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S-Cationoid reagents in organic synthesis

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Abstract. The review is devoted to the methods of preparation, properties, and applications in organic synthesis of compounds of divalent, tetravalent, and hexavalent sulfur which may bear a positive charge on the sulfur atom, such as sulfenium, sulfonium, and sulfoxonium (oxosulfonium) reagents. The bibliography includes 178 references.

I. Introduction

During the last 10 – 15 years, the development of the chemistry of organic compounds of sulfur has been characterised by the extensive application of S-cationoid reagents, which play the extremely important role of active intermediates in many synthetic reactions, such as, for example, the selective oxidation of alcohols, the transfer of various functional groups, the introduction of a carbon – carbon double bond, the generation of radical-cations, ylides, etc. Such intermediates play an extremely important role in biological methylation processes occurring in living organisms[1,2] and also in processes involving the cleavage of peptides at the methionine units.

The majority of the S-cationoid reagents are unstable under the usual conditions, so that they are generated and employed as a rule in situ during the chemical reaction. Of the S-cationoid intermediates known at the present time, sulfonium salts have been the most thoroughly investigated. Convenient preparative methods of synthesis of the latter have been developed, their physicochemical properties have been investigated comprehensively, and their synthetic applications have been discovered. Some of the sulfonium salts, for example dimethylbromosulfonium bromide, dimethylchlorosulfonium chloride, dimethyl(*N*-succinyl)sulfonium chloride, etc., have entered the reference literature on preparative organic chemistry as important reagents for organic synthesis.

The interest manifested in sulfonium salts induced at the relevant time the appearance of a series of review publications,[1-3] which fully reflected the state of the chemistry of sulfonium salts during that period, but by now many new S-cationoid reagents have appeared and will be considered in the present review (the literature up to 1993 inclusive is considered).

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II. Cationoid sulfenium reagents

The cationoid sulfenium reagents include complexes having the general formula RS^+Y^-, in which the sulfenium cation RS^+ (R = Alk, Ar) is stabilised by an anionoid species Y^- of the type BF_4^-,[4-9] $SbCl_6^-$,[10] ClO_4^-,[11-13] etc.

$$RSX + MY \longrightarrow RS^+Y^- + MX$$

R = Me, Ph; X = Cl, Br; M = Ag, Li;

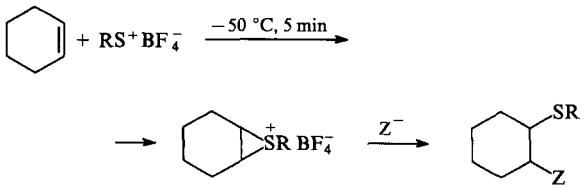
Y = BF_4, ClO_4, $SbCl_6$.

According to Cappozzi et al.,[14] the problem of the structure of these complexes still remains unsolved. In connection with the relatively low stability of cationoid sulfenium reagents, they are generated in situ in inert organic solvents (methylene chloride, nitromethane, dichloroethane) at low temperatures (−50 to −20 °C). Their synthesis is based on an exchange reaction.

The resulting solutions of cationoid sulfenium reagents are relatively stable in the temperature range indicated and are used in the synthesis of polyfunctional sulfides. These syntheses are based on the electrophilic addition of cationoid sulfenium reagents to alkenes and the subsequent interaction of the intermediate episulfonium cations with nucleophiles introduced into the reaction medium in the last stage.[4,5]

The use of cationoid sulfenium reagents in reactions with alkenes makes it possible to carry out the electrophilic addition in two stages, the stages involving the addition of the electrophile RS^+ and the nucleophile Z^- being separated in time and independent of one another (Scheme 1).

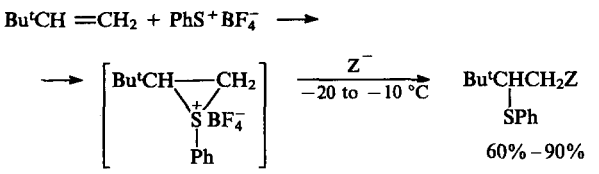
Scheme 1



R = Me, Ph; Z = OH, MeO, Cl, Br, OAc, $(EtCO_2)_2CH$, AcNH.

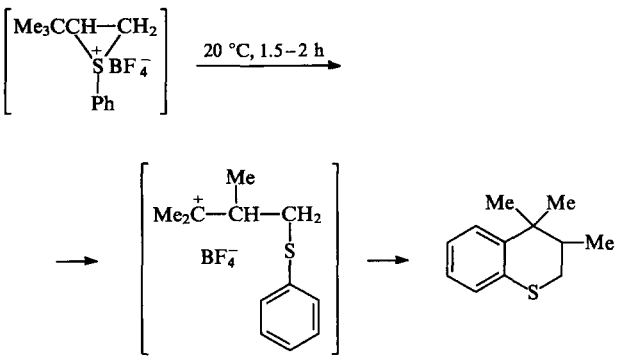
It is noteworthy that, in the addition of cationoid sulfenium reagents to alkenes with a branched structure, it is possible to direct the addition reaction towards the formation of products with a rearranged skeleton. For example, the episulfonium ion formed in the reaction of *tert*-butylethene with the complex

$PhS^+BF_4^-$ reacts at −20 to −10 °C with nucleophiles, affording polyfunctional sulfides in 60%–90% yields.[4]

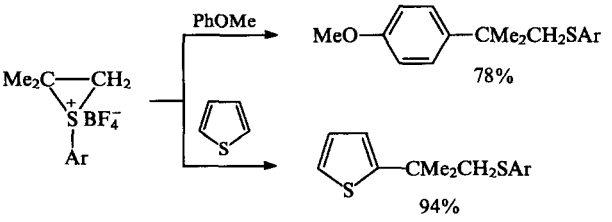


Z = OH, OMe, $MeCO_2$, H, $(EtCO_2)_2CH$, NEt_2.

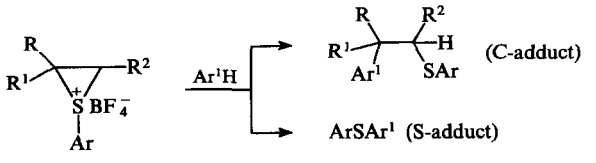
However, if the solution of the episulfonium complex obtained at −20 °C is maintained at 20 °C for 1.5–2 h, the main reaction product is 3,4,4-trimethylthiochroman regardless of the nature of the nucleophile Z,[4] which is due to the rearrangement of the episulfonium complex at the higher temperature to an intermediate carbonium ion, which in fact participates in the alkylation reaction.



It has been shown[9,15] that the stable *S*-arylepisulfonium complexes are capable of reacting not only with active nucleophiles but also with aromatic π-donors, which greatly expanded the limits of the applicability of the cationoid sulfenyl reagents in the synthesis of polyfunctional sulfides. For example, the interaction of episulfonium complexes with certain aromatic and heterocyclic compounds takes place in the absence of catalysts under mild conditions (−20 to 0 °C) in accordance with the general mechanism of the Friedel–Crafts reaction and leads to the formation of aryl(heteroaryl)-substituted sulfides.[15]

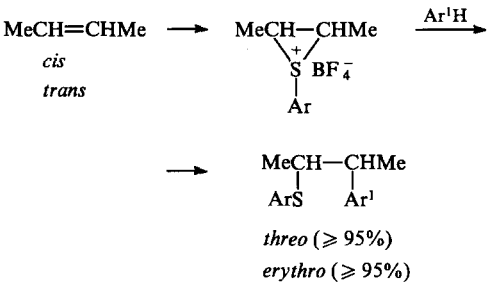


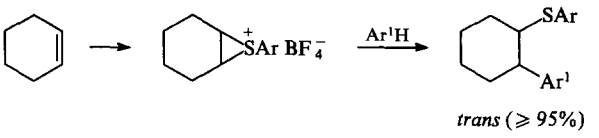
However, one should note that the reactions of the episulfonium complexes with aromatic compounds do not take place unambiguously, especially in the case of nonactivated aromatic compounds. This is due to the ambident nature of the episulfonium cation, which may react with the aromatic π-donor with participation of both a carbon atom (to form C-adducts) and the sulfur atom (to form S-adducts).[15]



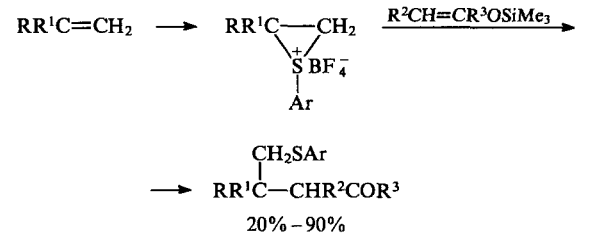
R, R^1, R^2 = H, Alk.

This disadvantage may be eliminated to some extent by varying the nature of the substituent at the sulfur atom. Thus in the reaction of the *S*-mesitylepisulfonium complex with aromatic compounds, the yield of the S-adduct does not exceed 5%–10%.[9] In the interaction of asymmetric episulfonium complexes with aromatic compounds, adducts of the Markovnikov type are formed exclusively, while in the case of the episulfonium complexes obtained from *cis*- or *trans*-but-2-ene and cyclohexene the stereochemistry of the products corresponds to the stereospecific anti-opening of the episulfonium ring by the aromatic π-donor, which indicates, according to Ibragimov and coworkers,[15,16] that the reaction proceeds via the intermediate formation of a bridged carbenium ion and not an open-chain β-arylthiocarbenium ion.



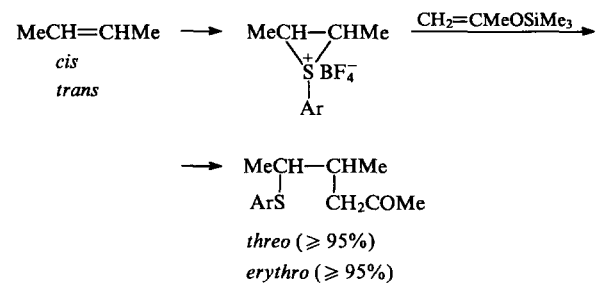


The trimethylsilyl ethers of enols proved to be active π-donors in reactions with episulfonium complexes. It has been shown[9,16] that the episulfonium complexes interact with such ethers even at −30 °C (1–2 h), affording γ-carbonyl-substituted sulfides, the structure of which corresponds to the Markovnikov and *trans*-stereospecific opening of the episulfonium ring by the nucleophile.

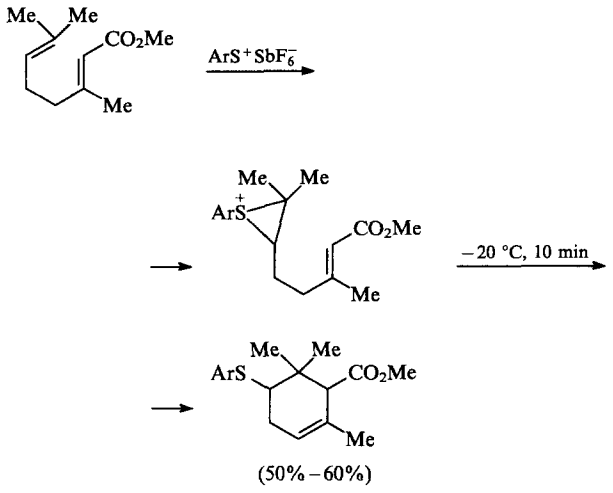


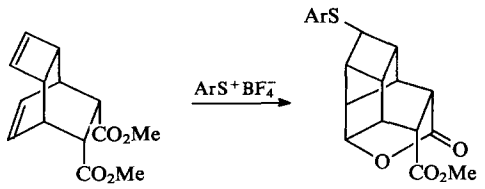
R = Me, Ph, H; R^1 = H, Me; R^2 = H; R^3 = Ph;

$R^2+R^3 = -(CH_2)_4-$.

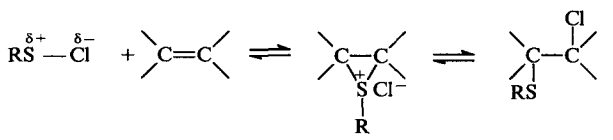


In the interaction of cationoid sulfenium reagents with dienes, the intermediate episulfonium cation may react with the π-electron system of the second double bond, giving rise to cyclic products.[9]

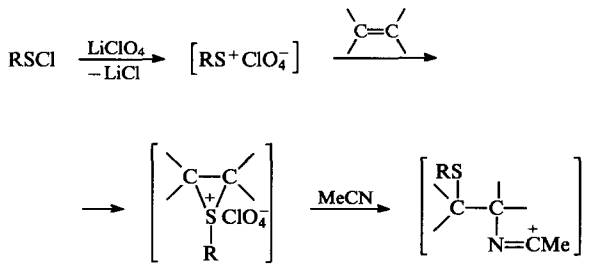




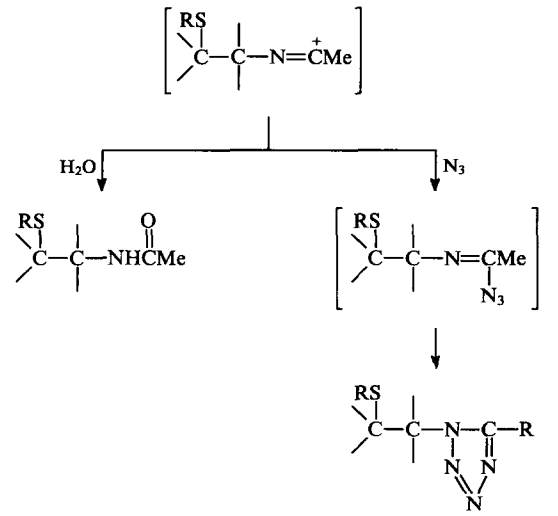
It is known[1] that the addition of sulfenyl chlorides to alkenes proceeds in accordance with the Ad_E2 mechanism, in which the cationic intermediate is the episulfonium cation—a weak electrophile which does not react with weak nucleophiles.



The method of the coupled addition of sulfenyl chloride to alkenes in the presence of a strong electrophile, for example lithium perchlorate, developed by Zefirov and coworkers,[11–13] is therefore of special interest. In this case, the sulfenyl chloride reacts even with acetonitrile, which is a weak nucleophile.



