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Sulfenyl† chlorides in organic synthesis

I V Koval'

Contents

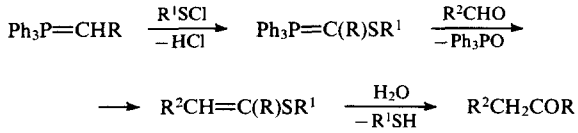
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Abstract. The results of studies concerned with the use of sulfenyl chlorides in organic synthesis are described systematically and surveyed. The methods of synthesis of sulfenyl chlorides are also considered. The bibliography includes 271 references.

I. Introduction

Sulfenyl chlorides, which are compounds of divalent sulfur, are highly reactive, and this has led to their extensive employment in organic synthesis. As a consequence of the high polarity and low strength of the S–Cl bond, sulfenyl chlorides readily react with both nucleophiles and electrophiles, which permits their employment for the synthesis of compounds with S–C, S–N, S–O, S–S, S–P, S=O, S=N, etc. bonds. These compounds include sulfides, disulfides, sulfenamines, sulfenates, sulfonates, sulfonyl chlorides, and other valuable products of fine organic synthesis.

Sulfenyl chlorides play an important role in multistep reactions, where they are employed to generate the sulfide functional group, the subsequent specific transformation of which may lead to a wide variety of products of organic synthesis.[1,2] For example, the synthesis of ketones from phosphorus ylides includes a stage in which the sulfide group is generated with the aid of sulfenyl chlorides, this being followed by its removal in the last stage of the synthesis.[3,4]



R = H, Me, COOEt, CN, COPh, 2-$NO_2C_6H_4$;

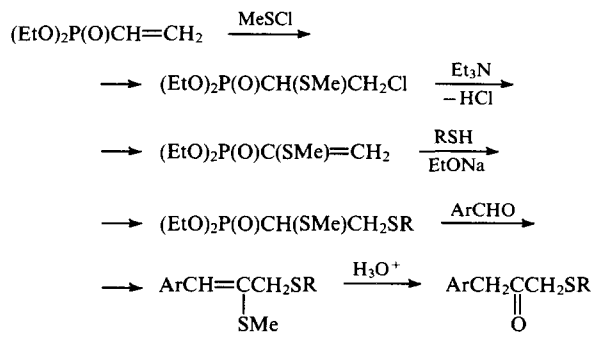
R^1, R^2 = Alk, Ar.

† It is appreciated that the name 'sulfenyl' is no longer accepted terminology under IUPAC recommendations [*A Guide to IUPAC Nomenclature of Organic Compounds, Recommendations 1993* (Oxford: Blackwell Scientific)]. The extensive use of the term, however, in the Russian literature makes it impracticable to effect a change in this review, but modern nomenclature is more likely in any subsequent review.

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A similar synthetic procedure is employed in the preparative synthesis of α-alkylthioketones from diethyl vinylphosphonates.[1]



The primary products of the reactions of sulfenyl chlorides, for example β-chloroalkyl aryl sulfides, which play an extremely important role in β-arylthioalkylation reactions, have also found extensive applications in organic synthesis.

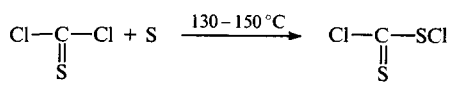
Bifunctional sulfenyl chlorides, i.e. compounds containing together with the sulfenyl chloride group also other functional groups (Cl, Br, C=O, S–Cl, ClC=O, ClC=N, etc.) are synthetically very important. A whole series of preparative methods of synthesis of diverse sulfur-containing heterocyclic compounds from these products have been developed.

Apart from fine organic synthesis, certain sulfenyl chlorides are employed in macromolecular chemistry as monomers,[5] in the production of widely known biologically active preparations such as phthalan, captan, euparen, and euparen M,[6–8] and also in the manufacture of pharmaceutical preparations[7] and vulcanising agents,[9] which makes them promising for practical purposes.

II. Methods of synthesis

1. Syntheses based on elemental sulfur and its inorganic derivatives

Elemental sulfur is relatively rarely employed in the synthesis of sulfenyl chlorides, which is due to the need for its activation.[10] A single instance of the direct application of elemental sulfur in the synthesis of chlorothiocarbonylsulfenyl chloride by its reaction with thiophosgene has been described in the literature.[11]



Inorganic derivatives of sulfur, for example sulfur chlorides, are much more frequently used in the synthesis of sulfenyl chlorides. Sulfur monochloride is employed in the form of the $SF_4-HF-S_2Cl_2$ system. Several ways of using this system in the synthesis of sulfenyl chlorides have been developed. One of them involves the interaction of the system with alkenes. For example, the reaction of the system with 1,2-dichlorodifluoroethene leads to the formation of 1,2-dichloroperfluoroethanesulfenyl chloride.[12] It is believed[13] that SF_4 and HF promote in this instance the ionisation of S_2Cl_2 and hence its addition to the double bond. The formation of a sulfenyl chloride is also favoured by the presence of fluoride and chloride anions in the reaction mixture.

$$S_2Cl_2 \xrightarrow{HF,\ SF_4} Cl^- + \overset{+}{S}SCl$$

$$SF_4 + 4\,Cl^- \xrightarrow[-4\,F^-]{} SCl_4 \longrightarrow SCl_2 + Cl_2$$

$$CFCl{=}CFCl + \overset{+}{S}SCl \longrightarrow \left[\overset{+}{C}FClCFClSSCl \xrightarrow{F^-} CF_2ClCFClSSCl\right] \xrightarrow{Cl_2} CF_2ClCFClSCl + SCl_2$$

Perfluoroethane-, perfluoro(1-methylethane)-, and perfluoro(1-methylpentane)sulfenyl chlorides have been synthesised similarly.[14,15]

It has been established[12] that the interaction of the $SF_4-HF-S_2Cl_2$ system with asymmetric alkenes, for example with chlorotrifluoroethene, leads to the formation of a mixture of two regioisomers, which is a disadvantage of the method.

$$CF_2{=}CFCl \longrightarrow CF_3CFClSCl + CF_2ClCF_2SCl$$

A second aspect of the use of this system to synthesise sulfenyl chlorides involves its reaction with certain inorganic and organic reagents and subsequent chlorolysis of the products.[16,17]

$$(EtOOC)_2CH_2 \xrightarrow[60\,^\circ C,\ 12\ h]{SF_4-HF-S_2Cl_2} [(EtOOC)_2CFS-]_2 \xrightarrow[28\,^\circ C,\ 4\ h]{Cl_2} (EtOOC)_2CFSCl$$

$$RCF{=}CF_2 \xrightarrow{SF_4-HF-S_2Cl_2} \left[\underset{CF_3}{\overset{|}{RCFSCl}} + \underset{CF_3}{\overset{|}{RCFSSCl}} + \underset{CF_3\ \ CF_3}{\overset{|\quad|}{RCFSSSCFR}}\right] \xrightarrow[100\,^\circ C]{Cl_2} \underset{CF_3}{\overset{|}{RCFSCl}}$$

R = F, CF_3, Bu, C_6H_{13}.

$$CS_2 \xrightarrow{SF_4-HF-S_2Cl_2} [CF_3SSCF_3 + CF_3SSSCF_3] \xrightarrow{Cl_2} CF_3SCl$$

Several versions of the synthesis of sulfenyl chlorides from sulfur dichloride have been developed. The first of these consists in its addition to the multiple bonds of unsaturated compounds. For example, the synthesis of phosphorus-containing sulfenyl chlorides by the addition of SCl_2 to the C=C bonds of vinyl- and allyl-phosphonates has been described.[18]

$$(AlkO)_2P(O)CH{=}CH_2 \xrightarrow{SCl_2} (AlkO)_2P(O)CH(CH_2Cl)SCl$$

$$R_2P(O)CH_2CH{=}CH_2 \xrightarrow{SCl_2} R_2P(O)CH_2CH(Cl)CH_2SCl$$

R = Cl, C_2H_5O.

The formation in certain cases of a mixture of two isomeric sulfenyl chlorides which are difficult to separate, as happens, for example, in the reaction of SCl_2 and methyl methacrylate,[19] should also be included among the disadvantages of this method.

$$MeOCOC(Me){=}CH_2 + SCl_2 \longrightarrow \begin{cases} MeOCOC(Me)(SCl)-CH_2Cl & 71\% \\ MeOCOC(Me)(Cl)-CH_2SCl & 29\% \end{cases}$$

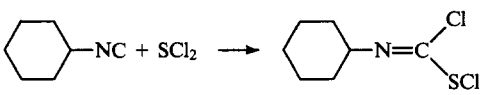
In the presence of fluorosulfonic acid, sulfur dichloride reacts with hexafluoropropene by a coupled addition mechanism, the subsequent elimination of hydrogen chloride, and the formation of the corresponding sulfenyl chloride.[20,21]

$$CF_3CF{=}CF_2 \xrightarrow[-HCl]{SCl_2,\ HSO_3F,\ 40-60\,^\circ C} \underset{SCl}{\overset{|}{CF_3-CF}}-CF_2OSO_2F \quad 75\%$$

Under the conditions of specific solvation of the S–Cl bond (in acetonitrile, benzonitrile, SO_2, etc.), SCl_2 reacts with hexafluorodimethylketene, affording the corresponding sulfenyl chloride.[22]

$$(CF_3)_2C{=}C{=}O + SCl_2 \longrightarrow (CF_3)_2C\begin{cases} C(O)Cl \\ SCl \end{cases}$$

The addition of sulfur dichloride to isonitriles is used in the synthesis of chloroiminomethanesulfenyl chlorides.[11]



The second version of the use of sulfur dichloride in the synthesis of sulfenyl chlorides involves the sulfenylation of CH acids, for example isobutyronitrile in the synthesis of α-cyanoisopropanesulfenyl chloride.[23]

$$Me_2CHCN + SCl_2 \longrightarrow \underset{CN}{\overset{|}{Me_2C}}-SCl$$

2. Syntheses based on thiols

The chlorolysis of the S–H bond in thiols on treatment with chlorinating agents is used very frequently in the synthesis of sulfenyl chlorides. A series of preparative methods of synthesis of arene-,[24] polyfluoroalkane,[25,26] and trichlorothiophene-sulfenyl chlorides[27] have been developed on the basis of this reaction. In order to avoid the hydrolysis of the sulfenyl chlorides formed and also to diminish the possibility of *C*-chlorination, the reaction is carried out in anhydrous inert solvents in the absence of ultraviolet light. This is a three-stage process with participation of disulfides as intermediates.[24,28]

$$RSH + Cl_2 \longrightarrow RSCl + HCl$$

$$RSH + RSCl \longrightarrow RSSR + HCl$$

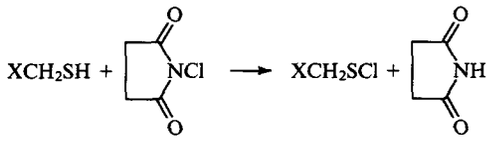
$$RSSR + Cl_2 \longrightarrow 2\,RSCl$$

Sulfuryl chloride is a milder chlorinating agent than chlorine.[24,28] It too can induce *C*-chlorination, which has been observed in the case of methane-thiols with functional group substituents.[29,30]

$$XCH_2SH + 3\,SO_2Cl_2 \longrightarrow XCCl_2SCl + 3\,HCl + 3\,SO_2$$

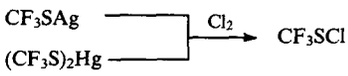
X = CN, $PhSO_2$, ArNHCO, RCO etc.

N-Chlorosuccinimide is frequently employed as a chlorinating agent in order to avoid the chlorination of α-C–H bonds.[31,32]



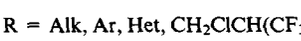
X = Ph, EtOOC, HOOC.

In the case of unstable or gaseous thiols, the use of their silver or mercury salts is more convenient.[33]



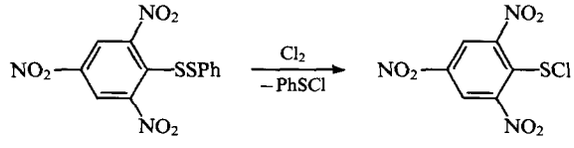
3. Syntheses based on disulfides

The chlorolysis of the S–S bond in disulfides on treatment with chlorine or other chlorinating agents in anhydrous organic solvents is one of the commonest methods of synthesis of sulfenyl chlorides.[24,28,32–44]



R = Alk, Ar, Het, $CH_2ClCH(CF_3)$, $CF_3CHClCH_2$, $CF_3OCFClCF_2$, CF_2ClCF_2, CCl_2FCF_2, $CF_3CF_2CF_2$, $CF_3(CF_2)_6$, $(CF_3)_2CFOCF_2$, $(CF_3)_2CF$ etc.

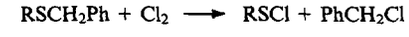
Since the rate of chlorolysis of the S–S bond in disulfides depends on the nucleophilicity of the sulfur atoms, electron-accepting groups attached to a sulfur atom hinder the process. In such cases, it is recommended[45,46] that catalysts such as iodine, aluminium and iron chlorides, oleum, sulfuric acid, etc. be employed. In order to reduce the influence of strong electron-accepting groups on the chlorination process, asymmetric compounds, containing an electron-donating group as well as an electron-accepting group, are sometimes employed instead of symmetrical disulfides.[47]



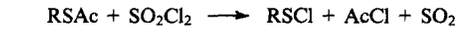
In the case of disulfides containing α-C–H bonds, there is a possibility, of the chlorolysis also of C–H bonds together with that of the S–S bond.[24,28,48] In order to avoid this process, it is recommended that sulfuryl chloride,[49–53] *N*-chlorosuccinimide,[54] and other *N*-halo-derivatives[55,56] be used as chlorinating agents.

