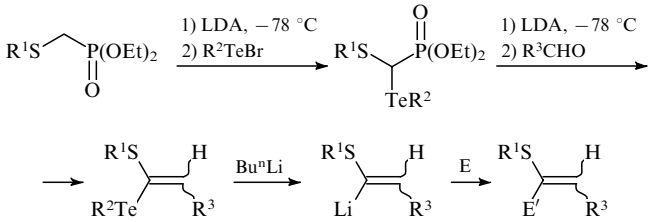



$R^1$ = Me, Ph; $R^2$ = Ph, 4-$Me_2NC_6H_4$.

Quaternary ammonium bases and crown-ethers are used as catalysts in phase-transfer reactions. In this case, the ratio of (*E*)- and (*Z*)-vinyl sulfides formed varies depending on the catalyst.[170]

High yields of vinyl sulfides are an indisputable advantage of the given method; however, in some cases the synthesis of sulfur-containing Wittig reagents presents a complicated synthetic problem.

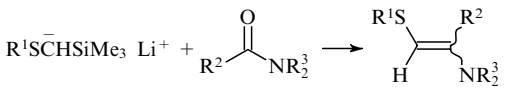
The use of the Wittig – Horner reaction enables the synthesis of some thio(telluro)acetals of substituted ketenes where the aryltelluro groups can be readily and selectively modified.[171]




$R^1$ = Me, Ph; $R^2$ = Ph, $Bu^n$; $R^3$ = H, Ph, 2-furyl, 4-$MeC_6H_4$, 4-$ClC_6H_4$, $Pr^n$, $Pr^i$; E = $H_2O$, MeI, PhCHO; E′ = OH (62%), Me (86%), PhCHOH (85%).

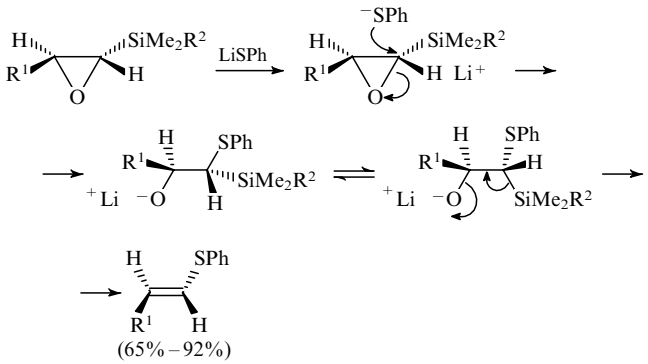
### b. Synthesis of vinyl sulfides using the Peterson reaction

The Peterson reaction, *i.e.*, the synthesis of vinyl sulfides from α-metallosilanes, plays an important role in organic synthesis. Thus lithium derivatives of arylthiomethyltrimethylsilanes react with ketones to give vinyl sulfides.[172] Various carboxylic acid derivatives, *e.g.*, amides, can be used for the synthesis of β-substituted vinyl sulfides instead of ketones.



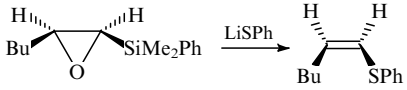

$R^1$ = Me, Ph; $R^2$ = H, $Bu^t$, Ph; $R^3_2$ = $Me_2$, $(CH_2)_2$, $(CH_2)_5$.

A method for the synthesis of vinyl sulfides has been developed which is based on the reaction of epoxysilanes with lithium phenylsulfide and subsequent Peterson *syn*-α,β-elimination.[173] This method is distinguished for high yields, regio- and stereospecificity.




(65% – 92%)

$R^1$ = H, Bu, Ph, $SiMe_3$, $SiMe_2Ph$; $R^2$ = Me, Ph.



## VII. Conclusion

The choice of a method for the synthesis of vinyl sulfides is determined by the nature of the substrate as well as by the stability and availability of the starting reagents. Some of the methods considered in this review, *e.g.*, the addition of sulfenyl chlorides to acetylenes or nucleophilic substitution for the thiolate ion, were developed as early as the middle of the last century, but are still widely employed owing to the simplicity of equipment and experimental procedures. However, the yields of such classical reactions are not always satisfactory, which stimulates the search for more complex, perhaps, but nevertheless more efficient methods for the synthesis of vinyl sulfides.

Among a variety of methods recently developed for the synthesis of vinyl sulfides, reactions of arenesulfenamides with alkynes in the presence of phosphorus oxyhalides hold especially great promise.[69–74] The simplicity of equipment, the availability of starting reagents and high yields of reaction products make this method a reasonable alternative to the existing chloro- and bromosulfenylation procedures. Addition of thiols to alkynes in the presence of metal complex catalysts is yet another promising approach,[15, 144–149] which allows regioselective sulfenylation of nonsymmetrical alkynes. The success of the synthesis of the target regioisomer depends on the choice of a metal complex catalyst.

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