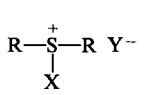
The immonium ion formed under these conditions is converted into the final products on treatment with various reagents.



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

III. Sulfonium reagents

A characteristic feature of divalent sulfur compounds, for example sulfides, is their ability to react with electrophiles, which is due to the presence of a free electron pair at the sulfur atom by virtue of which the atom can participate in the formation of a third covalent bond. The positive charge arising at the sulfur atom is as a rule stabilised by the negative charge of the anion. The compounds formed under these conditions have the general name of sulfonium salts and are divided into several types depending on the nature of the groups surrounding the sulfonium centre: trialkyl(aryl)sulfonium, halosulfonium, aminosulfonium, alkoxysulfonium, aryloxysulfonium, acyloxysulfonium, alkyl(aryl)thiosulfonium salts, etc.



R = Alk, Ar; Y = Cl, Br, BF_4, ClO_4 etc.;

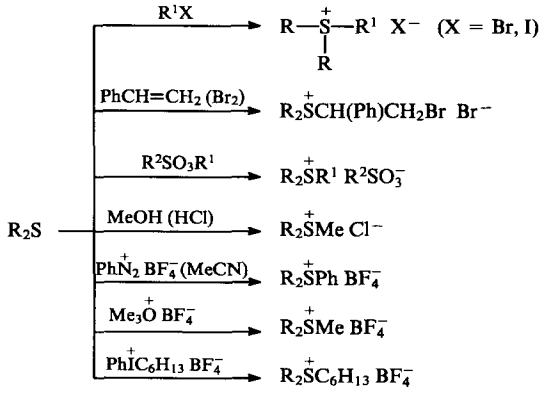
X = Alk, Ar, Cl, Br, I, F, OAc, NR'_2, OR', SR' (R' = Alk, Ar).

1. Trialkyl(aryl)sulfonium salts

a. Methods of synthesis of trialkyl(aryl)sulfonium salts

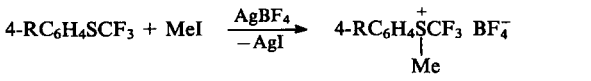
Preparation from sulfides. The alkylation (arylation) of sulfides by aryl halides,[12,17–19] alkenes,[2,20] sulfonic acid esters,[21,22] alcohols,[23] and diazonium,[2] oxonium,[2] and iodonium[24] salts is very frequently used to obtain trialkyl(aryl)sulfonium salts (Scheme 2).

Scheme 2



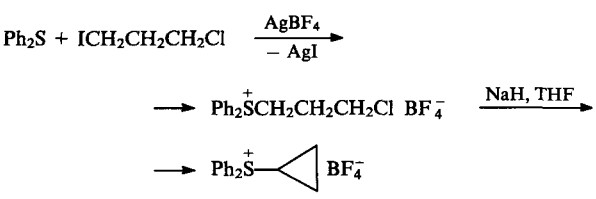
Dialkyl sulfides react with alkyl halides relatively easily, whereas diarylsulfides, as well as sulfides containing strongly electron-accepting groups at the sulfur atom, are alkylated by alkyl halides only in the presence of catalysts ($FeCl_3$, $AgBF_4$, etc.). For example, despite the reduced nucleophilicity of the sulfur atom in aryl trifluoromethyl sulfides, the latter were methylated by methyl iodide in methylene chloride in the presence of $AgBF_4$ (Scheme 3).[25,26]

Scheme 3

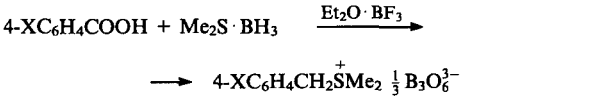


R = H, Me, Cl, NO_2.

The same catalyst has been used in the synthesis of cyclopropyldiphenylsulfonium tetrafluoroborate.[27,28]

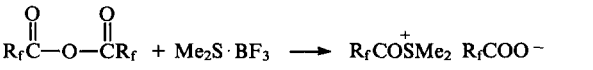


In the synthesis of trialkyl(aryl)sulfonium salts, the complexes of sulfides with BH_3 and BF_3 as well as various systems based on sulfides are used instead of the sulfides themselves. The reduction of aromatic carboxylic acids by the borane–dimethyl sulfide complex has been described.[29] The reduction products then react with dimethyl sulfide in the presence of boron trifluoride etherate to form the corresponding sulfonium salts.

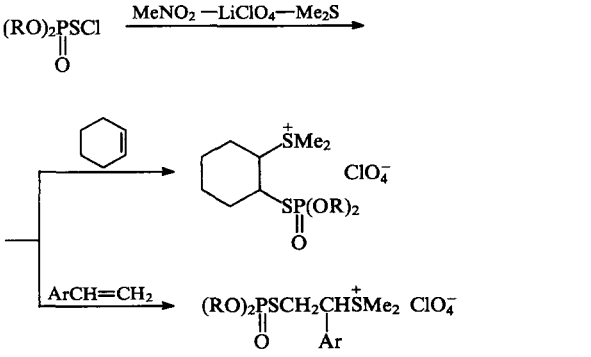


X = MeO, HO, H_2N.

The complex between Me_2S and BF_3 reacts relatively easily with the anhydrides of perfluorocarboxylic acids to form the corresponding sulfonium salts.[30]

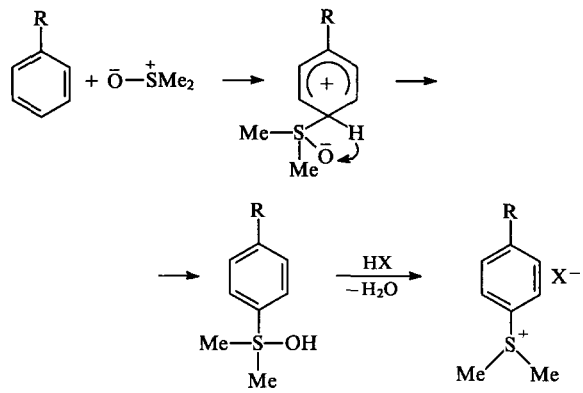


It has been shown[31] that the addition of dialkoxyphosphonylsulfenyl chlorides to ethene hydrocarbons in the presence of the $MeNO_2$–$LiClO_4$–Me_2S system leads to sulfonium salts containing dialkoxythiophosphonyl groups.



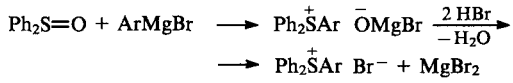
R = Me, Pr^i; Ar = Ph, 4-$MeOC_6H_4$.

Preparation from sulfoxides. By virtue of the presence of the electron-deficient sulfur atom, dialkyl sulfoxides react as electrophiles with an aromatic ring activated by electron-donating groups (OH, OR, etc.), forming dialkylarylsulfonium salts.[1] The reaction is catalysed by a strong inorganic acid (HCl, H_2SO_4, etc.).



R = OH, OR; X = Cl, HSO_4.

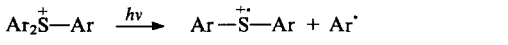
Triarylsulfonium salts are formed in the reaction of diphenyl sulfoxides with arylmagnesium bromides.[1,2]



It has been noted[32] that, in the interaction of dimethyl sulfoxides with 5-R-6-methyl-2,4-diphenyl-3-azapyrylium perchlorate in acetic anhydride, the product is a sulfonium salt, which is converted on heating in alcohol into the salt $PhCH_2NHC(Ph)=C(R)COCH_2S^+Me_2\ ClO_4^-$.

b. Applications of trialkyl(aryl)sulfonium salts in organic synthesis.

Generation of sulfonium radical-cations. One of the characteristic features of trialkyl(aryl)sulfonium salts is their photolytic instability. On irradiation with UV light at a certain wavelength, they are cleaved, affording a mixture of products. The primary step in the photolytic process is the homolysis of one of the three C–S bonds with formation of sulfonium radical-cations, which give rise to secondary photolysis products on interaction with the solvent or solutes. For example, on pulsed laser irradiation, the photolytic cleavage of triarylsulfonium salts begins with the homolysis of the Ar–S bond.[33]



The diarylsulfonium radical-cations formed in this process are initiators of the polymerisation of alkenes.[33]

On irradiation of the sulfonium salt $(4\text{-}Bu^tOCOOC_6H_4)_3S^+.CF_3SO_3^-$ with light at wavelengths of 254 and 266 nm in acetonitrile or dimethylformamide (DMF), the sulfonium radical-cation $(4\text{-}Bu^tOCOOC_6H_4)_2S^{\bullet+}$ and trifluoromethanesulfonic acid are formed as the primary reaction products. Their further reactions lead to the sulfide $(4\text{-}HOC_6H_4)_2S$ and the sulfonium ions $(4\text{-}Bu^tOCOOC_6H_4)_2S^+(C_6H_4OH\text{-}4)$, $(4\text{-}HOC_6H_4)_3S^+$, and $(4\text{-}HOC_6H_4)_2S^+(C_6H_4OOCOBu^t\text{-}4)$.[34]

The photolysis of the isomeric sulfonium salts $RMeS^+PhSbF_6^-$ (R = 1-, 2-, 9-$C_{14}H_9$), which proceeds on UV irradiation at wavelengths in the range from 260 to 400 nm, has been described.[35] The primary step in the photolysis is the homolysis of the Me–S bond accompanied by the formation of the sulfonium radical-cation $PhRS^{\bullet+}$, the interaction of which with the solvent leads to acid products.

Generation of sulfonium ylides. The deprotonation of trialkylsulfonium salts by a base B is one of the commonest methods for the generation of sulfonium ylides.[36]

$$Me_3S^+ + B \rightleftharpoons Me_2\overset{+}{S}-\bar{C}H_2 + BH^+$$

The mobility of the proton in the alkyl group of the sulfonium salt depends on many factors and in the first place on its acidity, the nature of the solvent, and also on the presence of other substances in the solution. Various combinations of bases and solvents, such as aqueous solutions of NaOH or KOH in the presence of tetraalkylammonium halides,[36,37] KOH in dimethyl sulfoxide (DMSO),[28,30] sodium hydride in tetrahydrofuran (THF)[28] or in DMSO,[36] *tert*-butyllithium in THF,[38] potassium *tert*-butoxide in THF,[2,28] and sodium dimethyl sulfoxide in DMSO or THF [36,39] are used to increase the mobility. In the presence of strongly electron-accepting groups in the α-position in the alkylsulfonium salt, the ylide may be formed even on treatment with organic bases, such as, for example, 1,5-diazabicyclo[5.4.0]undec-5-ene.[40]

In the preparation of an ylide from triarylsulfonium salts, one aryl group is replaced by an alkyl group (for example, the butyl group) with its subsequent deprotonation.[36]

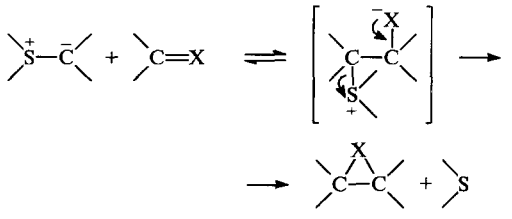
$$Ph_3S^+BF_4^- + BuLi \xrightarrow[-PhLi]{THF} Ph_2\overset{+}{S}Bu\ BF_4^- \longrightarrow Ph_2\overset{+}{S}-\bar{C}HPr$$

Sulfonium ylides are also obtained by adding nucleophiles to vinylsulfonium salts.[2]

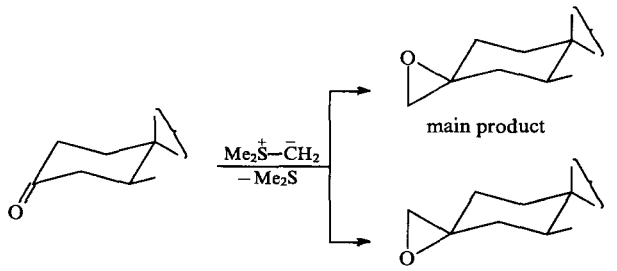
$$R_2\overset{+}{S}-CH=CR^1_2 + \bar{N}u \rightleftharpoons R_2\overset{+}{S}-\underset{\displaystyle Nu}{\underset{|}{\bar{C}H}}CR^1_2$$

When R = Me and R^1 = H, the methylation of the nucleophile via an S_N2 reaction competes with the addition reaction.

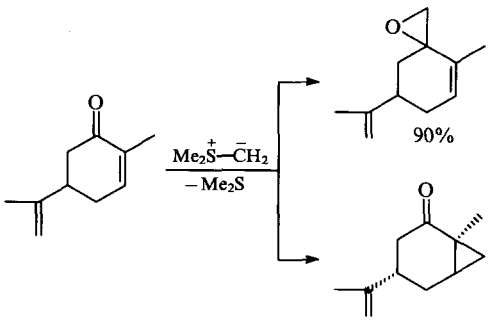
The high nucleophilicity of the carbon atom in the ylide group and also the tendency of the sulfonium centre to be converted into the readily eliminated sulfide group, are responsible for the principal application of sulfonium ylides in organic synthesis, namely the transfer of alkylidene groups to an electrophilic double bond via the intermediate formation of a betaine, which cyclises via direct substitution at the carbon atom.[2,41]



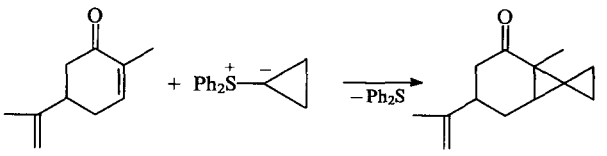
Depending on the structure of the ylide and the alkene, their addition to one another may lead to the formation of diastereoisomeric or structurally isomeric betaines. The cyclisation of such betaines gives various combinations of products. For example, the interaction of dimethylsulfonium methylide with cholestan-3-one leads to two isomeric products, with the isomer having an axial disposition of the epoxide substituent predominating.[2]



The addition of dimethylsulfonium methylide to carvone leads to two different products, with the epoxide predominating.[2]

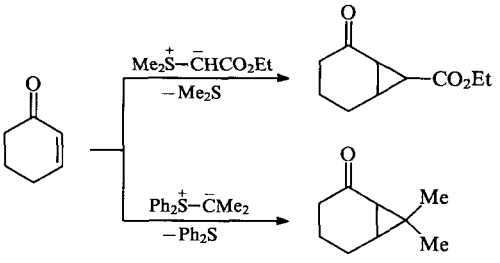


On the other hand, the addition of the diphenylsulfonium cyclopropylide to carvone takes place at the C=C bond with formation of one product.