4. Syntheses based on sulfides

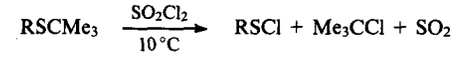
One of the important methods of synthesis of sulfenyl chlorides is the specific chlorolysis of one of the C–S bonds in sulfides. This method makes it possible to obtain sulfenyl chlorides with a wide variety of structures, including those containing powerful electron-accepting groups attached to the sulfur atom. The ease of chlorolysis of the C–S bond in sulfides is determined primarily by the nature of the leaving group, the structure of the initial sulfide, and the chlorolysis conditions. Sulfides containing a readily removable group such as the benzyl,[57–65] acyl,[61,66–68] and *tert*-butyl[69] groups are most often employed in the synthesis of sulfenyl chlorides.



R = 2,4,6-$(NO_2)_3C_6H_2$, CHF_2, CCl_2F, CF_3, C_2HF_4, $(CF_3)_2CHCF_2$, CF_3CFCl, $(CF_3)_2CF$, $CHFClCF_2$, $(CF_3)_2C{=}CF$, $(CF_3)_2C{=}C(I){-}C_2F_5$ etc.

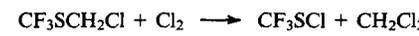


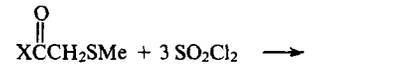
R = Me, Bu, Bu^i, Bu^t, 2-MeC_6H_4, Ph, $PhCH_2$, 4-$NO_2C_6H_4$, $MeOCOCH_2CH_2$, $PhC{\equiv}C$.



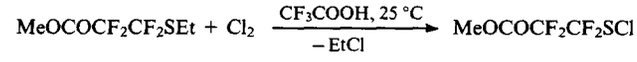
R = $MeOCOCH(CF_3)CF_2$, $MeOOC{=}CF(CF_3)$.

A series of methods of synthesis of sulfenyl chlorides involving the chlorination of sulfides containing leaving groups such as the chloromethyl,[33] methyl,[70] and ethyl[71] groups have been described.

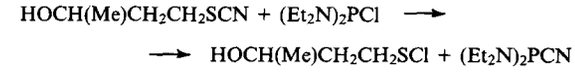




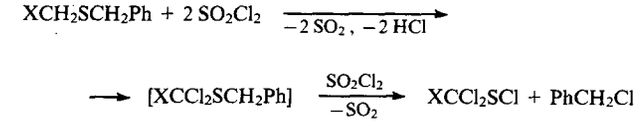
X = $Ph{-}N(CHMe_2){-}$



It has been noted[72] that the interaction of 1-thiocyanatobutan-3-ol with phosphorochloridous tetraethyldiamide in the presence of triethylamine at 30 °C proceeds with the cleavage of the C–S bond and the formation of 3-hydroxybutanesulfenyl chloride.

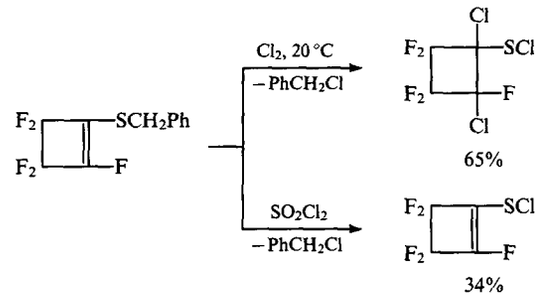


The chlorolysis of the C–S bond in sulfides containing active α-C–H bonds is accompanied by the *C*-chlorination of the alkyl group, which is used in the synthesis of dichloromethanesulfenyl chlorides with functional group substituents.[70,73]

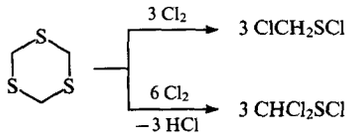


X = CN, $C_6H_4SO_2$, EtOCO, 4-ClC_6H_4OCO, HOCO, Alk_2NCO, ArNHCO, CF_3 etc.

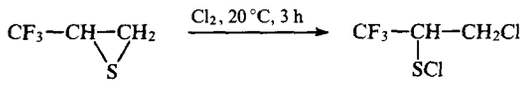
The chlorolysis of the C–S bond in alkenyl benzyl sulfides is accompanied as a rule by the addition of chlorine to the C=C bond.[58,63] The use of sulfuryl chloride instead of chlorine rules out the side reaction, as happens, for example, in the chlorination of benzyl pentafluorocyclobutenyl sulfide.[58]



Cyclic sulfides undergo chlorolysis to form sulfenyl chlorides. For example, the chlorination of trithiane with chlorine leads to chloromethane- and dichloromethane-sulfenyl chlorides depending on the conditions.[74]

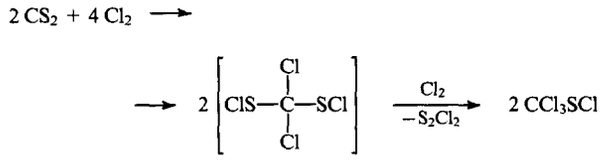


The analogous chlorination of trifluoromethylthiirane yields 1-chloro-2-chlorosulfenyl-3,3,3-trifluoropropane.[75]

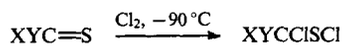


5. Syntheses based on thiocarbonyl compounds

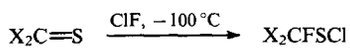
The use of thiocarbonyl compounds in the synthesis of sulfenyl chlorides is based on the addition of chlorine to the C=S bond. For example, reaction of Cl_2 with carbon disulfide is the basis of the industrial synthesis of trichloromethanesulfenyl chloride (TCMSC).[33]



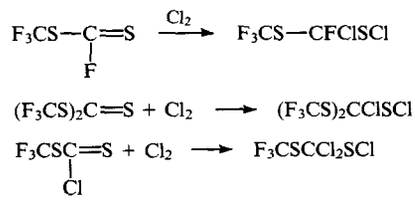
This reaction has been used to synthesise perhaloalkanesulfenyl chlorides.[63,76-83]



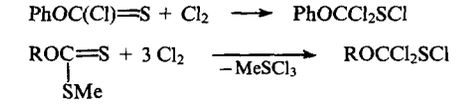
X = Cl, Br, F, CF_3, Et; Y = Br, F, $(CF_3)_2CH$, $(CF_3)_2CCl$.



X = Cl, Br, F.

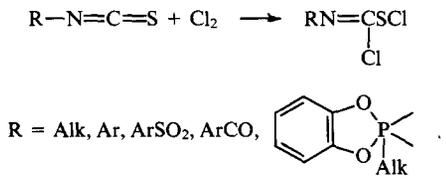


The addition of chlorine to the C=S bond in chlorides and esters of thiocarbonic and dithiocarbonic acids is the basis of the synthesis of α,α-dichloromethanesulfenyl chlorides with functional group substituents.[74]



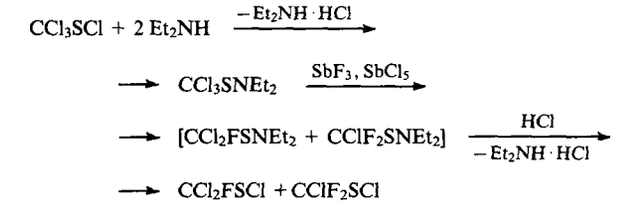
R = Me, Et.

One of the methods of synthesis of chloroiminomethanesulfenyl chlorides is based on the addition of chlorine to the C=S bond in isothiocyanates.[28,83,84]

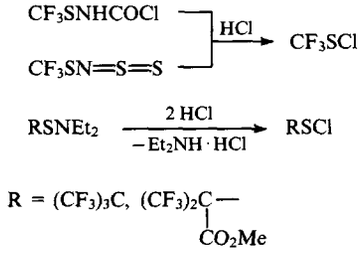


6. Syntheses based on sulfenamides

A familiar procedure for the formation of the sulfenyl chloride group involves heterolytic cleavage of the S–N bond in sulfenamides on treatment with gaseous HCl.[85-87] However, this reaction is used fairly rarely, since in most cases sulfenamides are obtained from the sulfenyl chlorides into which they are converted on hydrochlorolysis of the S–N bond. As a synthetic procedure, the conversion of the sulfenyl chloride group into the sulfenamide group with subsequent hydrochlorolysis of the S–N bond is used to protect the sulfenyl chloride group in the modification of groups attached to the sulfur atom, as happens, for example, in the conversion of TCMSC into dichlorofluoro- and chlorodifluoro-methanesulfenyl chlorides.[33]

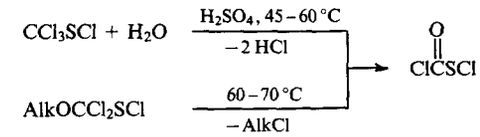


Instances of the synthesis also of other fluoroalkanesulfenyl chlorides using the hydrochlorolysis of the S–N bond in the corresponding sulfenamides are known.[88-90]



7. Modification of the functional groups in sulfenyl chlorides

The specific modification of the various functional groups attached to the sulfur atom in sulfenyl chlorides has been used very frequently in the synthesis of new types of these compounds. TCMSC is particularly valuable in this respect. Its partial hydrolysis in concentrated sulfuric acid leads to chlorocarbonylsulfenyl chloride,[11,33,74] which is also formed on thermolysis of alkoxydichloromethanesulfenyl chlorides.[11]



Alk = Me, Et.

The interaction of TCMSC with potassium fluoride can lead to the stepwise substitution of the chlorine atoms by fluorine.[33]

$$CCl_3SCl \xrightarrow[-KCl]{KF} CFCl_2SCl \xrightarrow[-KCl]{KF}$$

$$\longrightarrow CF_2ClSCl \xrightarrow[-KCl]{KF} CF_3SCl$$

A relatively large number of sulfenyl chlorides have been obtained by modification of the COCl group of chlorocarbonylsulfenyl chloride. For example, the replacement of the chlorine atom in this group by fluorine can be achieved with the aid of antimony trifluoride.[82]

$$ClC(=O)SCl \xrightarrow{SbF_3} FC(=O)SCl$$

The chlorine atom is replaced by the alkoxy-group in the interaction of chlorocarbonylsulfenyl chloride with alcohols in molar proportions of 1:1.[11]

$$ROH + ClC(=O)SCl \xrightarrow[-HCl]{} ROC(=O)SCl$$

R = Me, Et, Pr, C_8H_{17}, $ClCH_2CH_2$, $PhCH_2CH_2$, $MeOCH_2CH_2$.

8. Other methods of synthesis

Among other methods of synthesis, mention may be made of (a) the addition of sulfenyl chloride to the C=S bond in thiocarbonyl compounds:[82]

$$F_2C{=}S + F_3CSCl \longrightarrow CF_3CSCF_2SCl;$$

(b) the chlorolysis of the S–P bond in the alkyl esters of phosphorothioic acids:[68]

$$RSP(=O)(OEt)_2 \xrightarrow{SO_2Cl_2} RSCl + (EtO)_2P(O)Cl + SO_2,$$

R = $(CF_3)_2CHCF_2$, $(CF_3)_2CHCO$;

(c) the chlorolysis of the S–Si bond in thiosilanes.[91]

$$RSSiMe_3 \xrightarrow[-Me_3SiCl]{Cl_2} RSCl$$

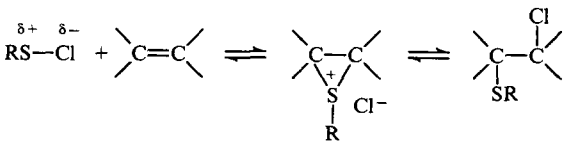
III. Syntheses based on sulfenyl chlorides

1. Syntheses of sulfides

The synthesis of sulfides from sulfenyl chlorides has been described in detail in the present author's earlier review[2] and in the literature quoted therein and only the synthesis of sulfides with functional group substituents, which play an important role in organic synthesis, will therefore be considered in the present review.

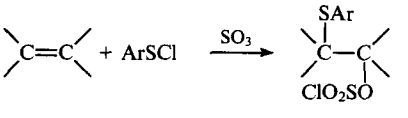
a. Synthesis of aryl β-chloroalkyl sulfides

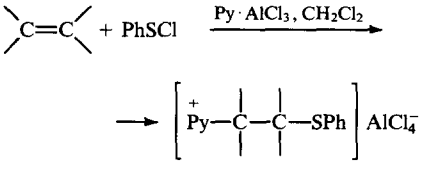
A classical method of synthesis of β-chloroalkyl sulfides involves the addition of sulfenyl chloride to the C=C bond in unsaturated compounds, which proceeds under mild conditions and with high yields.[2,4,24,28,46,92–97] The mechanism of this reaction has been discussed in detail in a series of review publications.[2,4,24,28,46] It has been suggested that the reaction proceeds via an Ad_E2 mechanism, in which an episulfonium ion is a cationic intermediate and which leads as a rule to stereospecific *trans*-addition.[28]



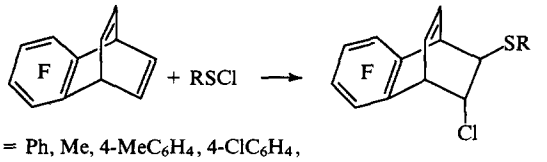
Quantum-mechanical calculations for the $C_2H_4SH^+$ ion have shown[98] that the bridged episulfonium ion is more stable as an intermediate than a linear carbenium ion. When the process is subject to kinetic control, the composition of the products of the addition reaction reflects the relative rate of substitution at the ring carbon atom of the episulfonium ion. The presence of α-substituents, which increase the reactivity in reactions of the S_N2 type (Ph, C=O, C≡N, CH=CH_2, etc.), increases the relative rate of addition, whereas alkyl groups or other bulky substituents diminish the relative rate of this reaction. Terminal alkenes therefore react with sulfenyl chlorides by anti-Markovnikov addition, whereas styrenes, acrylic acid derivatives, and dienes combine with sulfenyl chlorides in accordance with the Markovnikov rule.[28,99]

In order to increase the effective electrophilicity of the episulfonium ion and to substitute the chloride anion by other nucleophiles, it has been suggested that the coupled addition of sulfenyl chlorides be carried out in the presence of strong electrophiles such as $LiClO_4$,[100–103] SO_3,[104] and $PyAlCl_3$.[105] The episulfonium cations formed under these conditions react even with weak nucleophiles such as acetonitrile.[100–103]

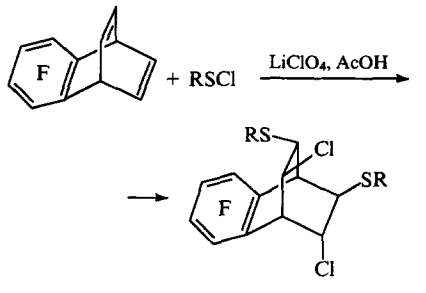




The use of lithium perchlorate in the reaction of sulfenyl chlorides with polycyclic dienes induces various side processes (skeletal rearrangements, etc.). For example, the addition of sulfenyl chlorides to tetrafluorobenzobarrelene in CH_3COOH, CH_3NO_2, and CH_2Cl_2 takes place in the *exo*-position with formation of *trans*- β-halo-substituted sulfides, whereas in the presence of lithium perchlorates the reaction proceeds with participation of two C=C bonds.[106]

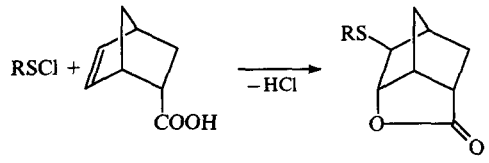


R = Ph, Me, 4-MeC_6H_4, 4-ClC_6H_4, 2-$NO_2C_6H_4$, 4-$NO_2C_6H_4$, 2,4-$(NO_2)_2C_6H_3$.



R = 4-MeC_6H_4.

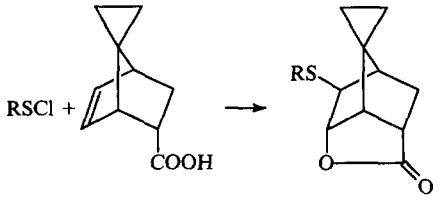
It has been noted[107] that the addition of polyfluoroalkanesulfenyl chlorides to norborn-5-ene-2-carboxylic acid under mild conditions (−20−0 °C) is accompanied by the lactonisation of the adducts.



R = $ClCH_2CH_2\underset{\displaystyle CF_3}{\underset{|}{C}}H$, CF_2ClCF_2, $CFCl_2CF_2$,

$ClCH_2\underset{\displaystyle CF_3}{\underset{|}{C}}Cl$, $MeOOC\overset{\displaystyle CF_3}{\overset{|}{C}}\underset{\displaystyle CF_3}{\underset{|}{}}$

Spiro(2-carboxybicyclo[2.2.1]hept-5-ene-7,1'-cyclopropane) reacts similarly with sulfenyl chlorides.[108]



R = $ClCH_2\underset{\displaystyle CF_3}{\underset{|}{C}}H$, $MeOOC\overset{\displaystyle CF_3}{\overset{|}{C}}\underset{\displaystyle CF_3}{\underset{|}{}}$

Under more severe conditions (20 °C and above), the formation of mixtures of the corresponding lactones and the products of the *endo*- and *exo*-addition to the C=C bond was observed.[108]

In certain cases, the stability of the episulfonium ion diminishes so much that the addition of sulfenyl chlorides to the C=C bond proceeds with participation of an open-chain carbenium ion with loss of stereospecificity.[15] Examples of such reactions are the addition of 2,4-dinitrobenzenesulfenyl chloride to *cis*-anethole[109] and also the addition of benzenesulfenyl chloride to strained cyclobutenes.[110] It has been noted[111] that the addition of sulfenyl chlorides to alkenes in weakly polar solvents proceeds via intermediates less polar than episulfonium salts. Kinetic studies of the addition of arenesulfenyl chlorides to *para*-substituted styrenes led to the conclusion[111] that a whole range of structures from nonpolar (σ-sulfurane) to ionic (episulfonium ion) as intermediates is possible. It has also been suggested that an ion-pair mechanism may be possible in the case of the addition of sulfenyl chlorides to alkenes in acetic acid.[112]

In the presence of Lewis acids ($TiCl_4$, $LiClO_4$) and also on dissolution in liquid SO_2, β-chloroalkyl sulfides are readily converted into episulfonium salts, which are widely used in β-arylthioalkylation reactions in order to expand the range of sulfides with functional group substituents.[10,112,113] However, it has proved more convenient to carry out this reaction using the aryl β-chloroalkyl sulfide–$TiCl_4$ (or $ZnCl_2$, $SnCl_4$) system, by-passing the stage involving the formation of a stable episulfonium salt, as happens, for example, in the interaction with trimethylsilyl ethers of enols (Scheme 1).[10,114–119]

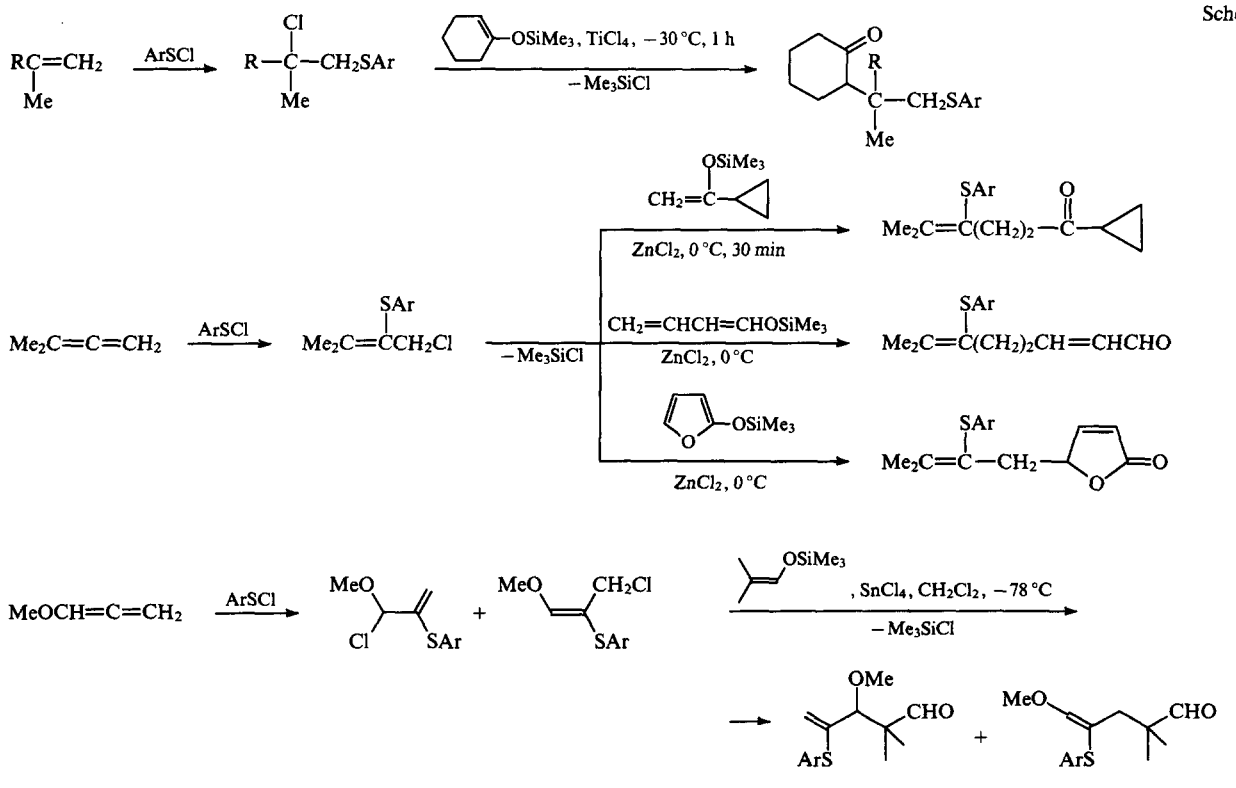
According to Ibragimov and Smit,[117] the β-arylthio-α-alkoxyalkylation of various types of trimethylsilylenol ethers is accompanied by their reaction with the products of the addition of arene-sulfenyl chlorides to vinyl ethers (Scheme 2).

According to Belen'kii[10] and Ibragimov et al.,[120] the overall outcome of these reactions reduces to the chemoselective aldol condensation of two carbonyl compounds with the simultaneous introduction of a γ-arylthio-substituent, which leads to the additional possibility of subsequent reactions at this centre.

Similar results have been obtained when methyl trimethylsilyl acetals of ketene were used as π-donors (Scheme 3).[10,121]

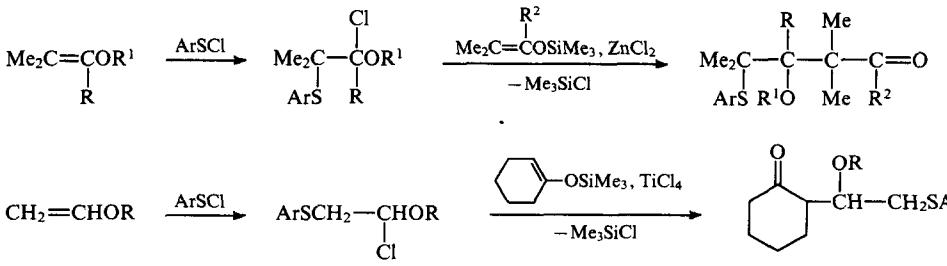
In the presence of $TiCl_4$ or $ZnBr_2$, allylsilanes also react with aryl β-haloalkyl sulfides (Scheme 4).[121–123]

Scheme 1

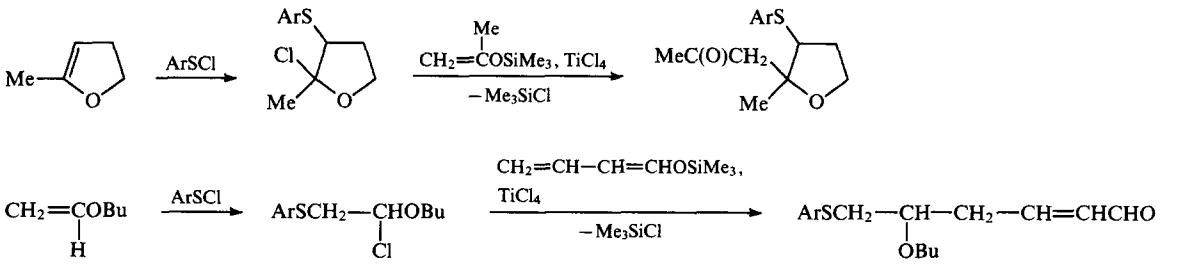


Ar = 4-MeC_6H_4, 4-ClC_6H_4, 2,4,6-$Me_3C_6H_2$.

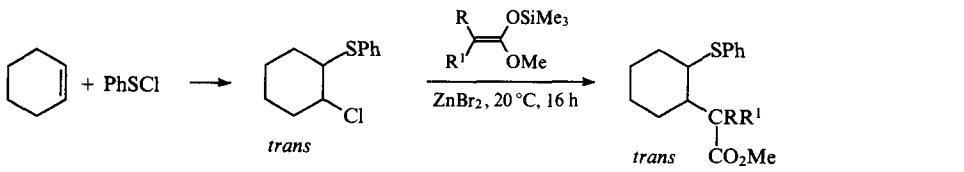
Scheme 2



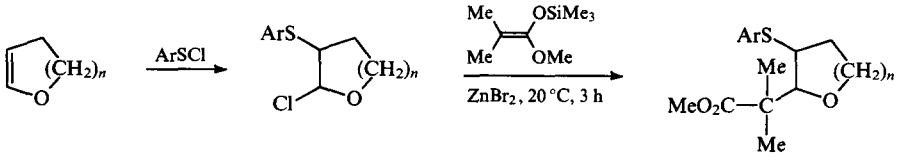
R = Me, Bu^t.



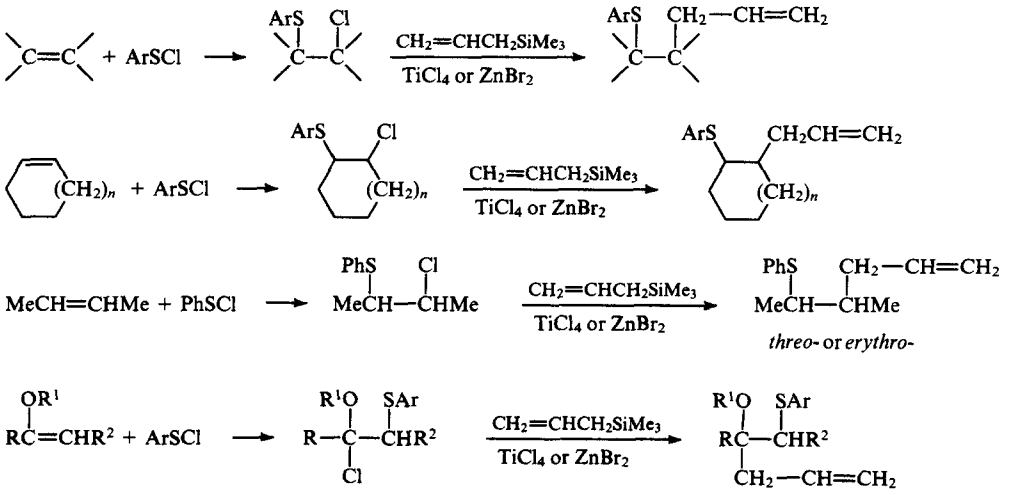
Scheme 3



R = R^1 = R^2 = R^3 = R^4 = H, Alk.