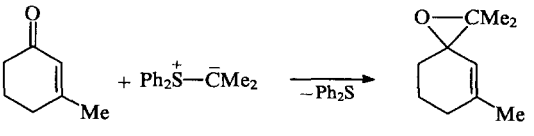


The addition of dimethylsulfonium ethoxycarbonylmethylide and diphenylsulfonium dimethylmethylide to cyclohexen-2-one also takes place at the C=C bond[2] (Scheme 4).

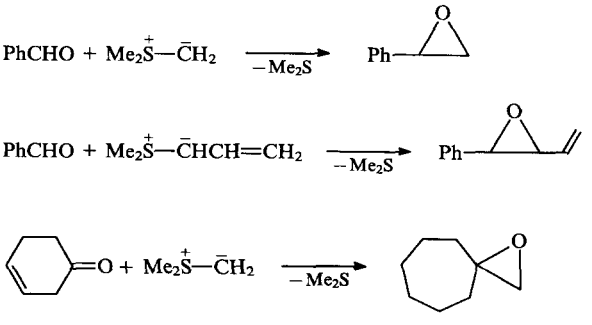
Scheme 4

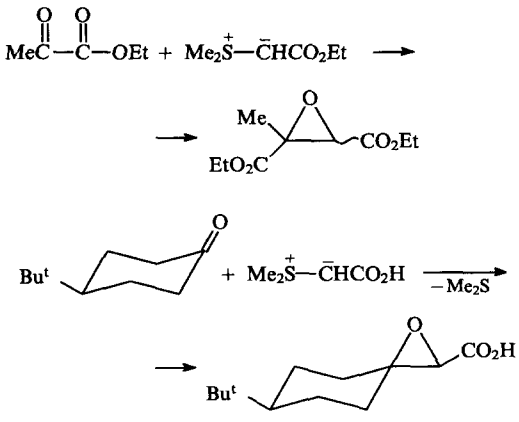


The introduction of an alkyl group in the 3-position in cyclohex-2-enone alters the mode of addition.[2]

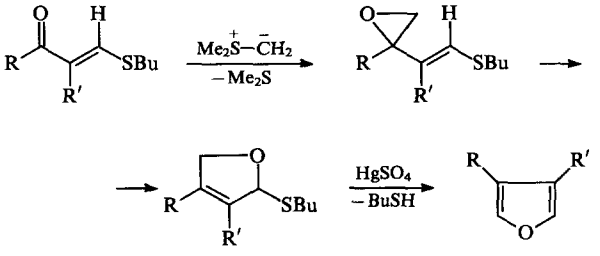


As a result of the diversity and ready availability of aldehydes and ketones, their condensation with sulfur ylides has become the most important synthetic method for the preparation of oxiranes with a wide variety of structures.[2,36,42,43]



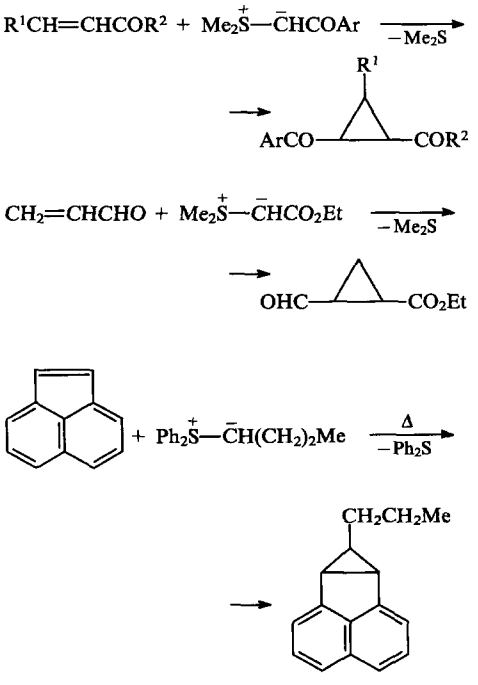


In the presence of a mobile hydrogen atom in the substrate molecule, the oxirane ring formed may be opened with subsequent formation of a five-membered ring, which is used in the synthesis of furans from dimethylsulfonium methylide and unsaturated ketones.[28]



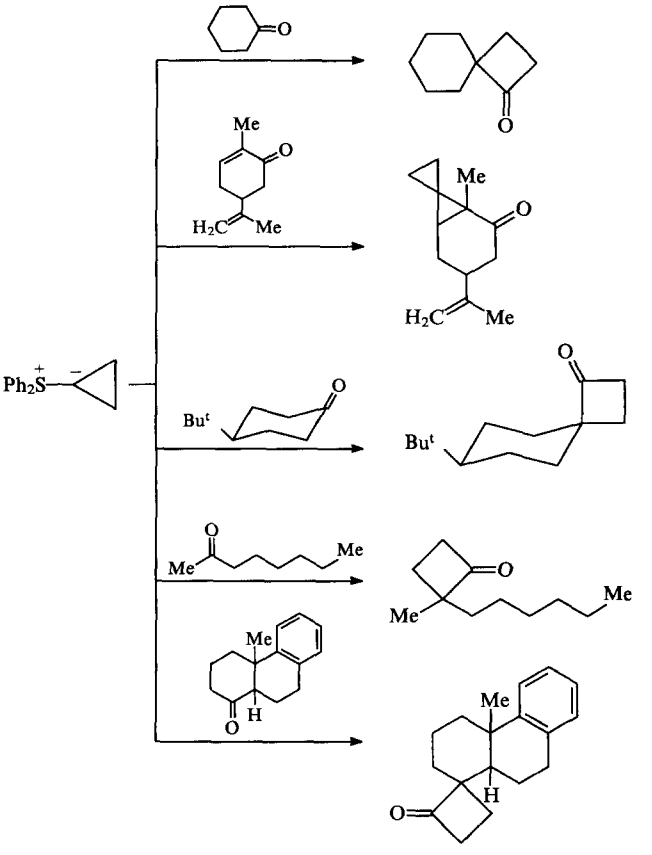
The availability of unsaturated compounds with a wide variety of structures makes it possible to employ the ylides for the synthesis of cyclopropanes (Scheme 5).

Scheme 5

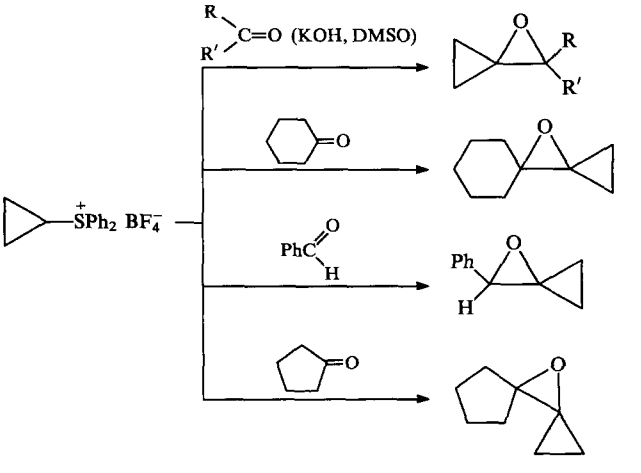


It has been suggested[44] that the biosynthesis of the cyclopropane ring in many natural products proceeds via the copper-catalysed transfer of the methylene group from the sulfonium methylide formed from *S*-adenosylmethionine.

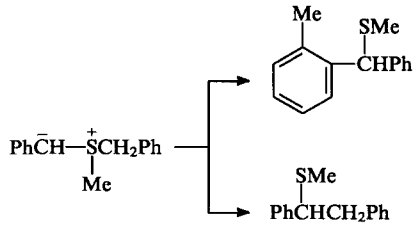
Diphenylsulfonium cyclopropylide, formed when cyclopropyldiphenylsulfonium tetrafluoroborate is treated with sodium dimethyl sulfoxide in THF, is widely used in the transfer of the cyclopropylidene group in preparative organic chemistry.[28] The interaction of this reagent with aldehydes and ketones and also with α,β-unsaturated ketones affords spirocycloalkanones and cyclic ketones.[27,28,44,45]



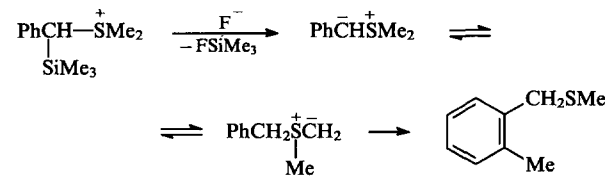
Oxaspiropentanes are intermediates in some of these reactions. They have been isolated by treating the carbonyl compounds with cyclopropyldiphenylsulfonium tetrafluoroborate.[46,47]



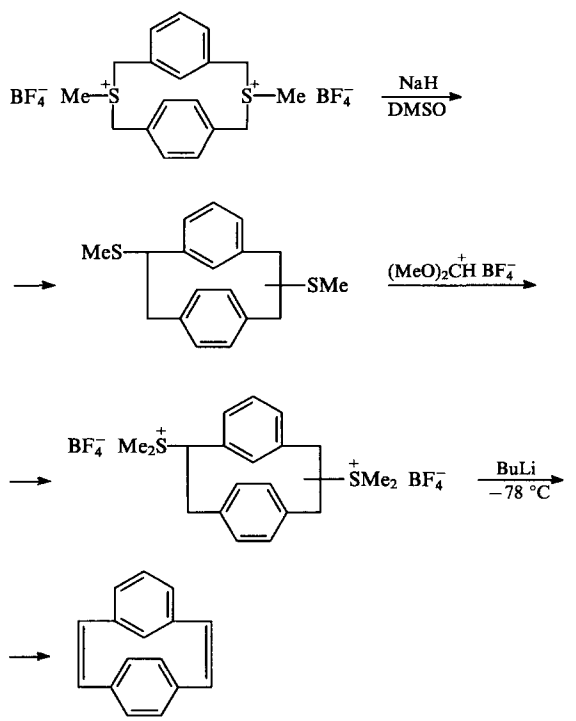
The tendency of sulfonium ylides to undergo rearrangements is frequently employed in the syntheses of various sulfides. For example, in the presence of strong bases, benzylsulfonium ylides undergo the [2,3]-sigmatropic rearrangement and also 1,2-shift rearrangements with formation of the corresponding sulfides.[2,15,48,49]



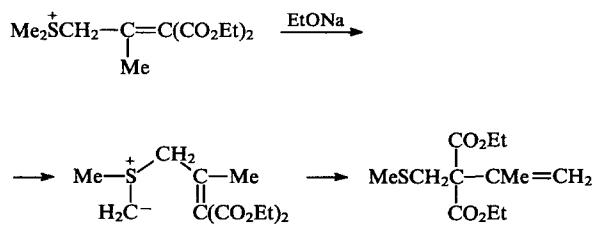
The [2,3]-sigmatropic rearrangement of the benzylsulfonium ylide, formed as a result of the desilylation of a α-trimethylsilylbenzylsulfonium salt by the fluoride anion, has been described.[50]

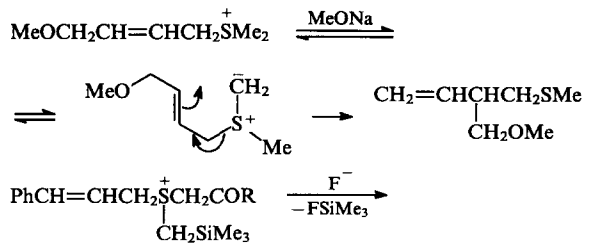


The 1,2-shift rearrangement of benzylsulfonium ylides constitutes the basis of the synthesis of cyclophanes.[36,51]

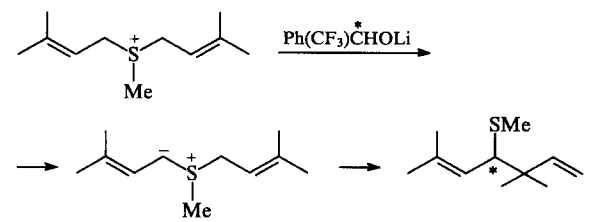


The [2,3]-sigmatropic rearrangements of allylsulfonium ylides, which take place on heating or on treatment with basic reagents, are used in the syntheses of but-3-enyl sulfides.[52-54]



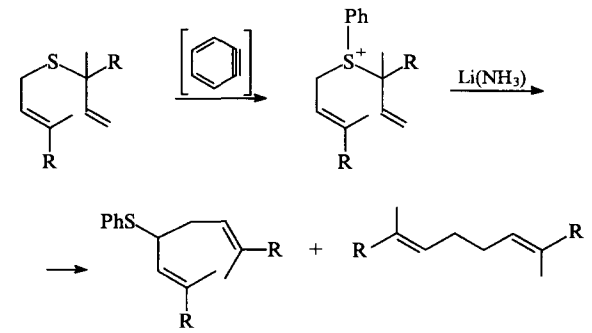


Thus the [2,3]-sigmatropic rearrangement of the sulfonium ylide generated from *S*-methyl-*S*,*S*-di(α,α-dimethylallyl)-sulfonium tetrafluoroborate in the presence of an optically active base led to an optically active sulfide.[54]



The synthesis of squalene has been achieved with the aid of the [2,3]-sigmatropic rearrangement of the corresponding allylsulfonium ylide (Scheme 6).[2]

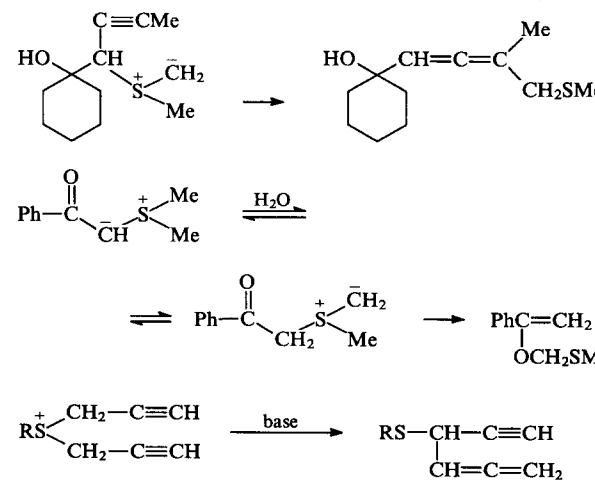
Scheme 6



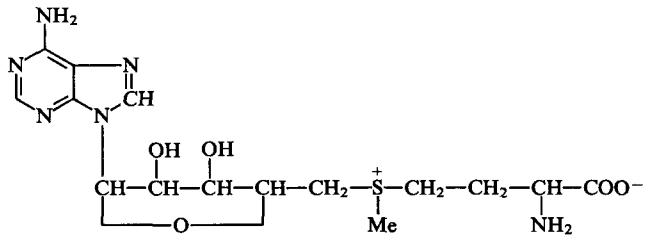
R = $Me_2C{=}CHCH_2CH_2C(Me){=}CHCH_2CH_2$.

Ylides and sulfonium salts containing triple bonds and heteroatoms can also participate in similar rearrangements (Scheme 7).[36,55]

Scheme 7



The transfer of alkyl and acyl groups. The high lability of the C–S bond in sulfonium salts makes possible their use as alkyl group transfer reagents, which has found application in biological methylation reactions[56] and in the biomimetic transalkylation of alkenes.[57] It has been suggested[1] that methylation in living organisms takes place with participation of the adenosylsulfonium salt of methionine.



The transfer of an alkyl groups to the sulfur atom of a thiolate anion[56,58,59] or sulfides[17,24,60] is used in the syntheses of asymmetric sulfides.

$$4\text{-}ClC_6H_4\overset{+}{S}(Me)\text{-}C_6H_4OMe\text{-}4\ SbF_6^- + 4\text{-}NO_2C_6H_4SNa \longrightarrow 4\text{-}NO_2C_6H_4SMe + 4\text{-}ClC_6H_4SC_6H_4OMe\text{-}4$$

$$Me_2\overset{+}{S}C_6H_{13}\ BF_4^- + Me_2S \longrightarrow MeSC_6H_{13} + Me_3\overset{+}{S}\ BF_4^-$$

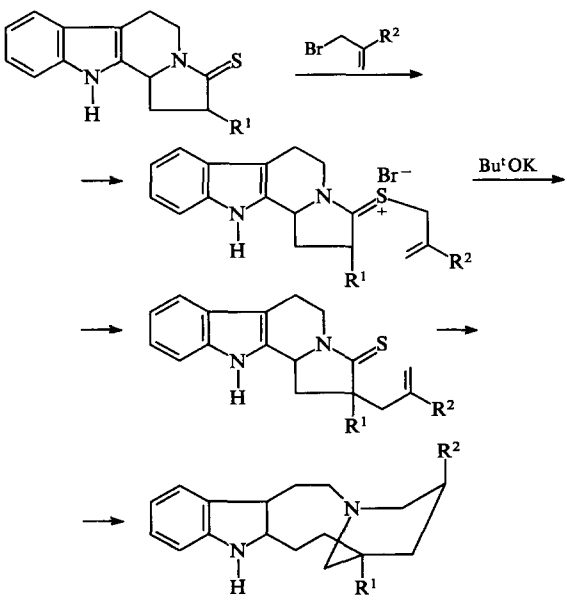
$$Me_2S + Me_2CHBr \longrightarrow Me_2\overset{+}{S}\text{—}CHMe_2\ Br^- \xrightarrow{Me_2S} Me_2CHSMe + Me_3\overset{+}{S}\ Br^-$$

$$Me_2S + Me_3SiCH_2\overset{+}{S}Me_2\ I^- \longrightarrow Me_3SiCH_2SMe + Me_3\overset{+}{S}\ I^-$$

An example of the intramolecular transfer of an alkyl group from the sulfonium centre to an oxygen atom is provided by the isomerisation of dialkylsulfonium salts containing the triphenylphosphonium group, which takes place at 190–230 °C under an argon atmosphere.[61] This leads to the preferential formation of the (*E*)-isomer of the corresponding α,β-disubstituted styryltriphenylphosphonium tetrafluoroborate.

$$Ph_3\overset{+}{P}\text{—}\underset{Ph\text{—}C\text{—}O^-}{\overset{\|}{C}}\text{—}\overset{+}{S}RR'\ BF_4^- \xrightarrow{190\text{–}230\ ^\circ C,\ argon} Ph_3\overset{+}{P}\text{—}\underset{Ph\text{—}C\text{—}OR'}{\overset{\|}{C}}\text{—}SR\ BF_4^-$$

The Claisen thio-rearrangement of sulfonium salts, used in the syntheses of certain alkaloids, is also of the type involving the intramolecular transfer of an alkylallyl group.[54]



It has been noted[62] that sulfonium salts containing a nitrogroup at a carbon atom adjoining the sulfonium centre are capable of being cleaved also in the presence of electrophiles. The cleavage then takes place at the S–C(NO_2) bond with transfer of the nitroalkyl fragment to the electrophilic part of the reagent.

$$R_2\overset{+}{S}\text{—}C(NO_2)_2Z\ A^- + \bar{Y}\text{—}\bar{X} \longrightarrow YC(NO_2)_2Z + R_2S\overset{+}{X}\ A^-$$

Y—X = Cl–Cl, Cl–N(COR)$_2$, Cl–SO_2Cl, Cl–RS.

Z = COR, H.

It has been shown[63–65] that the dimethylacylsulfonium salts $RCOS^+Me_2BF_4^-$ (R = Me, Bu^t, CF_3) act as acylating agents in reactions with alkenes, dienes, and ethynes, which is used in the synthesis of α,β-unsaturated ketones.

$$RCO\overset{+}{S}Me_2\ BF_4^- + CH_2{=}CHR' \xrightarrow[-HBF_4]{} RCOCH{=}CHR' + Me_2S$$

R = Me, Bu^t; R′ = Ph, CH_2=CMe.

Elimination of the sulfonium group. The sulfonium centre activates the β-hydrogen atoms in alkyl groups; the sulfonium group can also be the leaving nucleophile in elimination reactions. These factors have in fact determined the use of sulfonium salt in the syntheses of unsaturated compounds.[66]

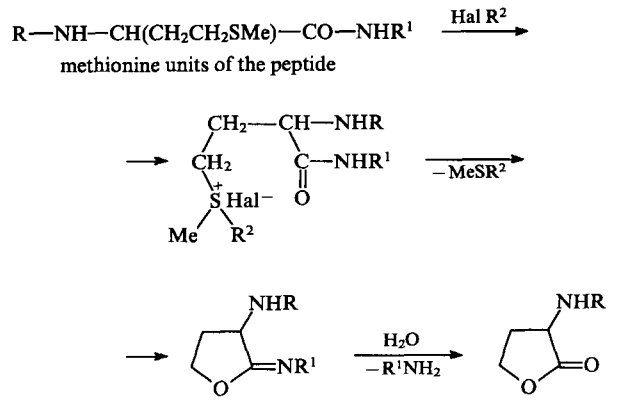
$$Me_2\overset{+}{S}\text{—}CH_2\text{—}\underset{H}{\overset{H\leftarrow:B}{C}}\text{—}R \xrightarrow[-BH]{} CH_2{=}CHR + Me_2S$$

The conversion of a sulfide functional group into a sulfonium group and the elimination of the latter are used as a method for the introduction of a carbon–carbon double bond, for example in the conversion of saturated ketones into α,β-unsaturated ketones.[66–68]

$$PhCH_2CH_2COMe \xrightarrow[LiNPr^i_2]{MeSSMe} PhCH_2\underset{SMe}{CHCOMe} \xrightarrow{CF_3SO_3CH_2CO_2Et} PhCH_2\underset{Me\text{—}\overset{+}{S}CH_2CO_2Et}{CHCOMe}\ CF_3SO_3^- \xrightarrow[-MeSCH_2CO_2Et]{base} PhCH{=}\underset{}{\overset{O}{\overset{\|}{C}}}CHMe$$

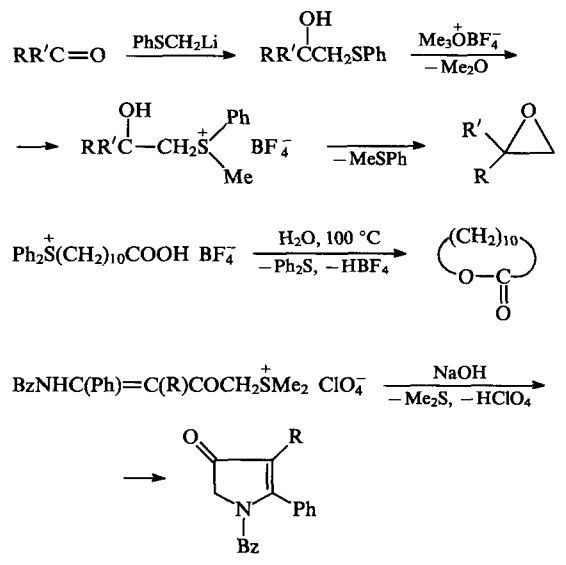
One of the methods for protecting the carboxyl group involves its conversion into an alkylthiomethyl ester group $-CO_2CH_2SR$, which is resistant to the action of weak alkalis and reductants. This is frequently employed in peptide and phosphatide syntheses.[66] In order to remove the alkylthiomethyl group, it is initially converted into a sulfonium group by treatment with methyl iodide and is then cleaved with a weak solution of alkali.

The intramolecular displacement of the sulfonium group by other nucleophilic groups with formation of cyclic products has come to be widely employed in organic synthesis. For example, a method has been developed for the specific cleavage of peptides in the methionine units, involving the intramolecular displacement of the sulfonium group by the oxygen atom of a neighbouring amide group.[66]

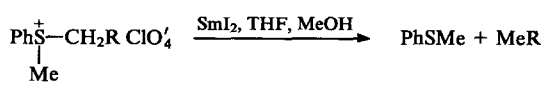


$HalR^2$ = BrCN, ICH_2CONH_2.

The intramolecular displacement of the sulfonium group is also used in the synthesis of oxiranes,[2] lactones,[68] and other heterocyclic compounds.[69]



The reduction of the sulfonium group by samarium diiodide in THF at 20 °C in the presence of 2 equiv. of methanol leads to the formation of the corresponding hydrocarbons and sulfides in quantitative yields.[70]

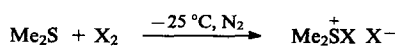


R = CN, 4-BrC_6H_4CO.

2. Halosulfonium salts

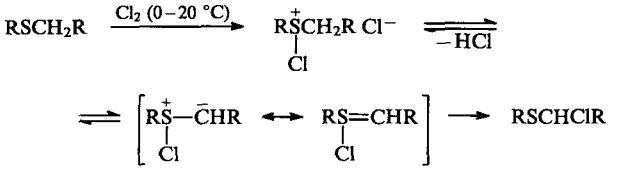
a. Methods for the generation of halosulfonium salts

Generation from sulfides. The interaction of sulfides with the halogens is one of the commonest methods for the generation of halosulfonium salts. The reaction is carried out at low temperatures (−50 to −25 °C) in anhydrous inert solvents (CCl_4, CH_2Cl_2, $CHCl_3$, etc.).[28,71,72]



X = Cl, Br

The solutions of the halosulfonium salts obtained may be stored in the dark without access of moisture for several weeks. At higher temperatures (0–20 °C), the halogenation of alkyl sulfides by the halogens leads to the formation of α-haloalkyl sulfides,[2,73] halosulfonium salts being formed as intermediates in this process.

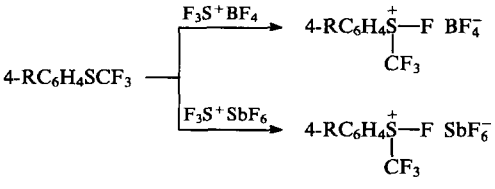


Apart from the halogens, *tert*-butyl hypochlorite,[74–78] sulfuryl chloride,[79] and sulfonic acid *N*-chloroamides[76,80,81] are also used as halogenating agents.

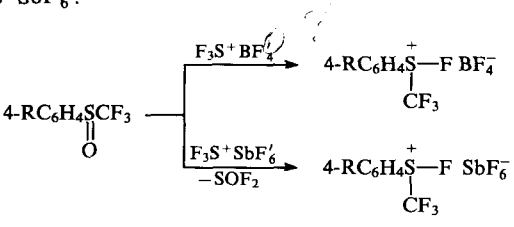


Z = BuO, SO_2Cl, $ArSO_2NH$.

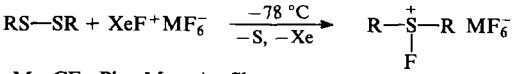
When aryl trifluoromethyl sulfides are treated with the complexes $F_3S^+BF_4^-$ and $F_3S^+SbF_6^-$, arylfluoro(trifluoromethyl)sulfonium salts are formed.[82]



Generation from sulfoxides. Arylfluoro(trifluoromethyl)-sulfonium salts are also formed when aryl trifluoromethyl sulfoxides are treated with the complexes $F_3S^+BF_4^-$ and $F_3S^+SbF_6^-$.[82]



Generation from disulfides. It has been noted[83] that, when disulfides interact with the complexes $FXe^+MF_6^-$ (M = As, Sb), the S–S and C–S bonds are cleaved with formation of fluorosulfonium salts.

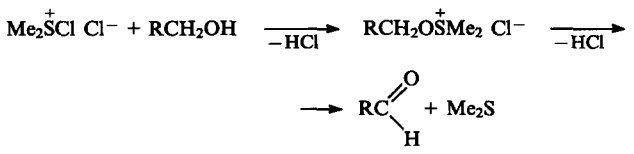


R = Me, CF_3, Ph; M = As, Sb.