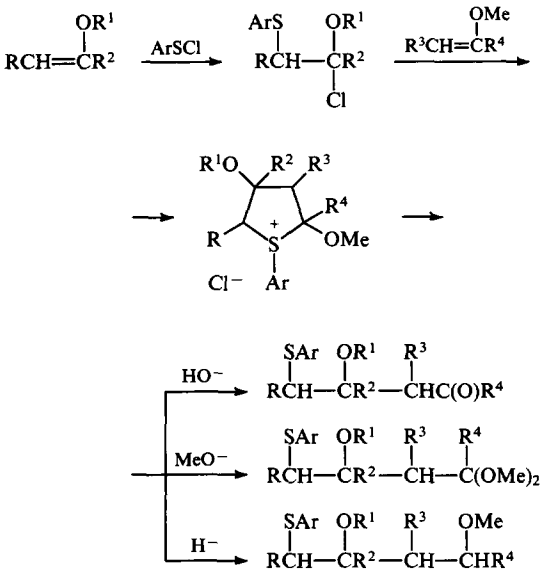


Scheme 4

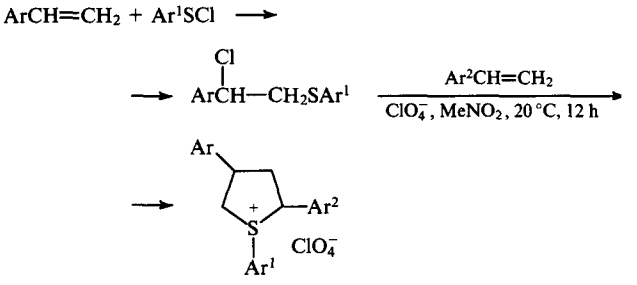


R = R^2 = H; R^1 = Et; R = H, R^1 + R^2 = $-(CH_2)_2-$; R = Me, R^1 + R^2 = $-(CH_2)_2-$.

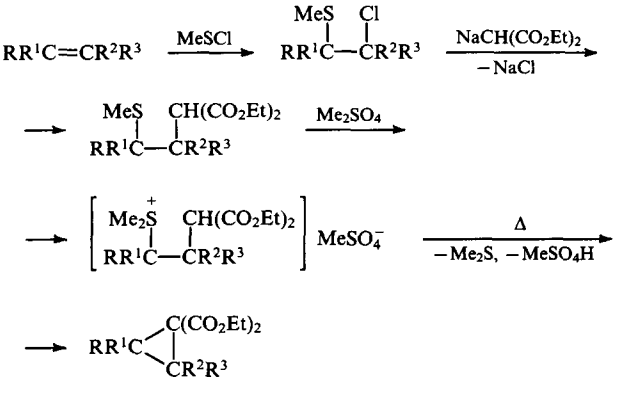
In the interaction of aryl β-chloroalkyl sulfides with vinyl ethers in proportions of 1:1, cyclic S-cationoid intermediates are formed. These react further with nucleophiles to form various sulfides having functional group substituents.[10,122,123]



β-Chloroalkyl sulfides react similarly with styrene and its homologues,[124] which involves the stabilisation of the intermediates in the form of tetrahydrothiophenium perchlorate.

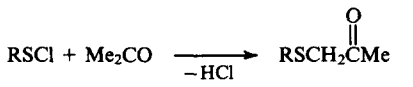


The reaction of β-chloroalkyl sulfides with *C*-nucleophiles, which may be used to create new carbon–carbon bonds, is synthetically very important. However, it is not always possible to achieve this reaction, since it has been noted,[10] for example, that, in the presence of *C*-nucleophiles such as organolithium or organomagnesium compounds, β-chloroalkyl sulfides undergo elimination. Only when sodiomalonic ester was used as the *C*-nucleophile was it possible to obtain the corresponding β-aryl(alkyl)thioalkylation products, which were subsequently converted into cyclopropane derivatives.[125]



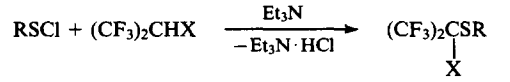
b. Syntheses of oxo-substituted sulfides

One of the commonest methods of synthesis of oxo-substituted sulfides is the sulfenylation of carbonyl compounds containing reactive C–H bonds. For example, sulfenyl chlorides react relatively easily in the cold with ketones having α-hydrogen atoms, forming β-oxo-substituted sulfides.[33]



R = Ar, Alk.

Fluorine-containing CH acids interact with sulfenyl chlorides only in the presence of triethylamine.[126]



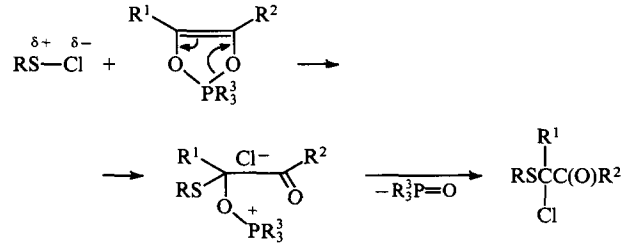
X = PhCO, CF_3CF_2CO, FCO.

In their reactions with sulfenyl chlorides, phosphorus ylides containing a carbonyl group readily exchange a hydrogen atom of the methylene group for an alkylthio- or arylthio-group even in the absence of bases.[3]

Dibenzoylmethane,[127,128] acetoacetic ester,[129,130] acetylacetone,[131] and even malonic ester[132,133] react similarly with alkanesulfenyl chlorides.

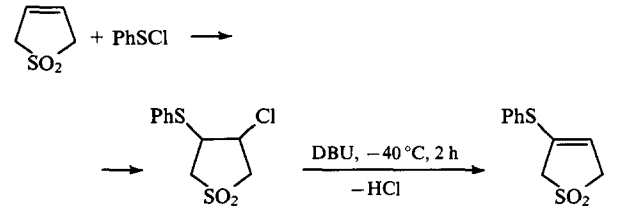
Another aspect of the use of sulfenyl chlorides in the synthesis of oxo-substituted sulfides involves the reaction of sulfenyl chlorides with vinyloxy[131–137] and divinyloxy-silanes[138] and also with the enols of dibutylborinates.[139] This reaction proceeds via stages involving 1,2-addition of the sulfenyl chloride and the elimination of chlorotrimethylsilane or dibutylchloroborane.

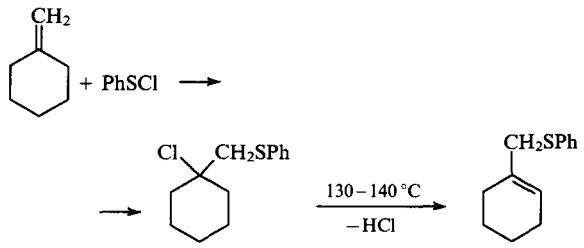
The synthesis of β-oxoalkyl sulfides from sulfenyl chlorides and 1,3,2-dioxaphospholenes has been described.[140] It has been suggested[28] that this reaction proceeds via a polar mechanism.

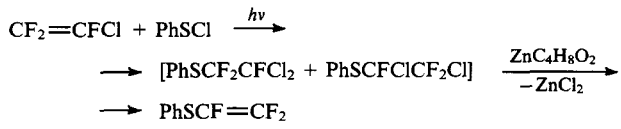


c. Synthesis of unsaturated sulfides

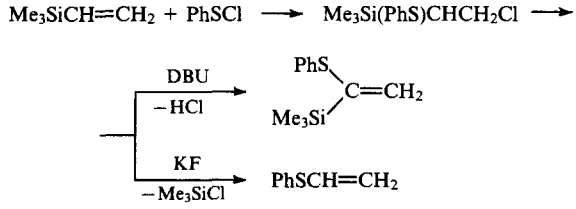
Several variants of the synthesis of unsaturated sulfides from sulfenyl chlorides have been developed. One of them involves the addition of sulfenyl chlorides to the C=C bond of unsaturated compounds with subsequent dehydrochlorination or dechlorination of the adducts. This variant has been used widely in the syntheses of vinyl[8,141] and allyl sulfides.[142,143] Potassium *tert*-butoxide, 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU), triethylamine, and other organic bases are used as the dehydrochlorinating agents.



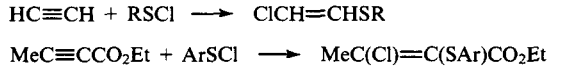




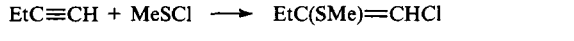
β-Chloro-α-(trimethylsilyl)ethyl phenyl sulfide, which is a product of the reaction of benzenesulfenyl chloride with trimethylvinylsilane, can undergo dehydrochlorination or dechlorotrimethyldesilylation, depending on the conditions, with formation of two different vinyl sulfides.[144]



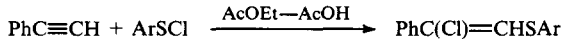
2-Chlorovinyl sulfides are formed as a result of the reaction of sulfenyl chlorides with ethyne and its homologues.[10,145,146]



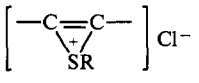
This reaction is slower than that of sulfenyl chlorides with alkenes, catalysts, for example aluminium chloride, being used sometimes to accelerate it.[10] The addition of sulfenyl chlorides to alkylethynes is mainly anti-Markovnikov and the products formed are not isomerised further.



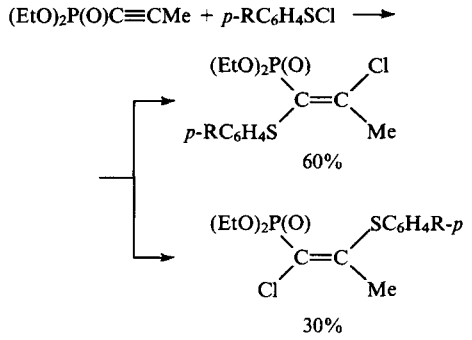
The mode of addition is influenced appreciably by the nature of the solvent and of the substituents. For example, the content of the Markovnikov addition product increases in acid media, a small amount of the *cis*-adduct being also formed together with the *trans*-adducts under these conditions.



It has been suggested[10] that Markovnikov addition occurs predominantly in those cases where the reaction conditions and the nature of the substituents favour the formation of a highly polar intermediate of the thiirenium salt type.

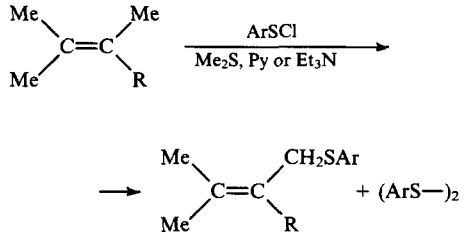


In anti-Markovnikov addition, the intermediate formed initially apparently decomposes. The addition of arenesulfenyl chlorides to diethyl propynylphosphonate takes place stereoselectively with formation of two regioisomers having the (*E*)-configuration in proportions of 2:1.[147]



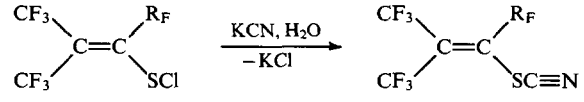
R = H, Me.

It has been noted[148] that, when internal alkenes reacted with arenesulfenyl chlorides in the presence of dimethyl sulfide, pyridine, or triethylamine, the hydrogen of the alkene methyl group is substituted by the arenesulfenyl fragment with formation of unsaturated sulfides. A proportion of the sulfenyl chloride is then converted into the disulfide.

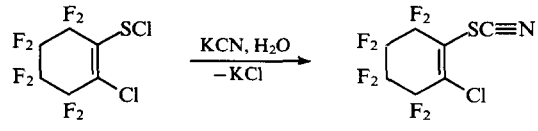


R = CH_3, 4-$MeOC_6H_4$; Ar = 4-MeC_6H_4, 4-ClC_6H_4.

The synthesis of perfluorinated α,β-unsaturated thiocyanates, by reaction of perfluorinated α,β-unsaturated sulfenyl chlorides with potassium cyanide in an aqueous medium, has been described.[149] This reaction proceeds under mild conditions (5–10 °C, 20 min) and gives high yields of the target products (50%–70%).

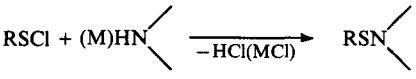


R_F = F, C_2F_5.



2. Syntheses of sulfenamides

One of the most important reactions of sulfenyl chlorides is that with compounds containing N–H or N–M (M = Na, K, Ag) bonds.



A whole series of preparative methods of synthesis of sulfenamides, including biologically active preparations, have been developed on the basis of this reaction.[13,85–87,150] Depending on the nature of the sulfenyl chloride and the compound containing the NH group, the sulfenylation is carried out in anhydrous inert organic solvents in the presence of hydrogen chloride acceptors (pyridine, triethylamine) or aqueous alkaline media. The sulfenylation of ammonia,[151–154] primary[155–159] and

secondary[160–165] amines, hydrazines and hydrazides,[28] the amides of carboxylic,[165–171] sulfonic,[172–177] and phosphoric[178,179] acids, cyanamide,[180,181] imides,[27,160] phosphine imines[182–184] and sulfine imines,[185,186] imidoesters,[187] sulfinamidines,[188] silazanes,[89,189–191] glycine derivatives,[192–197] and nitrogen-containing heterocyclic compounds[33,198] has been described. Instead of amines and amides, their silylated derivatives are introduced in certain cases into the reaction with sulfenyl chlorides. The interaction of these derivatives with sulfenyl chlorides entails the cleavage of the N–Si bond and the formation of the N–S bond.[199,200]

$$2\,ArSCl + (Me_3Si)_2NR \xrightarrow[-2\,Me_3SiCl]{} (ArS)_2NR$$

Ar = 4-$NO_2C_6H_4$, $PhCH_2$, Ac, $PhSO_2$

$$RSCl + Me_3SiN(Me)_2 \xrightarrow[-Me_3SiCl]{} RSN(Me)_2$$

R = Me, CCl_3, Ph, 2-$NO_2C_6H_4$.