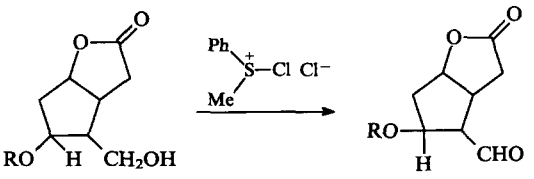
The interaction of the complex $FXe^+SbF_6^-$ with hydrogen sulfide at −78 °C leads to the formation of the fluorosulfonium salt $H_2S^+FSbF_6^-$.[83]

b. The use of halosulfonium salts in organic synthesis

Oxidation of alcohols. Chlorodimethylsulfonium chloride is widely used in organic synthesis as a mild oxidant which oxidises primary and secondary alcohols to carbonyl compounds.[28]

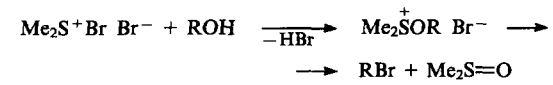


Chloro(methyl)phenylsulfonium chloride is used as a mild oxidant for the conversion of hydroxylactones into aldehydrolactones.[28]

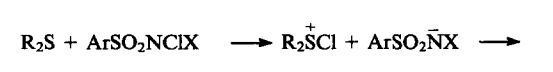


R = 4-PhC_6H_4CO.

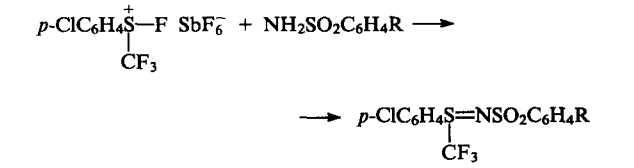
Preparation of alkyl bromides. Bromodimethylsulfonium bromide is widely used for the replacement of the OH group in an alcohol by bromine.[28] For this purpose, the sulfonium salt is treated with an excess of the alcohol for 4–5 h at 80 °C. The reaction takes place with inversion of the configuration.



Synthesis of sulfimides (sulfilimines). *N*-Arenesulfonylsulfimides[80,81,84–89] are obtained by the reaction of sulfimides with sulfonic acid *N*-chloroamides via the intermediate formation of the chlorosulfonium cation R_2S^+Cl and the sulfonamide anion $ArSO_2N^-X$ (X = H, Cl).



Arylfluoro(trifluoromethyl)sulfonium salts give rise relatively easily to *N*-arenesulfimides on interaction with sulfonic acid amides.[26,90]

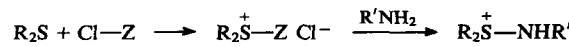


R = H, 4-Me.

3. Aminosulfonium salts

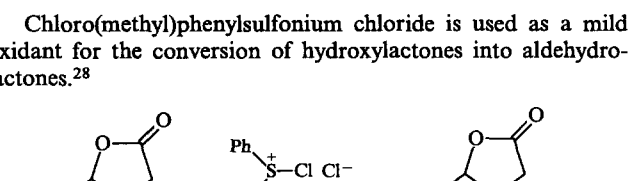
a. Methods for the generation of aminosulfonium salts

Generation from sulfides. Several variants of the generation of aminosulfonium salts from sulfides have been developed. According to one of them, the sulfides are converted into sulfonium salts by treatment with halogenating agents. The interaction of the sulfonium salts with amines leads to aminosulfonium salts.[80,91–98]

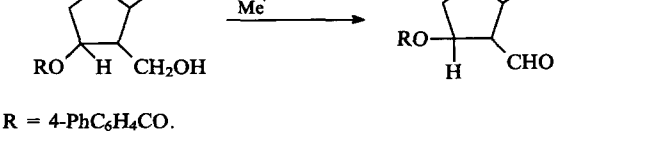


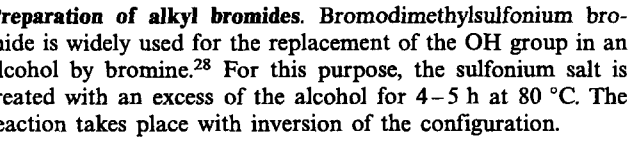
Z = Cl, Bu^{t}O, SO_2Cl, etc.

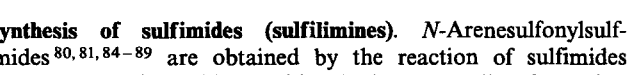
Another method is based on the reaction of sulfides with *N*-halo-compounds such as *N*-chloramine,[99] *N*-bromoacetamide,[100] *N*-chlorourethane,[100,101] *N*-chloramidines,[102] *N*-chloroguanidines,[102] *N*-chlorourea and its derivatives,[103,104] *N*-chlorosuccinimide,[28] *N*-chlorobenzotriazine,[105] and iminosulfonic acid *N*-chloroamides.[106]



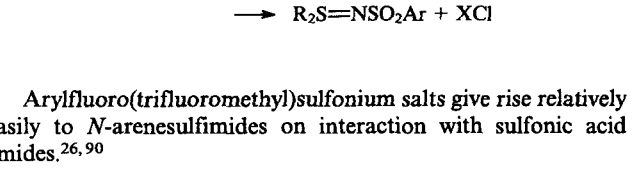
X = Cl, Br; Z = H, MeCO, EtOCO, PhC(=NH)–, $NH_2NHC(=O)$–, $NH_2C(=O)$–, NH_2–CH(OMe)–.



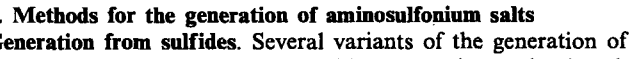




One of the modifications of these two variants for the generation of aminosulfonium salts involves the halogenation of sulfides in the presence of amines by halogenating agents such as *N*-chlorosuccinimide[107,108] and *tert*-butyl hypochlorite.[109]



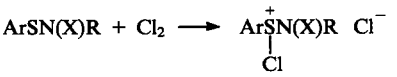
The third method for the generation of aminosulfonium salts from sulfides involves the interaction of the latter with certain derivatives of hydroxylamine, for example with hydroxyaminosulfonic acid,[80] *N*-arenesulfonyl-*O*-(*p*-nitrobenzenesulfonyl)-hydroxylamine,[80] *N*-ethoxycarbonyl-*O*-(*p*-nitrobenzenesulfonyl)hydroxylamine.[80] *O*-mesitylenesulfonylhydroxylamine,[110] and (+)-*O*-(α-bromocamphorsulfonyl)hydroxylamine.[111]



R = Alk; X = H, $ArSO_2$, EtOCO;

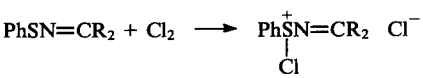
Y = HSO_3, 2,4,6-$Me_3C_6H_2SO_2$, 4-$NO_2C_6H_4SO_2$.

Generation from sulfenamides. The formation of aminosulfonium salts as intermediates in the reactions of sulfenamides with chlorine,[112–116] *N*-chloro- and *N*-dichloro-amides,[117–119] *N*-halosuccinimides,[120,121] *N*-chlorobenzotriazine,[122] and other halogenating agents has been noted.

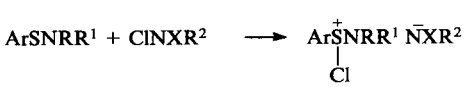


Ar = Ph, 4-MeC_6H_4, 2-$NO_2C_6H_4$, 4-$NO_2C_6H_4$;

R = Bu^t, $PhSO_2$; X = H, Na.

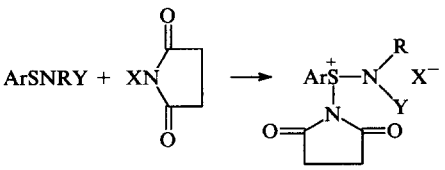


R = Ph, CF_3.



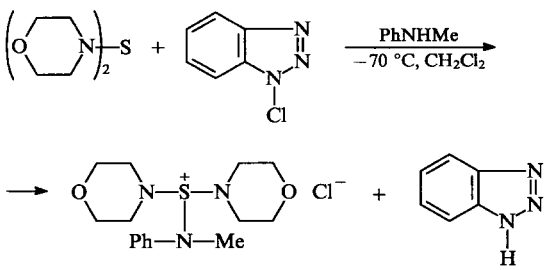
R = H, Alk; R^1 = Alk, Ar, $ArSO_2$;

X = H, Cl; R^2 = ArCO, $ArSO_2$.

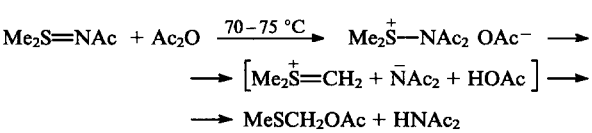


Ar = Ph, 2-$NO_2C_6H_4$;

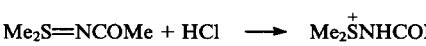
R = Me, $PhSO_2$; Y = Me, Na; X = Cl, Br.



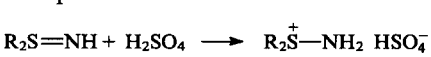
Generation from sulfimides. On heating in acetic anhydride, *N*-acyl-*S*,*S*-dimethylsulfimides enter into the Pummerer reaction, which proceeds via an intermediate stage involving the generation of aminosulfonium salts.[123]



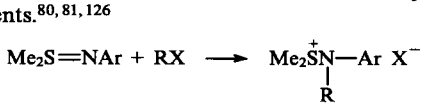
N-Acetyl-*S*,*S*-dimethylsulfimide is converted into an aminosulfonium salt on interaction with gaseous hydrogen chloride.[124]



Sulfimides unsubstituted at the nitrogen atom give rise to aminosulfonium salts on interaction with strong inorganic acids, for example with sulfuric acid.[125]



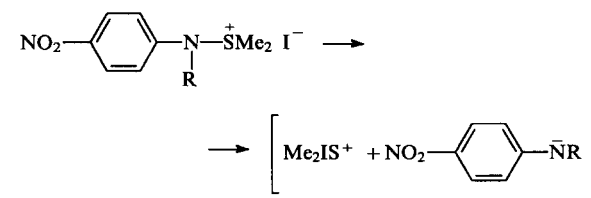
Unstable aminosulfonium salts have been obtained by the interaction of *N*-arenesulfilimides with alkylating or acylating agents.[80,81,126]



R = Me, X = Cl; R = EtOCO, X = Cl;

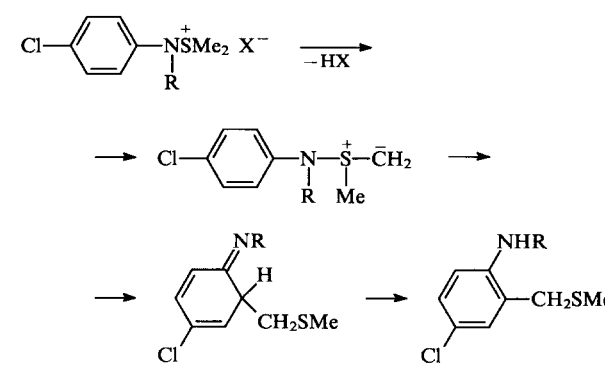
R = MeCO, X = MeOCO; Ar = *p*-$NO_2C_6H_4$, *p*-ClC_6H_4.

Further reactions of these salts are determined by the nature of the substituents in the benzene ring of the aryl group and by the basicity of X^-. In the case of strongly electron-accepting substituents (for example, NO_2) and highly basic X^-, X^- attacks the positively charged sulfur atom with subsequent dissociation of the S–N bond.



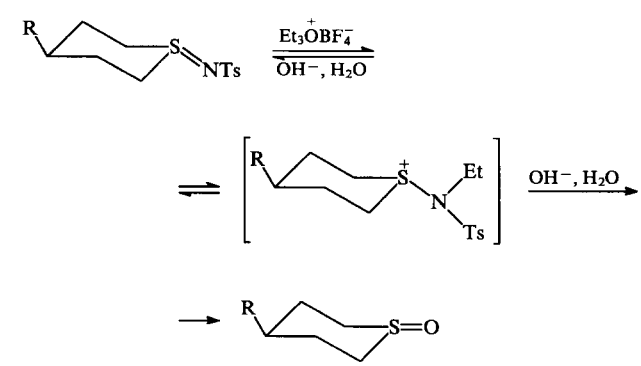
In the case of weakly electron-accepting or electron-donating substituents, the anion X^- abstracts a proton from the MeS group, giving rise to an intermediate ylide. The ylide then undergoes an intramolecular sigmatropic rearrangement, which leads to unstable cyclohexadiene derivatives and these are converted into the more stable benzene derivatives.

The replacement of one methyl group at the sulfur atom by the ethyl or propyl group does not alter the mode of abstraction of a proton — it is abstracted from the Me group as before, while on replacement of the methyl group by the benzyl group it is abstracted only from the latter, which is correlated with the decrease in acidity in the sequence $PhCH_2S$ > MeS > $AlkCH_2S$.



N-Arenesulfonylsulfimides give rise to aminosulfonium salts only on interaction with highly active acylating and alkylating agents such as oxonium salts,[80,81] methyl fluorosulfonate,[127] and complexes of carboxylic acid chlorides with $SbCl_5$.[127] The aminosulfonium salts formed in this case are relatively stable and undergo further reactions only on treatment with inorganic and organic bases (Scheme 8).

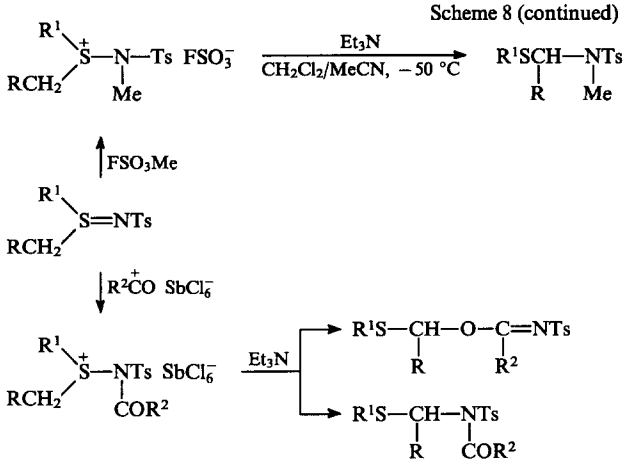
Scheme 8



R = Bu^t.

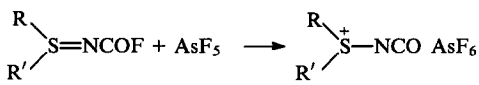
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Scheme 8 (continued)



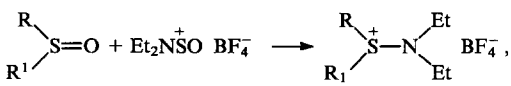
R = H, R^1 = R^2 = Me; R = H, R^1 = Me, R^2 = Et;
R = Ph, R^1 = Et, R^2 = Me;
R = H, R^1 = Me, R^2 = Ph; R = H, R^1 = Et, R^2 = Me.

It has been shown[128] that the reaction of fluorocarbonylsulfimide with arsenic pentafluoride proceeds with abstraction of a fluoride anion and the formation of an aminosulfonium salt.

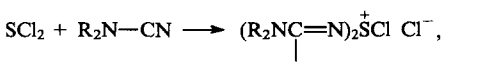


R = F; R′ = CF_3, NMe_2; R = CF_3; R′ = NMe_2.

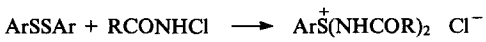
Other generation methods. Among other methods, mention should be made of the interaction of sulfoxides with *N*-sulfinyldialkylimmonium salts[129]



the reaction of sulfur dichloride with dialkylcyanamide[130]

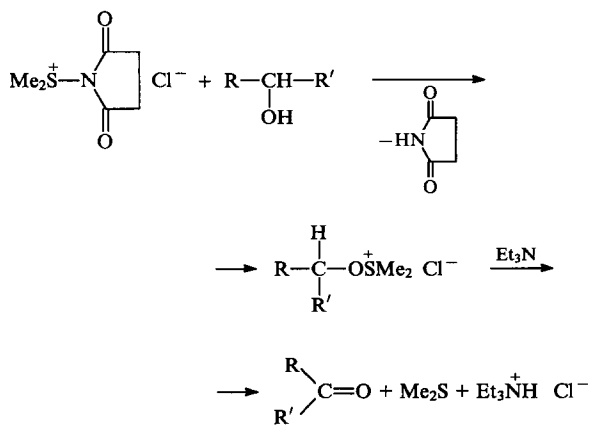


and the interaction of disulfides with carboxylic acid *N*-chloroamides;[131]

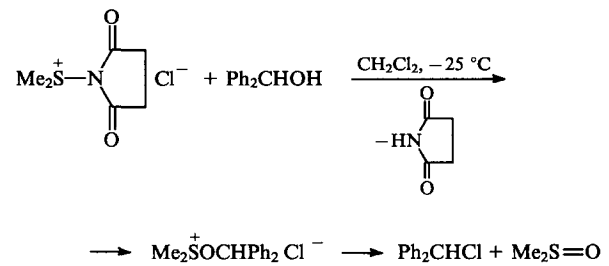


b. The use of aminosulfonium salts in organic synthesis

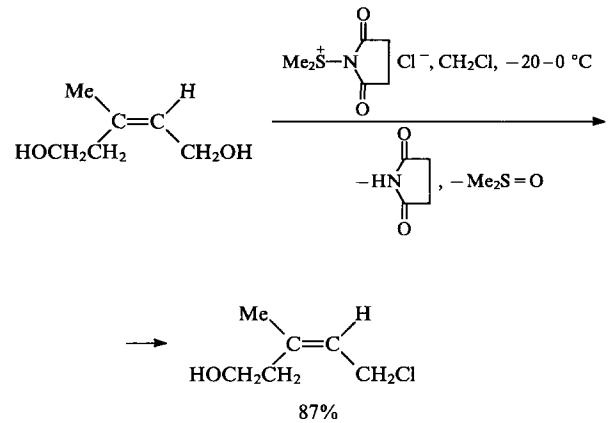
Dimethyl-*N*-succinylsulfonium chloride (the Corey–Kim reagent) has found extensive application in organic synthesis as a mild oxidant for alcohols,[28] which is superior in this respect to chlorodimethylsulfonium chloride.



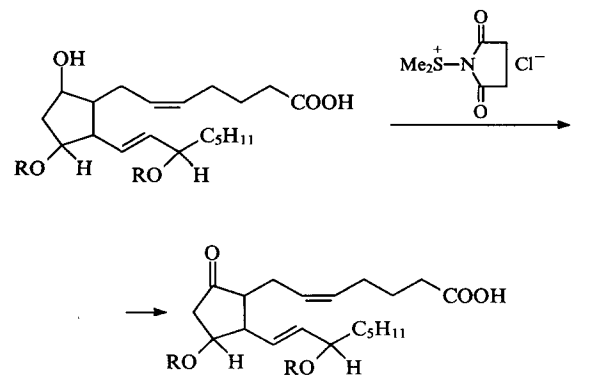
As an oxidant, the Corey–Kim reagent exhibits a high selectivity. For example, in contrast to primary and secondary aliphatic alcohols, allyl and benzyl alcohols are not oxidised by this reagent but are converted into the corresponding chlorides. In the case of diphenylmethanol, the yield of diphenylmethyl chloride reaches 95% in this reaction.[28]



Under the same conditions, cyclohex-1-en-3-ol is converted into 3-chlorocyclohexene in a yield exceeding 95%. The conversion of (*Z*)-3-methylpent-2-ene-1,5-diol into the allyl monochloride in 87% yield can also serve as a clear example of the selectivity of the Corey–Kim reagent.[28]

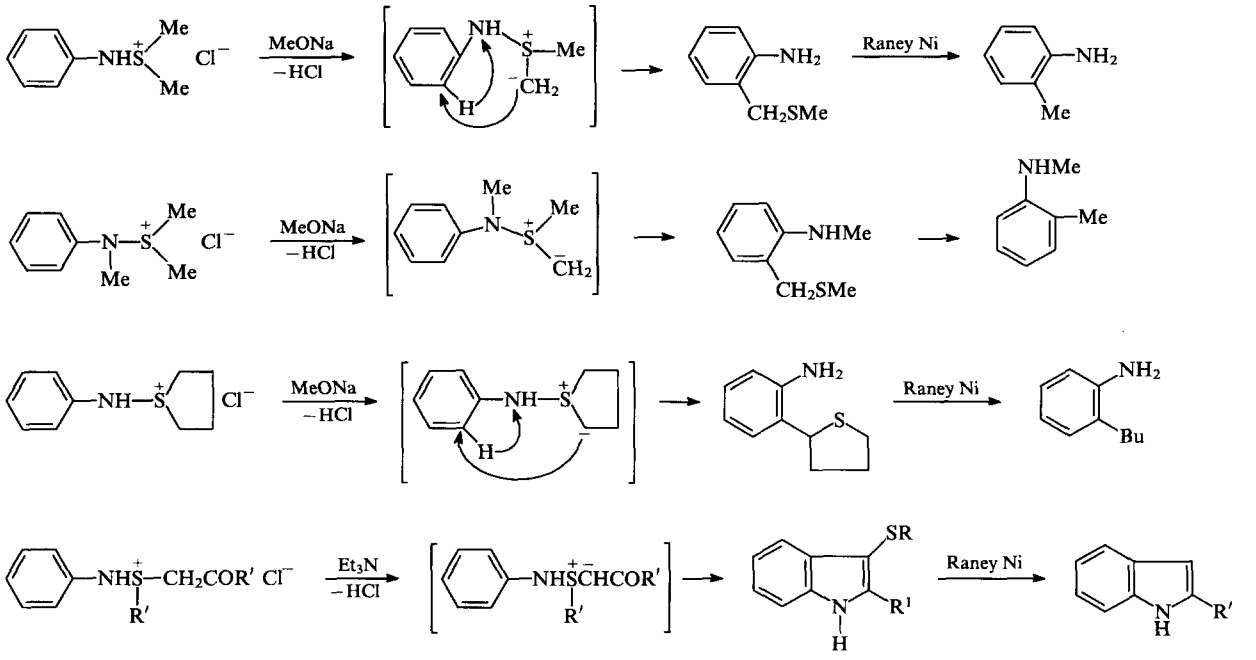


The Corey–Kim reagent is also used in an improved synthesis of prostaglandins for the conversion of a hydroxy-group into a keto-group in a yield exceeding 90%.[28]

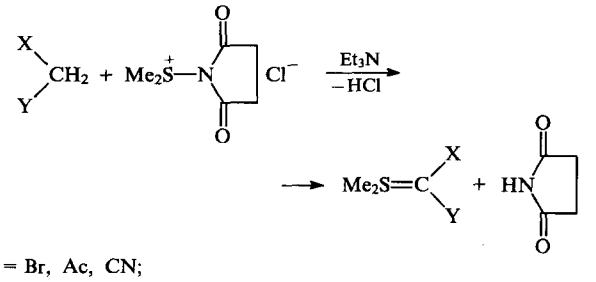


Generation of sulfur ylides. In the presence of bases, dialkylaminosulfonium salts may undergo C-deprotonation with formation of aminosulfonium ylides, which is also used in organic synthesis. For example, the conversion of dialkylaminosulfonium salts into aminosulfonium ylides with subsequent rearrangement of the latter is employed in the orthoalkylation or anilines[132] and in the synthesis of indoles (Scheme 9).[133]

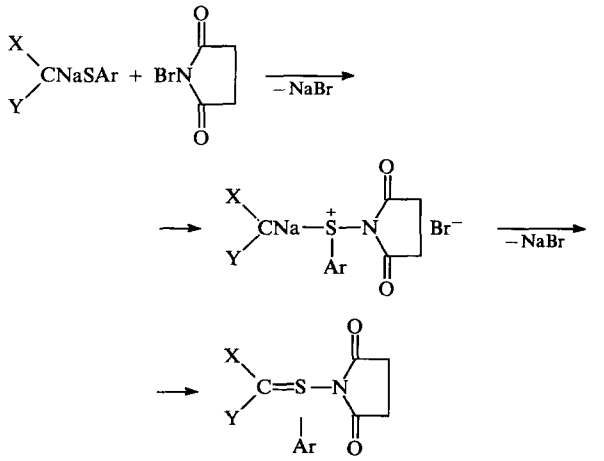
Scheme 9



It is worth noting that, in the case of aminosulfonium salts containing a hydrogen atom at the nitrogen atom, the formation of sulfur ylides may be accompanied by a side reaction — the formation of sulfimides. The rearrangement of aminosulfonium salts in the presence of bases, which results in the formation of sulfides,[134] also proceeds via a sulfonium ylide generation stage. The formation of sulfur ylides has also likewise been observed in the interaction of Corey–Kim reagents with CH acids in the presence of triethylamine.[135]



X = Br, Ac, CN;
Y = Br, Ac, CO_2Et, CO_2Me, Ph.

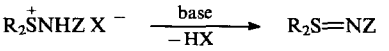


X = MeCO, Y = EtOCO, Ar = 2-$NO_2C_6H_4$;

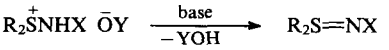
X = $PhSO_2$, Y = Ph, Ar = 4-$NO_2C_6H_4$.

It has been suggested[136] that the interaction of sodium salts of arylthio-CH acids with *N*-bromosuccinimide, which results in the formation of stable *S*-aryl-*S*-succinimidosulfonium methylides, proceeds via a stage involving the formation of aminosulfonium salts.

Synthesis of sulfimides. The N-deprotonation of aminosulfonium salts containing a hydrogen atom at the nitrogen atom is one of the commonest methods of synthesis of sulfimides.[80,81] Both organic and inorganic bases (Et_3N, NaOH, etc.) are used as the deprotonating agents.



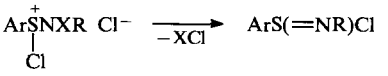
R = Alk, Ar, Het, X = Cl, Br; Z = H, MeCO, EtOCO, etc.



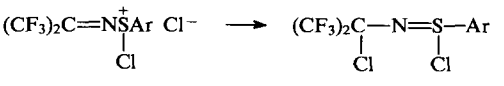
R = Alk, Ar; X = H, $ArSO_2$, EtOCO;

Y = HSO_3, 4-$NO_2C_6H_4SO_2$, 2,4,6-$Me_3C_6H_2SO_2$.

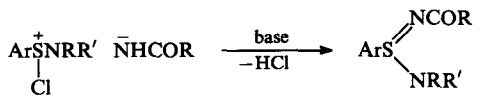
Synthesis of derivatives of iminosulfinic acids. The aminosulfonium salts formed on chlorination of *N*-substituted sulfenamides[112] or their sodium salts[113] are readily converted into iminosulfinic acid chlorides as a result of the elimination of HCl or NaCl.



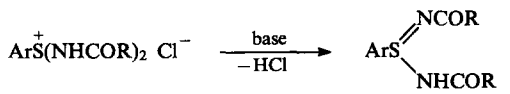
R = Bu^t, $PhSO_2$, ArCO; X = Na, H.



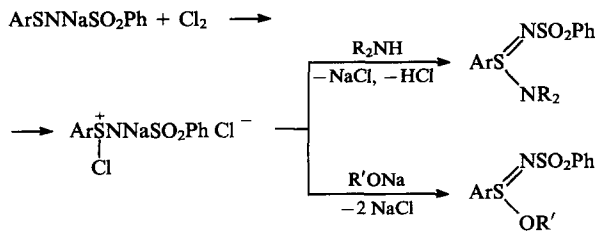
The dehydrochlorination of the aminosulfonium salts formed on interaction of *N*-chloroamides with sulfenamides[119] and disulfides[131] leads to the amides of iminosulfinic acids.



R = H, Alk; R′ = Alk, Ar, RCO



One cannot rule out the possibility that the chlorination of the sodium salts of *N*-arenesulfonylarenesulfenamides in the presence of various nucleophiles, which results in the formation of the amides[137] and esters[138,139] of iminosulfinic acids, also proceeds via a stage involving the formation of aminosulfonium salts.