The second aspect of the use of sulfenyl chlorides in the synthesis of sulfenamides involves their addition to the C≡N bond.[33] The reactions of TCMSC with 2,4-dimethylphenyl cyanate[33,201] and *N*-benzoylcyanamide,[202] of dichlorofluoromethanesulfenyl chloride with chlorocyanogen,[203] and of trifluoromethanesulfenyl chloride with tetracyanoethene[203] and chloro-cyanogen[204] take place in this way.

$$X{-}C{\equiv}N + ClSR \longrightarrow X{-}\underset{\displaystyle Cl}{\underset{|}{C}}{=}NSR$$

X = 2,4-$Me_2C_6H_3O$, PhCONH, $(NC)_2C{=}CCN$, Cl;

R = CCl_3, CF_3.

In the presence of mercury difluoride, trifluoromethanesulfenyl chloride adds readily to the C=N bond of chlorocyanogen and trifluoroacetonitrile and trichloroacetonitrile.[205] The interaction is accompanied by the substitution of chlorine by fluorine.

$$CF_3SCl \xrightarrow{HgF_2,\ 20\,^\circ C} \begin{cases} \xrightarrow{ClCN} CF_3N(SCF_3)_2 \\ \xrightarrow{CF_3CN} CF_3C(F){=}NSCF_3 \\ \xrightarrow{CCl_3CN} CCl_3C(F){=}NSCF_3 \end{cases}$$

The reactions of sulfenyl chlorides with cyanamide and its *N*-alkyl derivatives are accompanied by the sulfenylation of the amido-group.[206,207]

$$3\,XNHC{\equiv}N + 4\,RSCl \xrightarrow{0\,^\circ C,\ Et_2O} 2\,RSN(X)C(Cl){=}NSR + XNHCN\cdot 2\,HCl$$

R = CCl_3, $CFCl_2$, CF_3.

The third aspect of the use of sulfenyl chlorides in the synthesis of sulfenamides involves their conversion into sulfenyl isocyanates and subsequent treatment of the latter with ammonia, amines, or alcohols.[208–211] As a rule sulfenyl isocyanates are synthesised in situ by the interaction of sulfenyl chloride with AgOCN or NaOCN in anhydrous inert organic solvents.

$$RSCl + MOCN \xrightarrow[-MCl]{} RSNCO \longrightarrow$$

$$\xrightarrow{NH_3} RSNHC(=O)NH_2$$
$$\xrightarrow{R^1NH_2} RSNHC(=O)NHR^1$$
$$\xrightarrow{R^2_2NH} RSNHC(=O)NR^2_2$$
$$\xrightarrow{R^3OH} RSNHC(=O)OR^3$$

R^1 = R^2 = Alk, Ar; R^3 = Alk, Bz; M = Ag, Na.

3. Syntheses of thiocarbonyl compounds

On treatment with bases (triethylamine, NaOH, etc.), sulfenyl chlorides containing reactive α-C–H bonds generate thioaldehydes, which are used in organic synthesis as highly reactive intermediates.[1,43]

$$EtOCCH_2SCl \xrightarrow[-HCl]{Et_3N} EtOC(=S)C(=O)H$$

Certain sulfenyl chlorides give rise to thioaldehydes as a result of photolysis. For example, the photolysis of ethanesulfenyl chloride by irradiation with UV light at a wavelength of 365 nm has been recommended[212] as a preparative method of synthesis of thioacetaldehyde. Sulfenyl chlorides containing a *sp*-hybridised C atom at the S atom readily isomerise to thioketenes.[67]

$$PhC{\equiv}CSCMe \xrightarrow{SO_2Cl_2} [PhC{\equiv}CSCl] \longrightarrow \underset{Cl}{\overset{Ph}{}}C{=}C{=}S$$

Treatment of perhaloalkanesulfenyl chloride with a solution of Na_2CS_3 in chloroform or of $BaCS_3$ in the CH_3CN-H_2O mixture leads to the formation of the polysulfide derivatives of polythiocarboxylic acids $(RSS)_2C=S$ (R = CCl_3, CCl_3CCl_2, CF_3CCl_2, $CClF_2CCl_2$).[213] A series of preparative methods of synthesis of thiocarbonyl dihalides, based on the reduction of perhalomethanesulfenyl chlorides, have been developed. For example, heating of TCMSC with tetralin leads to the formation of thiophosgene.[24,33]

$$CCl_3SCl \xrightarrow[-Cl_2]{C_{10}H_{12},\ 200\,^\circ C} \underset{Cl}{\overset{Cl}{}}C{=}S$$

In the presence of tin, dichlorofluoromethanesulfenyl chloride and chlorodifluoromethanesulfenyl chloride are reduced to thiocarbonyl chloride fluoride and thiocarbonyl difluoride respectively.[33]

$$CFCl_2SCl \xrightarrow{40\,^\circ C} \underset{Cl}{\overset{F}{}}C{=}S$$

$$CF_2ClSCl \xrightarrow{20\,^\circ C} \underset{F}{\overset{F}{}}C{=}S$$

4. Syntheses of sulfenic acid esters

Sulfenic acid esters are formed in the reactions of sulfenyl chlorides with alkoxides (phenoxides) or with alcohols (phenols) in the presence of pyridine or triethylamine.[13,24,33,159] The reaction does not always proceed smoothly, especially in the case of aliphatic sulfenyl chlorides and alcohols. This is due to the fact that, by virtue of the high nucleophilicity of the sulfur atom, the sulfenate formed may react with the sulfenyl chloride to form a disulfide and other side products, which reduce the yield and hinder the isolation of the sulfenates.[28] The reaction proceeds more smoothly in the case of sulfenyl chlorides containing powerful electron-accepting groups at the sulfur atom, which reduce the nucleophilicity of the sulfur atom in the resulting sulfenate and therefore hinder its interaction with the sulfenyl chloride. For example, relatively stable sulfenates have been obtained in the reaction of polyfluoroalkanesulfenyl chlorides with alcohols on heating[69] and also in the presence of hydrogen chloride acceptors (triethylamine, pyridine)[214–216] or with alkali metal[217] and mercury[218] alkoxides and phenoxides.

$$R_FSCl + ROH \xrightarrow[-HCl]{\Delta} R_FSOR$$

$R_F = CF_3, (CF_3)_2CHCF_2$;

R = Et, 4-$MeOC_6H_4CH_2$, $CF_3SNHCH_2CH(Ph)$.

$$R_FSCl + ROH \xrightarrow[-HCl]{Et_3N \text{ or } C_5H_5N} R_FSOR$$

$R_F = CF_3, (CF_3)_2CHCF_2$; $CF_3CH(CH_2Cl)$;

R = Alk, Ar, 4-$MeOC_6H_4CH_2$.

$$R_FSCl + RONa \xrightarrow[-NaCl]{THF,\ 20\,^\circ C,\ 3\ h} R_FSOR$$

$R_F = CF_3CPh_2$;

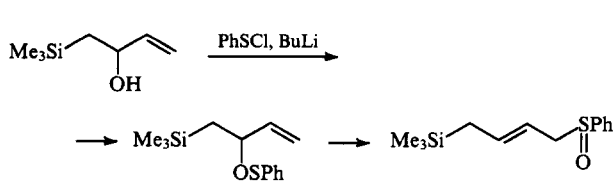
R = Bu^tCH_2, $PhCH_2O(CH_2)_2$, 4-$NO_2C_6H_4$, $Me(CH_2OCH_2)_3CH_2$.

$$R_FSCl + ROHgCl \xrightarrow[-HgCl_2]{0\,^\circ C,\ 24\ h} R_FSOR$$

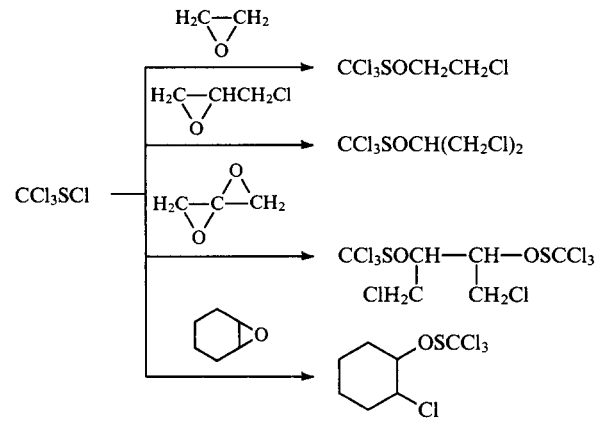
$R_F = CF_3, CF_3CO$; R = $(CF_3)_3C$.

The stable esters of 2,4,6-trinitrobenzenesulfenic,[47] 2,4-dinitrobenzenesulfenic,[4,28] trichloromethanesulfenic,[33] and dichlorofluoromethanesulfenic[33] acids have been described. In the sulfenylation of phenols and naphthols, it is better to employ their sodium salts, which rules out the competing electrophilic substitution of the hydrogen atoms of the benzene ring.[8] The introduction of the corresponding alkoxides instead of alcohols into the reaction with TCMSC, especially in the presence of an excess of the alkoxides, leads to the formation of alkyl orthocarbonates.[219] The above methods are unsuitable for the synthesis of allyl sulfenates, with the exception of the allyl esters of 2,4-dinitrobenzenesulfenic acid, because the esters formed are readily converted into allyl sulfoxides as a result of a 2,3-sigmatropic rearrangement.[33]

$$RSCl + HOCH_2CH{=}CH_2 \xrightarrow[-HCl]{C_5H_5N} [RSOCH_2CH{=}CH_2] \longrightarrow R\overset{\overset{O}{\|}}{S}CH_2CH{=}CH_2$$



The chloroalkyl esters of trichloromethanesulfenic acid are formed in the reaction of TCMSC with 1,2-epoxides.[33]



5. Syntheses of the thiolo-esters of sulfinic, sulfonic, carboxylic, and phosphoric acids

The hydrolysis of sulfenyl chlorides leads to the formation of a mixture of products in which the thiolo-esters of sulfinic or sulfonic acids predominate. This is determined both by the structure of the initial sulfenyl chloride and the hydrolysis conditions.[13,33] For example, in a study of the hydrolysis of dichlorofluoromethane- and chlorodifluoromethane-sulfenyl chlorides in a neutral medium, it has been possible[220] to isolate the thiolo-esters of sulfinic acids. The thiolo-esters of sulfonic acids are one of the products of the hydrolysis of sulfenyl chlorides in acid media.[221]

$$4\,RSCl + 2\,H_2O \xrightarrow{H^+} RSO_2SR + RSSR + 4\,HCl$$

The formation of the corresponding thiolosulfonate in the reaction of *p*-chlorobenzenesulfenyl chloride with anhydrous formic acid has been noted.[222] The interaction of sulfenyl chlorides with sulfinic acids[28,223] or their silver[28] and sodium[174] salts leads to asymmetric thiolosulfonates.

$$RSO_2H(M) + R^1SCl \xrightarrow[-HCl(MCl)]{} RSO_2SR^1$$

R, R^1 = Alk, Ar.

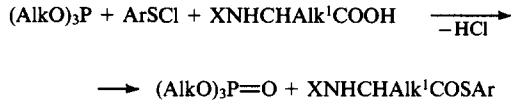
M = Na, Ag.

The thiolo-esters of carboxylic acids are formed on interaction of arenesulfenyl chlorides with triphenylphosphine or with trialkyl phosphites in the presence of carboxylic acid salts. It has been suggested[224] that the quasi-sulfonium salt **A** is an intermediate in this reaction. Its interaction with the carboxylate anion leads to the final products.

$$R_3P + ArSCl \longrightarrow \underset{\mathbf{A}}{(R_3PSAr)^+Cl^-} \xrightarrow[-NaCl]{R^1COONa} (R_3PSAr)^+R^1COO^- \longrightarrow (R_3POCOR^1)^+(SAr)^- \longrightarrow R_3P{=}O + RCOSAr$$

R = Ph, AlkO; R^1 = Ar, Alk.

The analogous reaction of arenesulfenyl chlorides with trialkyl phosphites and *N*-acylaminoacids in the presence of bases has been proposed as a preparative method of synthesis of the aryl thiolo-esters of carboxylic *N*-acylaminoacids.[225,226]



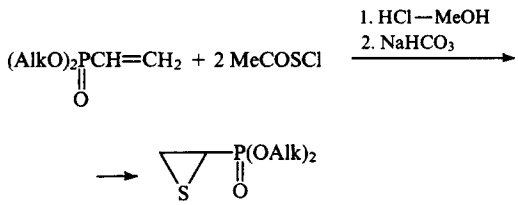
X = CF_3CO, Ph, $PhCH_2OCO$.

The syntheses of the thiolo-esters of phosphonic acids and other phosphorus-containing compounds from sulfenyl chlorides have been described in detail in a monograph[4] and also in a review[33] and in the literature quoted therein. For this reason they will not be considered here.