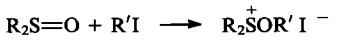
Ar = 2-$NO_2C_6H_4$, 4-$NO_2C_6H_4$;

R = Et, Bu, C_5H_{11}; R′ = Me, Et, Pr, Bu^i, Bu^n

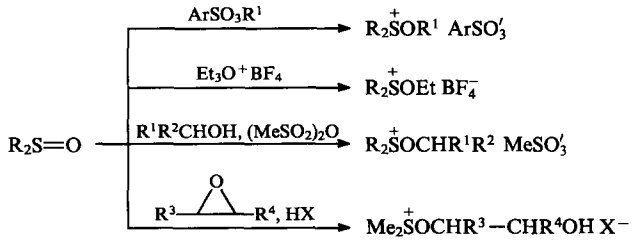
4. Alkoxy-, aryloxy-, and acyloxy-sulfonium salts

a. Methods for the generation of alkoxy-, aryloxy-, and acyloxy-sulfonium salts

Generation from sulfoxides. The commonest method for the generation of alkoxysulfonium salts involves the interaction of sulfoxides with alkyl halides.[1,2]



The alkyl esters of sulfonic acids,[28] triethyloxonium tetrafluoroborate,[2] alcohols (in the presence of the anhydride of methanesulfonic acid),[2] and epoxides (in the presence of strong acids)[2] are used as other alkylating agents.[2]

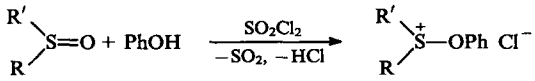


R = Alk, R^1 = Alk, Ar = 4-MeC_6H_4, 4-$NO_2C_6H_4$;

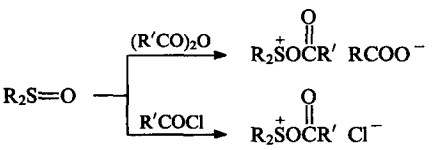
R^2 = Alk; R^3 = H, Alk, Ph; R^4 = H, Alk;

X = 2,4,6-$(NO_2)_3C_6H_2SO_3$.

The synthesis of a phenoxysulfonium salt by the reaction of sulfoxides with phenol in the presence of sulfuryl chloride has been described.[140]

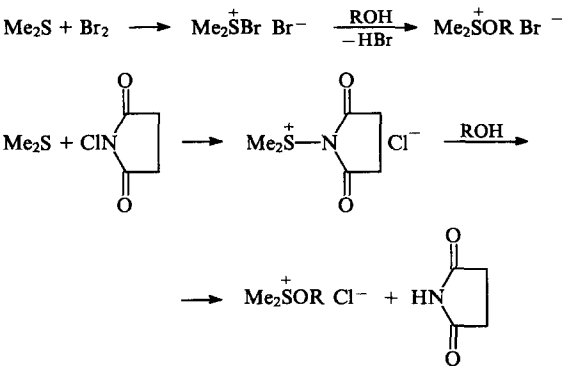


The interaction of the sulfoxides with carboxylic acid anhydrides[2,141,142] of halides[28] leads to the formation of acyloxysulfonium salts.

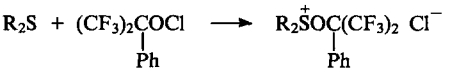


R = Me, Ph, CH_2=CH, etc.; R′ = Me, CF_3.

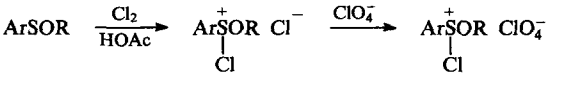
Generation from sulfides. Two alternative methods for the generation of alkoxysulfonium salts from sulfides have been developed. In the first method, the sulfide is converted into halo- or amino-sulfonium salts, which are subsequently treated with alcohols.[28]



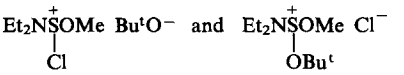
The second method involves the interaction of sulfides with alkyl hypochlorites.[105]



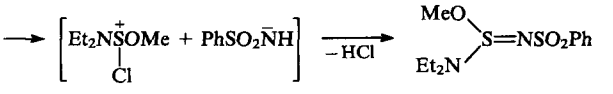
Generation from sulfenic and sulfinic acid esters. Alkoxysulfonium salts are formed on interaction of the alkyl esters of sulfenic acids with chlorine in acetic acid.[2]



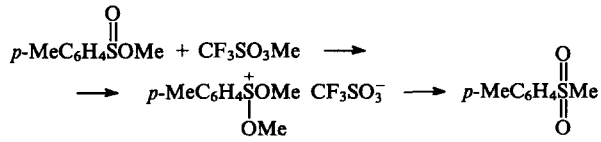
It has been noted[143,144] that the oxidation of *O*-methyl-*N*,*N*-dimethylaminosulfenates by *tert*-butyl hypochlorite to aminosulfinates proceeds via a stage involving the formation of alkoxysulfonium salts.



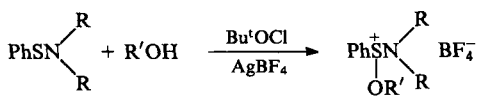
Evidently the oxidative imination of these compounds by the sodium derivatives of sulfonic acid chloramides[145] also proceeds via a stage in which alkoxysulfonium salts are generated.



The formation of a dimethoxysulfonium salt in the alkylation of methyl toluene-*p*-sulfinate by methyl trifluoromethanesulfonate has been postulated.[146]



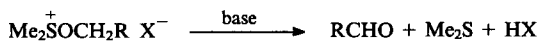
Generation from sulfenamides. It has been shown[147] that *N,N*-dialkylarenesulfenamides react with *tert*-butyl hypochlorite in the presence of alcohols and $AgBF_4$ to form alkoxyaryldialkylaminosulfonium salts.



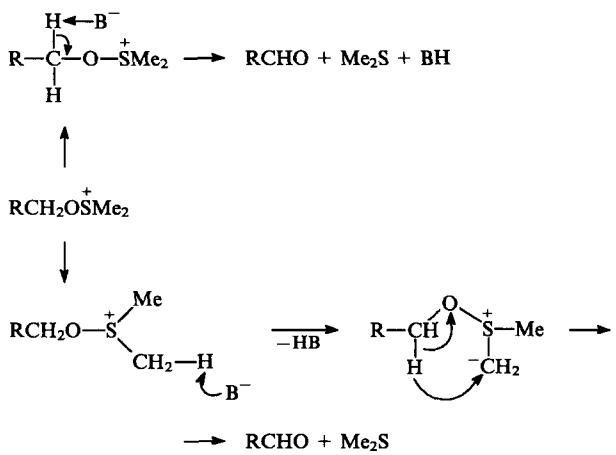
R = Me, $(CH_2)_5$, $(CH_2)_2O(CH_2)_2$; R′ = Me, Et, Pr^i, iso-C_6H_{11}.

b. Applications of alkoxysulfonium salts in organic synthesis

Synthesis of carbonyl compounds. On treatment with bases, alkoxysulfonium salts are cleaved, affording carbonyl compounds in relatively high yields.

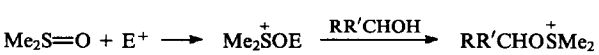


The cleavage can proceed in two ways.

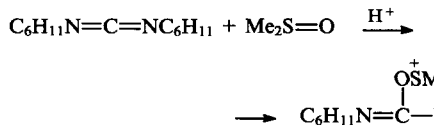


A whole series of convenient methods for the conversion of primary and secondary alcohols and also alkyl halides and tosylates into carbonyl compounds have been developed on the basis of this reaction. As a rule, alkoxysulfonium salts based on DMSO are used in these methods, which is evidently associated with their greatest availability. The advantage of these methods of synthesis of carbonyl compounds consist not only in the high yields of the target products but also in the fact that the oxidation of the aldehyde group to a carboxy-group is ruled out and other readily oxidised fragments, such as C=C and C–S–C, are not affected.

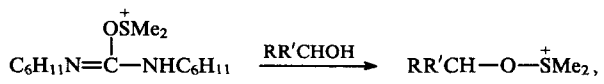
Depending on the method of generation of alkoxysulfonium salts, all these methods can be divided into several groups. The first group includes methods in which the alkoxysulfonium salt is formed as a result of the interaction of an alcohol with the alkoxysulfonium salt generated by the interaction of DMSO with the electrophilic species E^+ present in the reaction medium.[2]



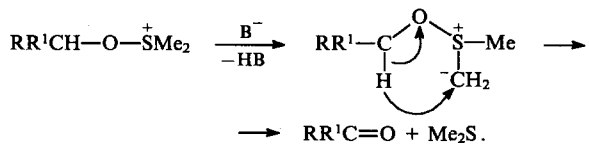
Here it is essential that the electrophilic species should react with DMSO faster than with the alcohol and that the OE group should be readily eliminated. Dicyclohexylcarbodiimide (DCC) combined with proton sources, for example pyridinium fluoroacetate, acetic anhydride, trifluoroacetic anhydride, and methanesulfonic acid anhydride is most often employed as the electrophile. When the last two compounds are used, the alcohol is introduced into the reaction medium after the reaction of dimethyl sulfoxide with the electrophile. The oxidation of the alcohol by the DMSO–DCC system includes three stages: the activation of DMSO by the electrophile with formation of a primary alkoxysulfonium salt:



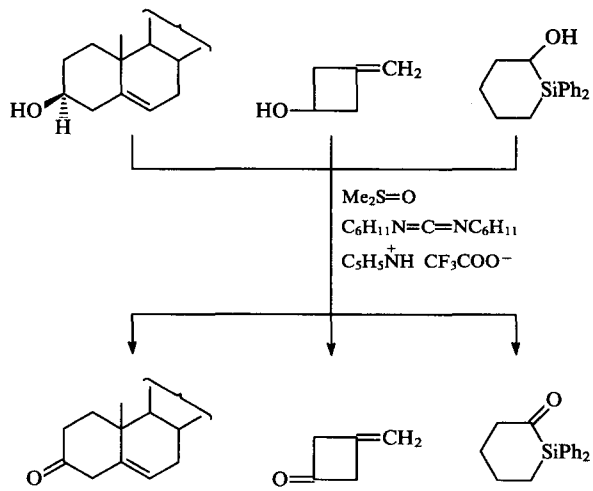
the interaction of the alkoxysulfonium salt with the alcohol to form a secondary alkoxysulfonium salt:



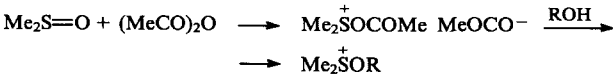
the decomposition of the secondary alkoxysulfonium salt:



Cholesterol, 3-methylenecyclobutanol, and 1,1-diphenylsilacyclohexan-2-ol have been oxidised to the corresponding ketones by means of the DMSO–DCC system.[2]

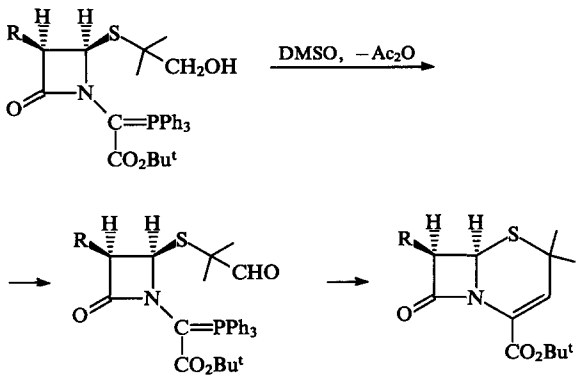


The acylsulfonium salt formed in the DMSO–$(MeCO)_2O$ system is converted into an alkoxysulfonium salt as a result of its interaction with the alcohol.[2]



This system is also used in the oxidation of hydrocarbons, sterically hindered alcohols, and also alcohols with readily oxidisible functional groups such as the sulfide and phosphorus-containing groups. For example, the conversion of a phosphorane, containing the β-lactam group, into a bicyclic

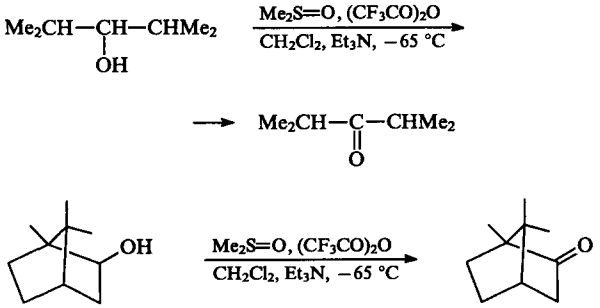
product takes place as a result of the Wittig reaction with participation of the aldehyde group formed on oxidation of an alcoholic group by the DMSO–$(MeCO)_2O$ system without change in the phosphorane and sulfide functional groups.



R = NHC(O)CH_2Ph.

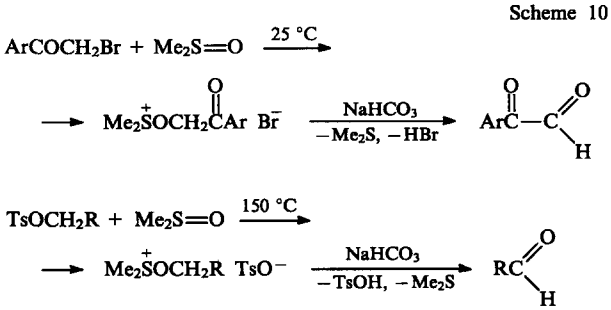
The formation of side products – acetates and methylthiomethyl ethers – must be regarded as a disadvantage of this system.