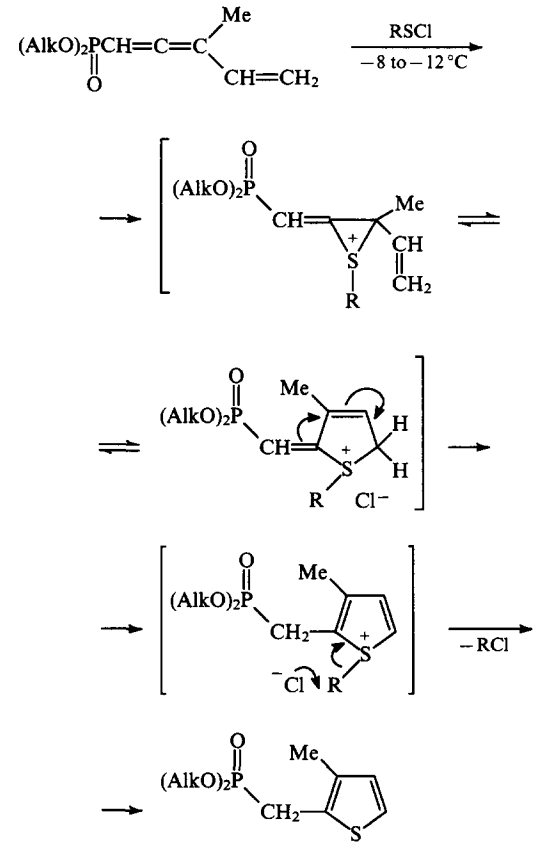
6. Syntheses of heterocyclic compounds

a. Syntheses based on monofunctional sulfenyl chlorides

The use of monofunctional sulfenyl chlorides in the synthesis of heterocyclic compounds is based on their addition to the C=C bond of unsaturated compounds with subsequent cyclisation of the resulting intermediates.[4,13,33] For example, the synthesis of the dialkyl esters of 1,2-epithioethylphosphonic acid has been described.[227] It is based on the addition of acetylsulfenyl chloride [1-oxoethanesulfenyl chloride (Ed. of translation)] to the alkyl esters of vinylphosphonic acid and subsequent treatment of the resulting adduct with a solution of hydrogen chloride in methanol and then with sodium bicarbonate.



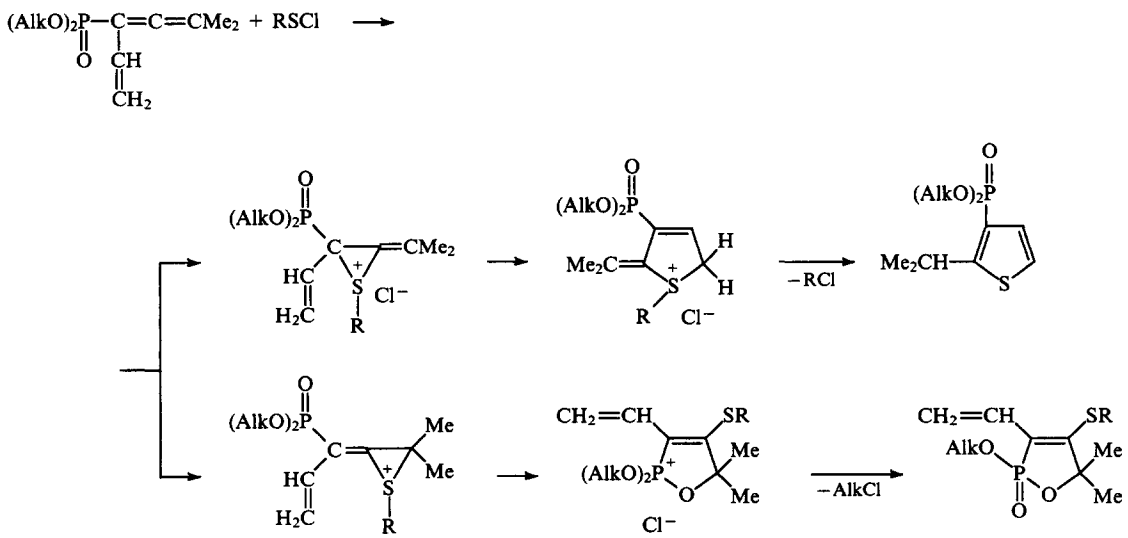
It has been noted[4,228,229] that the introduction of the vinyl group in the 3-position in allenylphosphonate leads to a system of double bonds, to which alkanesulfenyl chlorides add relatively easily with formation of an episulfonium ion capable of ring expansion to a five-membered cyclic compound followed by conversion into a thiophene derivative.

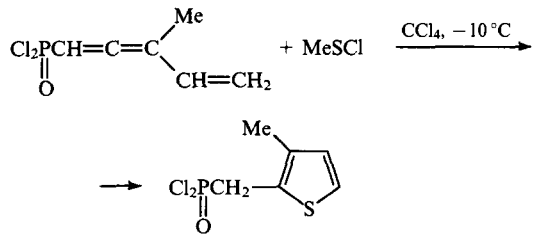


The analogous reaction of alkanesulfenyl chlorides with allenylphosphonates containing a vinyl substituent in the 1-position leads to a mixture of 3-vinyl-1,2-oxaphosphol-3-enes and phosphorylated thiophenes, the ratio of which is influenced by the reaction temperature (Scheme 5).[4,228,230]

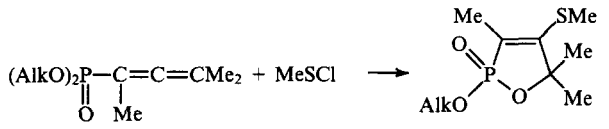
Derivatives of 2,2-dichlorophosphorylmethylthiophene are formed in 53% yield as a result of the addition of methanesulfenyl chloride to alkyl-1,2,4-trienylphosphonic dichlorides.[231]

Scheme 5

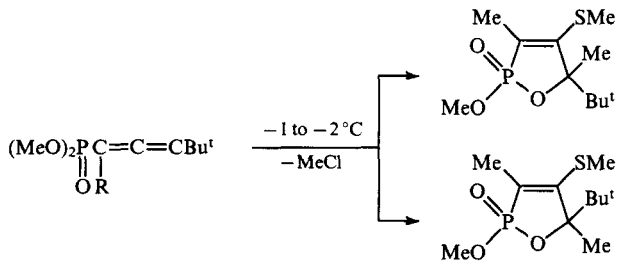




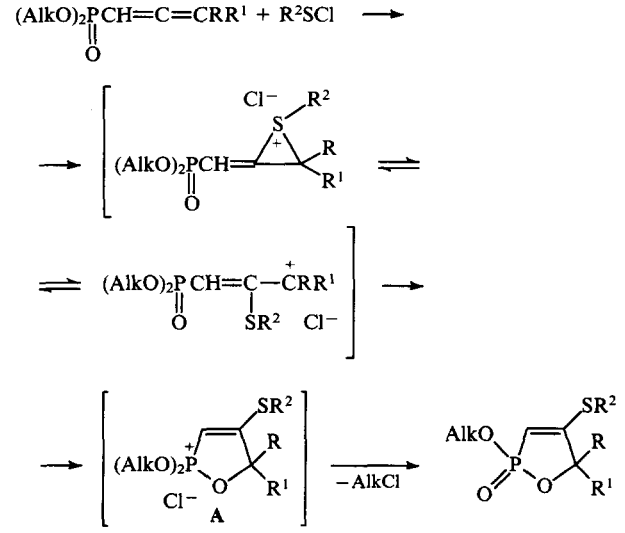
The addition of methanesulfenyl chloride to 1,3,3-trimethylallenylphosphonates leads to the derivatives of 1,2-oxaphosphol-3-ene.[228]



In the case of 1,3,3-trisubstituted allenylphosphonates containing the *tert*-butyl group in the γ-position, a mixture of two stereoisomers is formed. This has been demonstrated by NMR spectroscopy.[232]



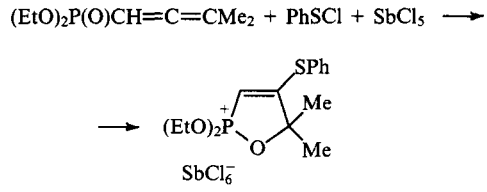
The addition of sulfenyl chlorides to the dialkyl esters of 3,3-disubstituted allenylphosphonic acids, the rearrangement of the episulfonium ion, cyclisation, and dealkylation result in the formation of 4-organylthio-1,2-oxaphosphol-3-enes.[233–237]



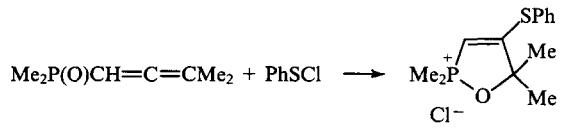
R, R^1 = Alk or R + R^1 = $-(CH_2)_5-$.

R^2 = Me, Et, Pr^i, Ph, 2,4-$(NO_2)_2C_6H_3$.

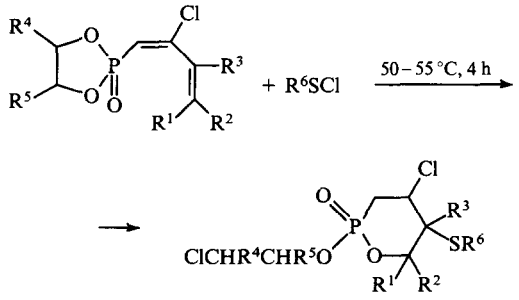
The formation of the intermediate phosphonium salt **A** has been demonstrated by its isolation in the form of 1,2-oxaphosphol-3-enium hexachloroantimonate.[238]



A quasi-phosphonium salt has also been isolated in the reaction of benzenesulfenyl chloride with dimethyl(3-methylbuta-1,2-dienyl)phosphine oxide in the cold.[234]



In chloroform or dichloroethane, alkanesulfenyl chlorides react with 1,3,3-dioxaphospholane 2-oxides to form 1,2-oxaphosphorines.[239]

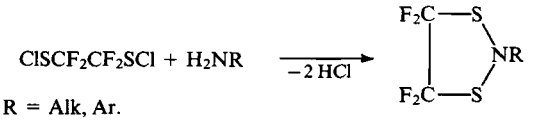


R^1 = R^2 = R^3 = R^4 = R^5 = H, Me; R^6 = Me, Pr^i.

The addition of arenesulfenyl chlorides to 2-allylphenols and subsequent cyclisation of the resulting adducts lead to the formation of 2-phenylthiomethylbenzofurans.[240]

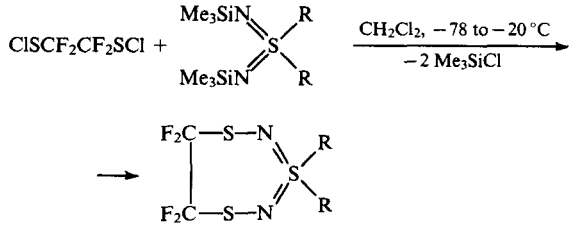
b. Syntheses based on bifunctional sulfenyl chlorides

Bifunctional sulfenyl chlorides are more widely used in the synthesis of heterocyclic compounds.[13] For example, a series of *N*-substituted 1,3,2-dithiazolidines have been obtained by the reaction of tetrafluoroethane-1,2-disulfenyl chloride with primary amines.[156]



R = Alk, Ar.

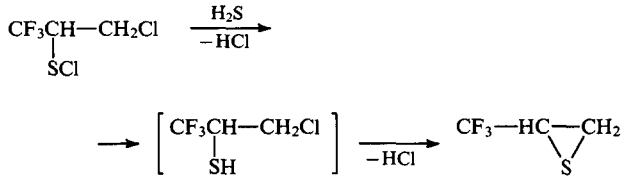
The interaction of the same disulfenyl chloride with *N*,*N*′-bis(trimethylsilyl)sulfodiimides affords high yields of 1,3,5-trithia-2,4-diazepines.[13]



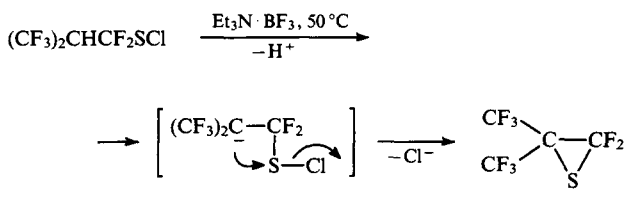
R = Alk, Ar.

Numerous heterocyclic compounds have been obtained from other polyfluoroalkanesulfenyl chlorides. The capacity of these sulfenyl chlorides for ring formation is determined primarily by

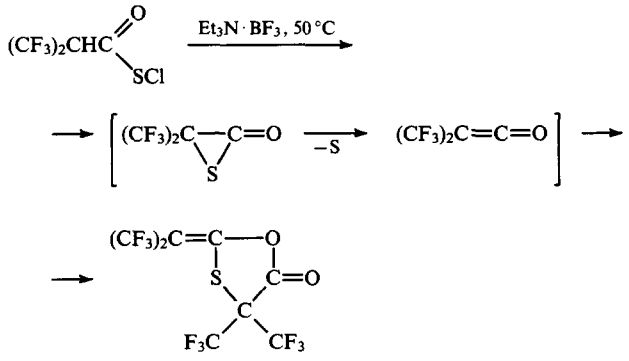
anionotropic transformations in the C–C–S three-centre systems.[13,241] It has been noted[242] that, on treatment with H_2S in *N*-methylpyrrolidinone, 3-chloro-1,1,1-trifluoropropane-2-sulfenyl chloride is readily converted into trifluoromethylthiirane. 3-Chloro-1,1,1-trifluoropropane-2-thiol is an intermediate in this reaction.



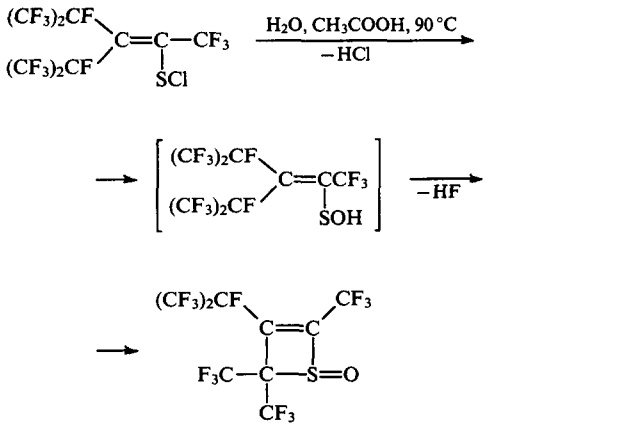
The dehydrochlorination of 2-hydroperfluoroisobutanesulfenyl chloride in the presence of the complex $Et_3N \cdot BF_3$ leads to the formation of perfluoro-2,2-dimethylthiirane.[69]



In the case of 3,3,3-trifluoro-2-(trifluoromethyl)-1-oxopropanesulfenyl chloride, the reaction proceeds in a more complex manner. The thiirane formed as a result of the 3-chlorination of this sulfenyl chloride is desulfurised under the reaction conditions, being converted into bis(trifluoromethyl)ketene, which subsequently react with the thiirane via a [3 + 2]-cycloaddition mechanism.[69]



The formation of the thietene ring has been observed[13,243] in the acid hydrolysis of perfluoro-3-isopropyl-4-methylpent-2-ene-2-sulfenyl chloride. An unstable sulfenic acid is an intermediate product of this reaction.



TCMSC has found extensive applications in the synthesis of heterocyclic compounds.[33] Thus the interaction of this compound with a 25% aqueous solution of ammonia in the benzene–water two-phase system leads to the formation of 2,3,7,8-tetrachloro-5,10,11,12-tetrathia-1,4,6,9-tetrazatricyclo-[5.3.11^{2,6}]-dodeca-3,8-diene.[244]

The interaction of TCMSC with aromatic amines results in the formation of unstable *N*-aryltrichloromethanesulfenamides, which are converted into 2,5-diaryl-3,3,6,6-tetrachloro-1,4-dithia-2,5-diazines in the presence of bases or on heating.[201]

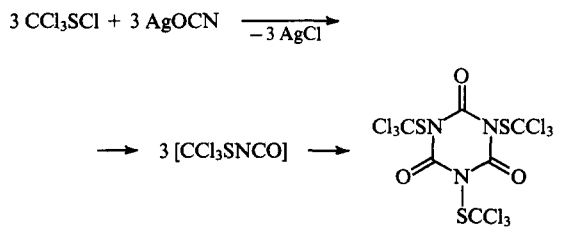
The reaction of TCMSC with 2-aminopyridine leads to the formation of 2-(*N*-trichloromethanesulfenyl)aminopyridine, which is converted into 3-(2-pyridylimino)-3*H*-1,2,4-thiadiazolo-[4,3-α]pyridine in the presence of an excess of the aminopyridine.[201,245]

When TCMSC is heated with carboxylic acid amides in dioxane, 5-aryl-1,3,4-oxathiazol-2-ones are formed.[246] *N*-Aroyltrichloromethanesulfenamides are intermediates in this reaction. In the presence of bases, they undergo the heterocyclisation reaction.[86,175,247,248]

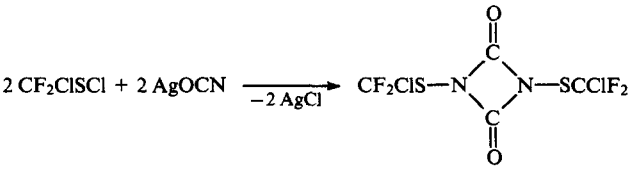
A series of 1,2,4-thiadiazole derivatives have been obtained by the reaction of TCMSC with carboxylic acid amidines and *S*-alkylisothiuronium salts.[33]

Dichloromethane- and dichlorofluoromethane-sulfenyl chlorides react similarly with carboxylic acid amidines.[28,33]

Treatment of TCMSC with silver isocyanate leads to the unstable trichloromethanesulfenyl isocyanate, which trimerises to 1,3,5-tris(trichloromethanesulfenyl)-2,4,6-trioxo-1,3,5-triazine.[249]



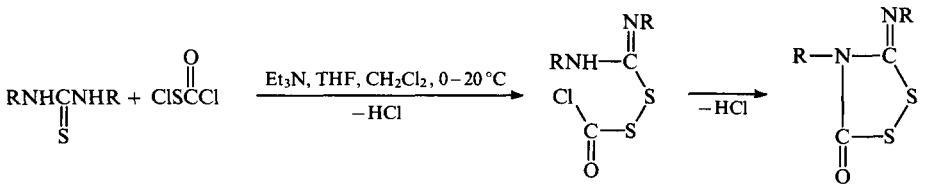
The analogous reaction of silver isocyanate with chlorodifluoromethanesulfenyl chloride leads to the formation of 1,3-bis(chlorodifluoromethanesulfenyl)-2,4-dioxo-1,3-diazetidine.[208,209]



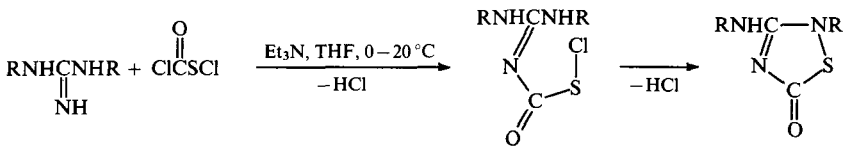
Chlorocarbonylsulfenyl chloride is of considerable preparative importance for the synthesis of various five-membered nitrogen and sulfur-containing heterocyclic compounds.[11] The two reaction centres (sulfur and carbon) as well as the high lability of the S–Cl and C–Cl bonds impart to this reagent a set of properties which are extremely valuable for heterocyclisation reactions. Depending on the nature of the bifunctional compound, chlorocarbonylsulfenyl chloride may react with the latter, a C or the S atom participating in the first stage of the reaction, while in the second stage the second reaction centre is involved, as happens, for example, in the interaction of chlorocarbonylsulfenyl chloride with thiourea, urea, and guanidine derivatives (Scheme 6).[250]

A whole series of preparative methods of synthesis of various five-membered heterocyclic compounds from chlorocarbonylsulfenyl chloride and 1,3-bifunctional compounds, presented in Scheme 7, have been developed.[11]

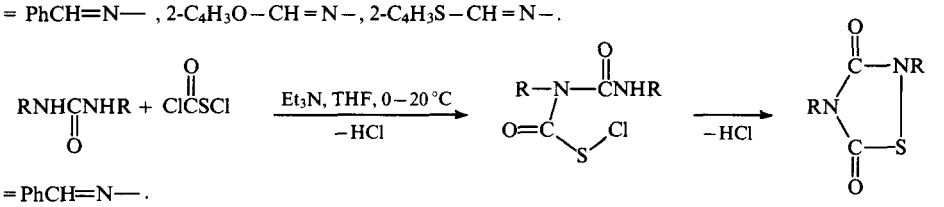
Scheme 6



R = Ph, XCH=N— (X = Ph, 2-C_4H_3O, 2-C_4H_3S, 2-C_5H_4N, 3-C_5H_4N).



R = PhCH=N— , 2-C_4H_3O–CH=N–, 2-C_4H_3S–CH=N–.

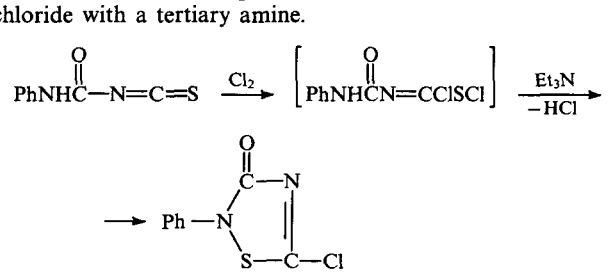


R = PhCH=N—.

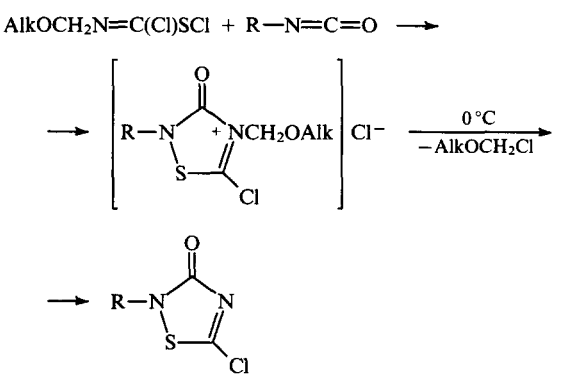
The interaction of chlorocarbonylsulfenyl chloride with derivatives of benzamide oxime in acetonitrile in the presence of triethylamine leads to the formation of two products — 3-aryl-1,2,4-thiadiazol-5-ones and 3-aryl-1,2,4-oxadiazol-5-ones.[251]

The condensation of chlorocarbonylsulfenyl chloride with 2-aminothiazole in tetrahydrofuran in the presence of bases takes place with formation of 2,3 fused thiadiazolone, whereas the condensation in chloroform leads to 3,4 fused thiadiazolone.[252]

Numerous methods of synthesis of five-membered nitrogen-containing heterocycles have been developed on the basis of chloroiminomethanesulfenyl chlorides. However, many of these methods have so far been inadequately tested and it is not clear whether they are of a general character. On the other hand, the majority of these compounds are unstable, their synthesis and their reactions being carried out in situ, which also limits their application in the syntheses of heterocycles. For example, the synthesis of 5-chloro-3-oxo-2-phenyl-1,2,4-thiadiazoline, described in the literature,[11] involves the chlorination of phenylcarbamoyl isothiocyanate followed by the treatment of the intermediate chloro(phenylcarbamoylimino)methanesulfenyl chloride with a tertiary amine.

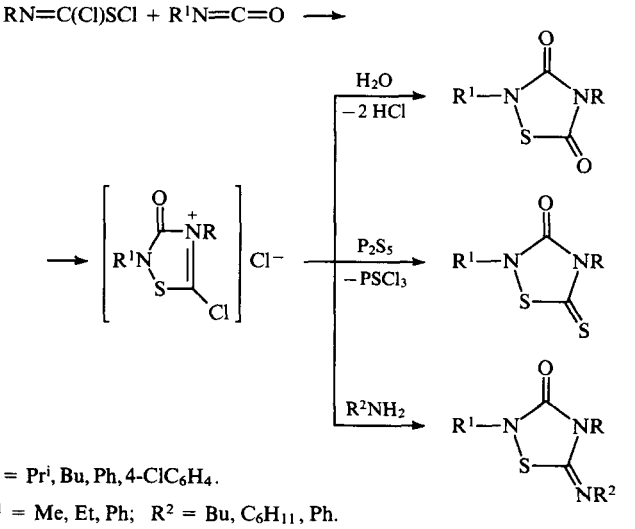


Similar compounds are formed in the interaction of alkoxymethylimino(chloro)methanesulfenyl chlorides with isocyanates. The intermediate formed in the first stage of this reaction is converted into the final product by elimination of an alkyl chloromethyl ether.



R = Me, Pr^i, Ph, 2-BrC_6H_4, 3,4-$Cl_2C_6H_3$, 4-$EtOC_6H_4$.

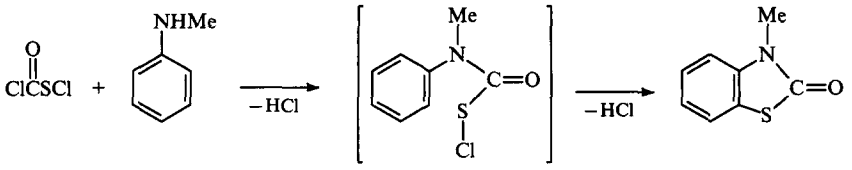
The intermediates formed in the reactions of chloro(imino)-methanesulfenyl chlorides with isocyanates interact relatively easily with various nucleophiles, affording five-membered heterocyclic compounds containing both sulfur and nitrogen.[253,254]

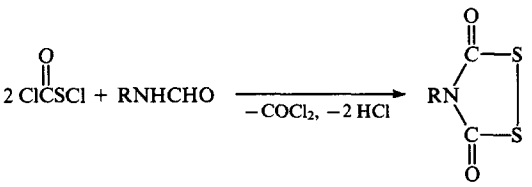


R = Pr^i, Bu, Ph, 4-ClC_6H_4.

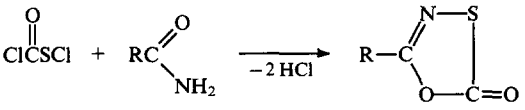
R^1 = Me, Et, Ph; R^2 = Bu, C_6H_{11}, Ph.

Scheme 7

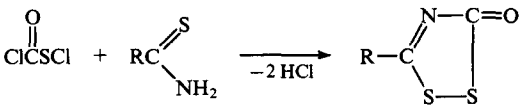


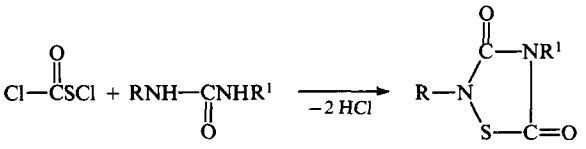


R = Me, C_5H_{11}, Ph, 3,4-$Cl_2C_6H_3$, 3-Cl-4-$MeOC_6H_3$.



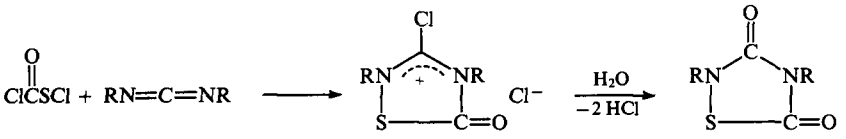
R = 2-$MeOC_6H_4$, 3-$MeOC_6H_4$, 4-$MeOC_6H_4$, 2-BrC_6H_4, 2-IC_6H_4, 2-MeC_6H_4.

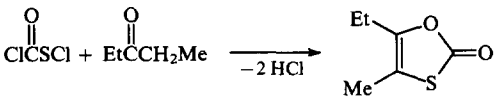


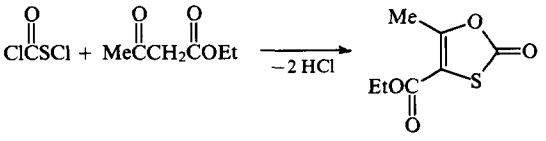


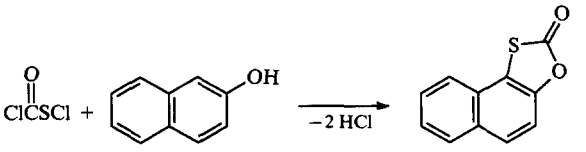
R = Me, $MeOCH_2$, C_6H_{11}, Ph, 2-$CF_3C_6H_4$, 3,4-$Cl_2C_6H_3$, 3-Cl-4-MeC_6H_3;

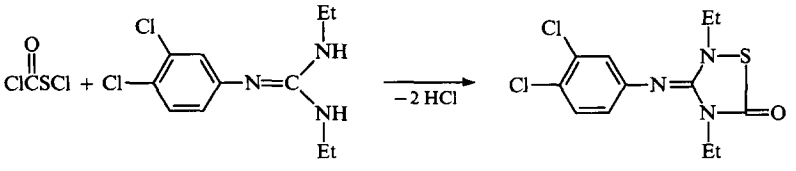
R^1 = Me, $MeOCCH_2$, C_6H_{11}, Ph.



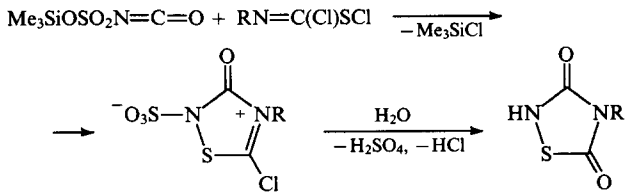






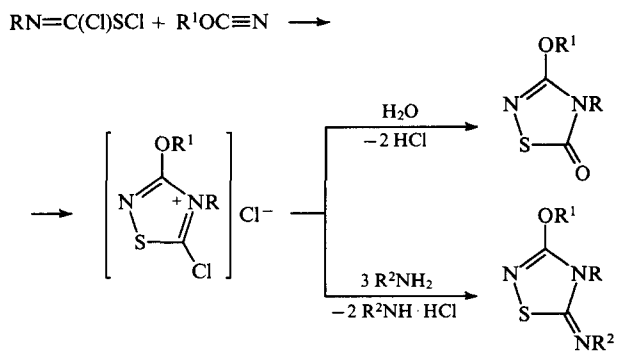


The interaction of chloro(imino)methanesulfenyl chlorides with trimethylsiloxysulfenyl isocyanate takes place with cleavage of the Si–O bond and the formation of a product having a dipolar structure, the hydrolysis of which affords 1,2,4-thiadiazolidine-3,5-diones.[254]



R = Me, Bu, $PhCH_2$, Ph, 3,4-$Cl_2C_6H_3$.

The addition of chloro(imino)methanesulfenyl chlorides to the C≡N bond of cyanates also proceeds with formation of intermediates, the hydrolysis and aminolysis of which lead to derivatives of 1,2,4-thiadiazoline.[11]



R = Me, Ph; R^1 = CCl_3CH_2, Ph, 3-$NO_2C_6H_4$.

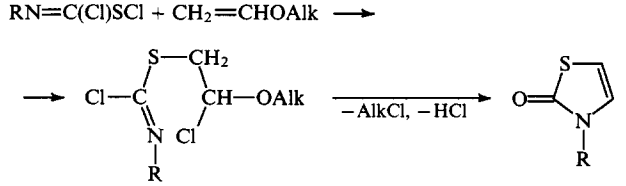
R_2 = Me, 4-ClC_6H_4.

The addition of chloro(imino)methanesulfenyl chlorides to the C=C bond of alkenes is accompanied by the formation of adducts, the hydrolysis of which leads to the S-esters of thiocarbamic acid, which cyclise to 2-oxo-1,3-thiazolidines.[255]



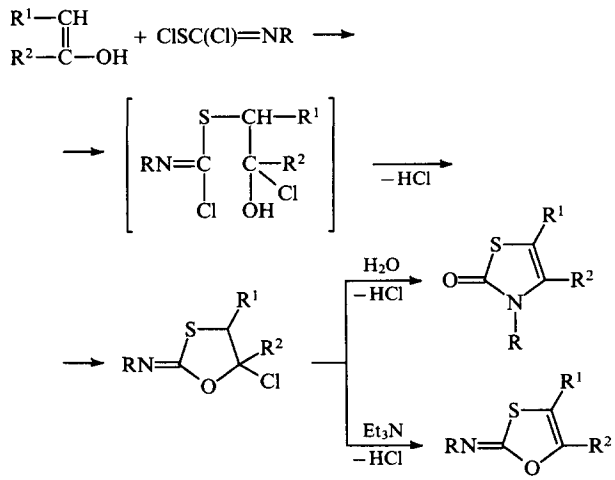
R = Me, Ph, R^1 = Alk.

In additions to vinyl ethers, the cyclisation of the adducts proceeds with elimination of an alkyl halide and hydrogen chloride and the formation of 2-oxo-1,3-thiazolines.[256]

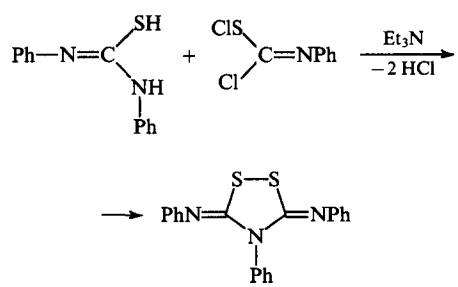


R = Me, Bu, Ph.

The enolic form of ketones react with chloro(imino)-methanesulfenyl chlorides to give adducts which are stabilised on intramolecular cyclisation.[256]



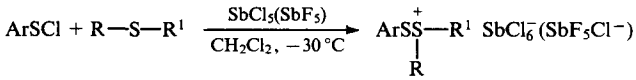
Diphenylthiourea reacts with chloro(*N*-phenylimino)-methanesulfenyl chloride in the thiolo-form with formation of 3,5-bis(phenylimino)-4-phenyl-1,2,4-dithiazolidine.[11]



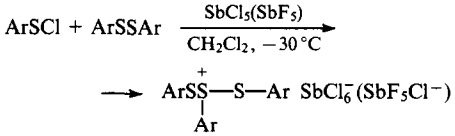
7. Syntheses of compounds of tetravalent and hexavalent sulfur

a. Syntheses of arylthiosulfonium and aryl(bisarylthio)sulfonium salts

Arylthiosulfonium and aryl(bisarylthio)sulfonium salts belong to a special type of derivatives of tetravalent sulfur, namely to the class of S-cationoid compounds with a positive charge on one of the sulfur atoms. These salts are formed relatively easily on interaction of sulfenyl chlorides with sulfides[257] and disulfides[258] in the presence of Lewis acids such as $SbCl_5$ or SbF_5.



Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4; R = R^1 = Me, Ph;

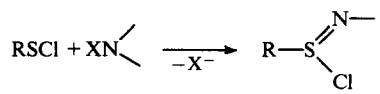


Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4.

Arylthiosulfonium and aryl(bisarylthio)sulfonium salts have found applications in organic synthesis as agents transferring the RS^+ groups in Ad_E reactions with alkenes.[259]

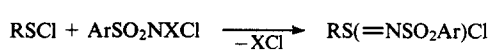
b. Syntheses of iminosulfinic acid chlorides.

The use of sulfenyl chlorides in the synthesis of iminosulfinic acid chlorides is based on their oxidative imination by *N*-halo-compounds, as a result of which the valence of the sulfur atom of the sulfenyl chloride increases by two units and combines with the imino-group.[186,260,261]



X = Cl, Br.

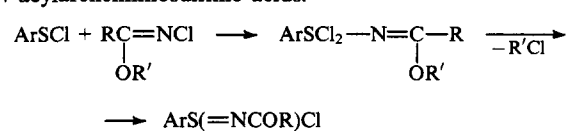
For example, it has been noted that arenesulfenyl chlorides react in anhydrous organic solvents with *N*-chloro- and *N,N*-dichloroamides of arenesulfonic acids with formation of the chlorides of *N*-arenesulfonylareneiminosulfinic acids.[260,261]



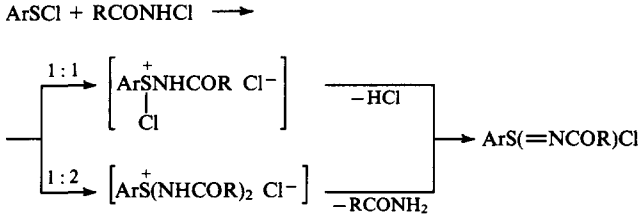
R = Ph, 4-MeC_6H_4, 4-$NO_2C_6H_4$, 4-ClC_6H_4, 2-$NO_2C_6H_4$.

Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4; X = Na, Cl, Me_3Si.

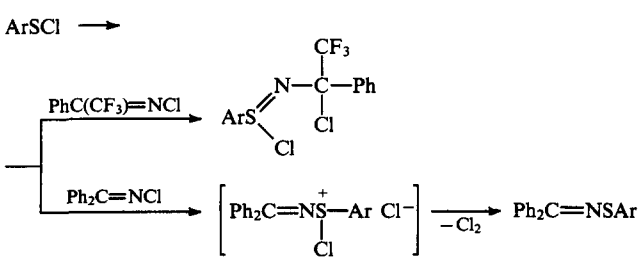
N,N-Dichlorourethanes and esters of *N*-chloroiminocarbonic acid,[260] *N*-chloro-*N*-trimethylsilyl-*tert*-butylamine,[262] the *N*-chloroamides of carboxylic acids,[263] and *N*-chloroketimines[264] are used as iminating agents in order to obtain the chlorides of *N*-substituted iminosulfinic acids containing other substituents at the nitrogen atom. The reactions of arenesulfenyl chlorides with *N*-chloroiminocarbonic acid esters proceed with formation of sulfuranes in the first stage. As a result of the elimination of an alkyl halide, the sulfuranes are converted into the chlorides of *N*-acylareneiminosulfinic acids.[265]



Depending on the reactant ratio, *N*-acylamino(aryl)chlorosulfonium chlorides or bis(*N*-acylamino)(aryl)sulfonium chlorides are intermediates in the reactions of arenesulfenyl chlorides with the *N*-chloroamides of carboxylic acid.[263]



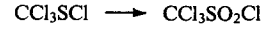
Arenesulfenyl chlorides do not react unambiguously with *N*-chloroketimines.[264] The formation of the corresponding acid chlorides has been observed in the reaction of arenesulfenyl chlorides with *N*-trifluoromethylphenylketimine, whereas the reaction with *N*-chlorodiphenylketimine leads to the corresponding sulfenamide.



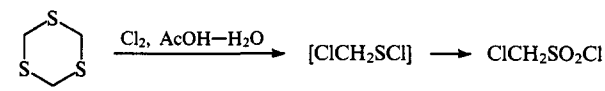
Arenesulfenyl chlorides do not react with *N*-chlorobis(trifluoromethyl) ketimine.[264]

c. Syntheses of sulfonic acid chlorides

Sulfenyl chlorides which are resistant to hydrolysis are relatively easily converted into sulfonic acid chlorides on treatment with oxidants, which is sometimes used in preparative organic chemistry.[13,33] For example, the oxidation of trichloromethanesulfenyl chlorides by various oxidants constitutes the basis of a preparative method of synthesis of trichloromethanesulfonic acid chloride.



Chlorine in an aqueous medium,[266] chlorine in acetic acid,[267] nitric acid,[268] and hydrogen peroxide[269] are used as oxidants. The same oxidants are employed in the synthesis of trifluoromethanesulfonic acid chloride[270] from trifluoromethanesulfenyl chloride. It has been noted[271] that the hydrolysis of trithiane in dilute acetic acid, which results in the formation of chloromethanesulfonic acid chloride, proceeds via an intermediate stage involving the formation of chloromethanesulfenyl chloride.



* * *

It is seen from the present review that the use of sulfenyl chlorides in fine organic synthesis, which has reached a large scale in recent years, is based on the characteristic features of their reactivity and in the first place on the high lability of the S–Cl bond, as a result of which sulfenyl chlorides are widely employed in reactions with diverse reagents in order to generate the S–C, S–N, S–O, S–S, S–P, S=O, S=N, etc. bonds. The ease of addition of sulfenyl chlorides to the C=C bond of unsaturated compounds with formation of β-chloroalkyl sulfides is likewise widely used in fine organic synthesis for the introduction of the β-arylthioalkyl groups into the molecules of various organic compounds. A feature of the reactivity of bifunctional sulfenyl chlorides which is of very great synthetic importance is their tendency to form heterocycles on interaction with various polyfunctional compounds, which has also been reflected in the present review.

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