Among other methods, mention should be made of the use of the DMSO – methanesulfonic acid anhydride system in DMF for the oxidation of testosterone to androst-4-ene-2,17-dione and of the DMSO – trifluoroacetic anhydride system in CH_2Cl_2.[148] The latter method has been used in the oxidation of sterically hindered alcohols. For example, in the presence of this system 2,4-dimethylpentan-3-ol and isoborneol are converted into diisopropyl ketone and camphor in 86% and 93% yields respectively.[149]



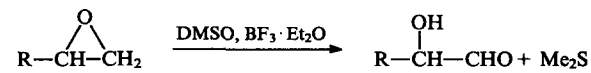
Methods in which the alkoxysulfonium salts are generated by the interaction of DMSO with halo-derivatives or tosylates in the presence of $NaHCO_3$ or collidine, which not only decompose the intermediate alkoxysulfonium salt but also neutralise the acid side products, are included in the second group of methods of synthesis of carbonyl compounds from alkoxysulfonium salts (Scheme 10).[2]

Scheme 10

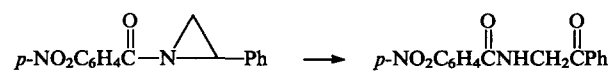


These methods are especially suitable in the case of halo-derivatives and tosylates, which tend to undergo S_N2 substitution reactions (α-halogenated esters and acids, phenacyl and benzyl halides, primary alkyl iodides, sulfonates). However, one should note that, when secondary halo-derivatives and tosylates are employed, the yields of the carbonyl compounds are low owing to the competing elimination reactions.

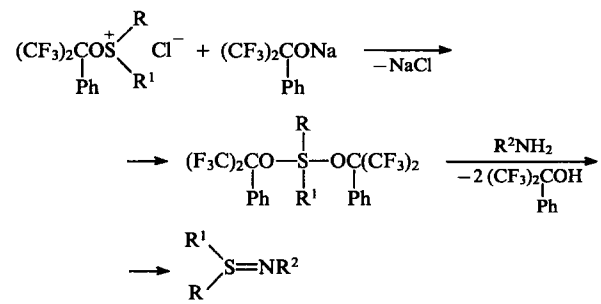
The third group comprises methods in which the intermediate alkoxysulfonium salts are the products of the interaction of DMSO with three-membered heterocyclic compounds in the presence of acid catalysts. For example, the interaction of DMSO with epoxides in the presence of $BF_3.Et_2O$ leads to the formation of α-hydroxyaldehydes.



On heating in DMSO at 115–120 °C, the ring in *N*-acylaziridines is opened with conversion into *N*-substituted amides.



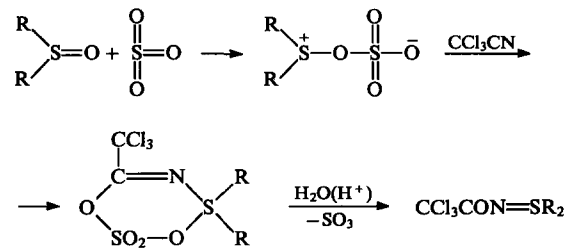
Synthesis of sulfimides. Several methods have been developed for the preparation of sulfimides from alkoxysulfonium salts. One of them involves the conversion of alkoxysulfonium salts by alkoxides into sulfuranes, which give rise to sulfimides on interaction with amines.[105]



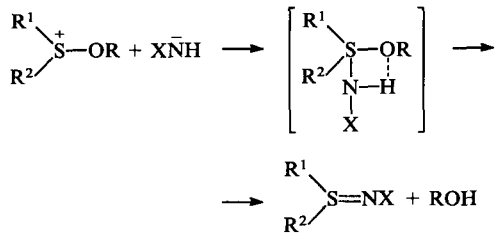
Another method is based on the interaction of alkoxysulfonium salts, generated from sulfoxides and active electrophiles E^+, with N-nucleophiles.[80,81]



The activating electrophiles employed are P_2O_5, $(CF_3CO)_2O$, SO_3, H_2SO_4, and BF_3.[80,81] Amines and amides of sulfonic and carboxylic acids are employed as the N-nucleophiles. The sulfonium salts formed in the reactions of sulfoxides with SO_3 also react with nitriles to form sulfimides.[149] The proposed reaction mechanism involves the attack by the electron-deficient carbon atom of the nitrile group on one of the oxygen atoms of the sulfonium salt, which occurs only in the case of nitriles containing strongly electron-accepting groups.



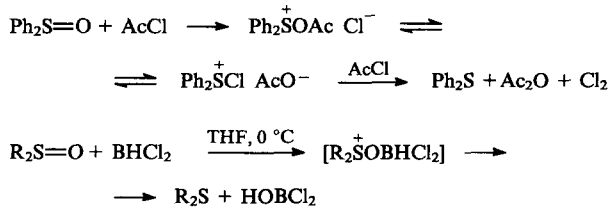
The synthesis of sulfimides by the reactions of the sodium derivatives of the amides and sulfonic and carboxylic acids with alkoxysulfonium salts has been described.[150] According to the authors, the reaction is stereospecific and proceeds with retention of configuration of the sulfur atom, which is due to the formation of an intermediate four-membered cyclic compound stabilised by an intramolecular hydrogen bond.



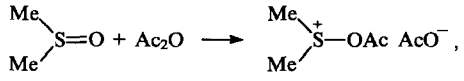
R = Me–C6H4–CHMe2, R^1 = 2-$MeOC_6H_4$, R^2 = Ph

X = $ArSO_2$, CH_2ClCO, $CHCl_2CO$, CF_3CO

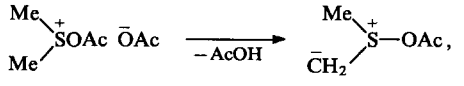
Synthesis of sulfides. Several methods have been developed for the synthesis of sulfides from sulfoxides involving an intermediate stage in which alkoxy- or acyloxy-sulfonium salts are generated. One of them amounts to the reduction of sulfoxides by an excess of acetyl chloride[151] and by dichloroborane.[152]



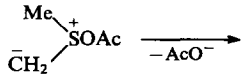
However, the method has not found extensive application, since more effective and convenient procedures have been developed for the reduction of sulfoxides and sulfides. Reactions leading to the formation of sulfides differing in structure from those employed for the synthesis of the sulfoxides are frequently used. One of them is based on the Pummerer rearrangement, which takes place when sulfoxides are heated in acetic anhydride.[2,153] The mechanism of this rearrangement includes the following stages:
the formation of an acyloxysulfonium salt:



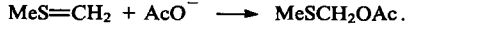
the conversion of the acyloxysulfonium salt into an ylide:



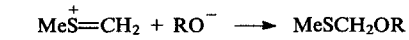
the formation of a sulfonium cation:



the interaction of the sulfonium cation with the acetate anion:

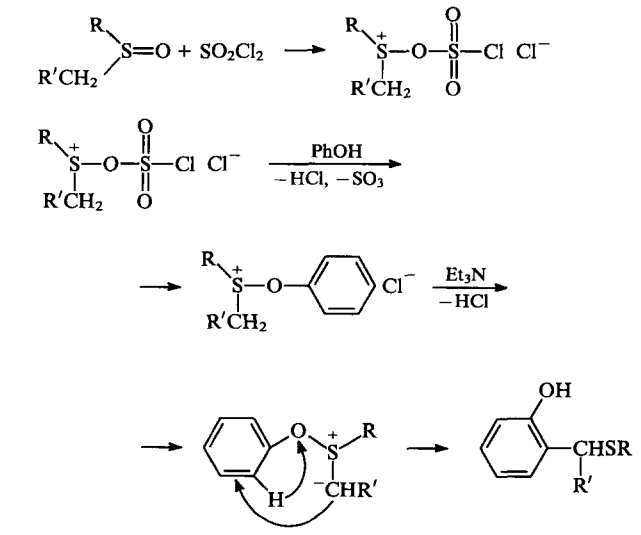


The presence of alkoxide anions in the reaction mixture leads to the formation of a methylthiomethyl ether or an alkoxymethyl methyl sulfide, which makes it possible to explain the formation of this compound as a side product in the oxidation of alcohols by the DMSO–$(MeCO)_2O$ system.

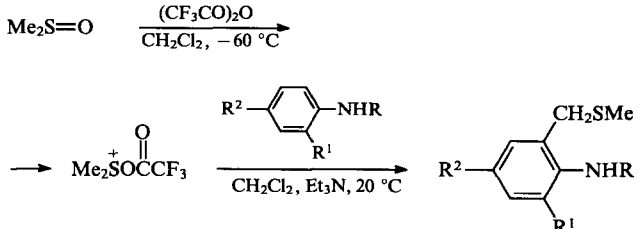


The regioselectivity of the Pummerer rearrangement, observed for asymmetric sulfoxides, can be predicted on the basis of the comparison of the relative acidities of the two α-protons in the acyloxysulfonium salt. Bearing in mind the ease of the conversion of sulfides into sulfoxides, the Pummerer rearrangement is a very important method for the conversion of one set of sulfides into another.

Other methods for the conversion of sulfoxides into sulfides are based on the intramolecular rearrangement of aryloxysulfonium salts proceeding via an ylide generation stage.[140] The final result of such 2,3-sigmatropic rearrangement is the introduction of an alkylthiomethylene group into the *ortho*-position in phenols.



An alkylthiomethylene group is introduced similarly into the *ortho*-position in aromatic amines.[141]

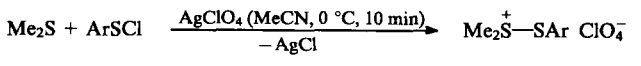


R = H, Me, Ph; R^1 = H, MeO; R^2 = H, Me, MeO

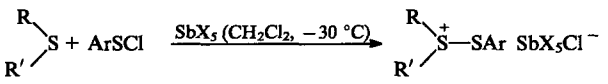
5. Alkyl(aryl)thiosulfonium and [dialkyl(aryl)]alkyl(aryl)-thiosulfonium salts

a. Methods of generation

Generation from sulfides. Dialkyl sulfides and certain diaryl sulfides react relatively easily with arenesulfenyl chlorides in the presence of silver perchlorate[154] or Lewis acids,[155] forming (dialkyl)arylthiosulfonium salts.



Ar = Ph, 4-MeC_6H_4

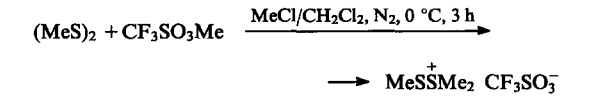


R = R′ = Me, Ph; R = Me, R′ = 4-ClC_6H_4; X = Cl, F

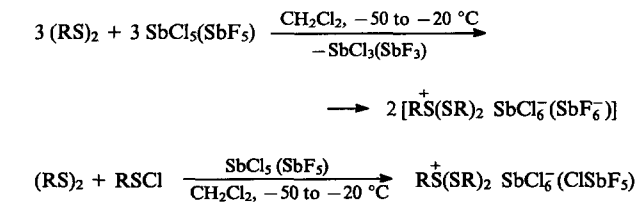
Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4, 2,4,6-$Me_3C_6H_2$, 4-$CF_3C_6H_4$.

Some of these salts are relatively stable and can be isolated in a crystalline state and analysed by ^1H and ^{13}C NMR spectroscopy.[155]

Generation from disulfides. (Dialkyl)alkylthiosulfonium salts have also been obtained by the interaction of dialkyl disulfides with methyl trifluoromethanesulfonate.[156]



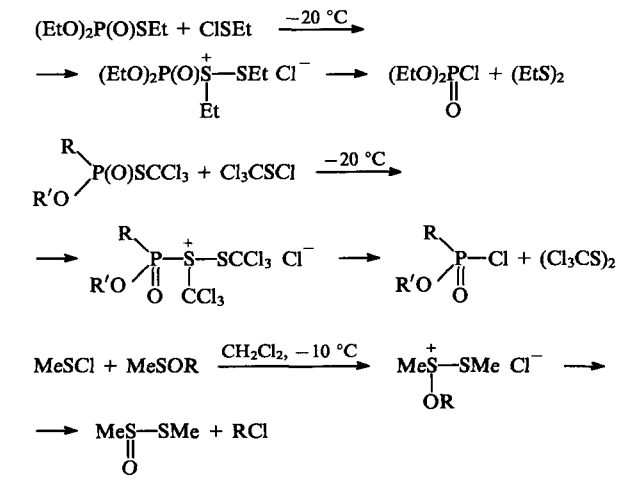
The interaction of dialkyl disulfides[157,158] and diaryl disulfides[159–161] with Lewis acids ($SbCl_5$, SbF_5) or with sulfenyl chlorides leads to the formation of [dialkyl(aryl)]alkyl(aryl)-thiosulfonium salts.



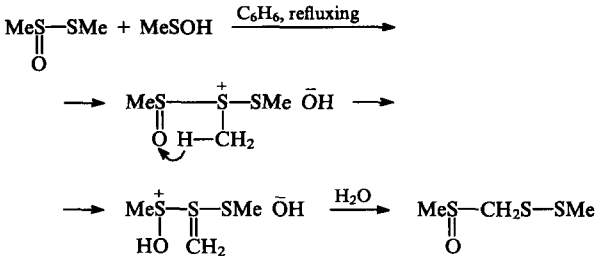
R = Me, Ph, 4-ClC_6H_4, 4-MeC_6H_4, 2,4,6-$Me_3C_6H_2$.

The salt solutions obtained can be stored without change for several hours at −50 to −20 °C. The formation of intermediates of analogous structure in the disproportionation of disulfides in an acid medium has been postulated.[162]

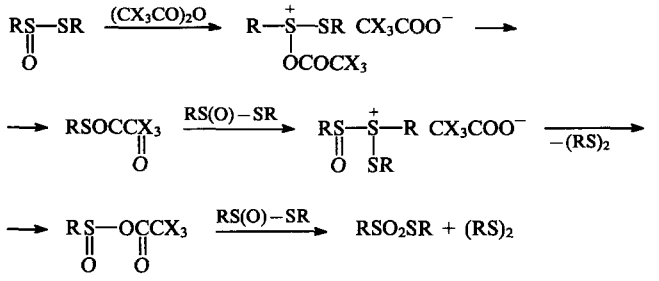
Other methods of generation. The formation of alkylthiosulfonium intermediates has been observed in the reactions of alkanesulfenyl chlorides with phosphorothiolates[163] and sulfenates.[2]



It has been suggested[164] that the sulfenic acids formed in the thermal dissociation of thiolosulfinates in the absence of trapping agents may react with the thiolosulfinates to form sulfinylthiosulfonium intermediates, which are converted into alkane-α-sulfinyl disulfides as a result of the Pummerer rearrangement.



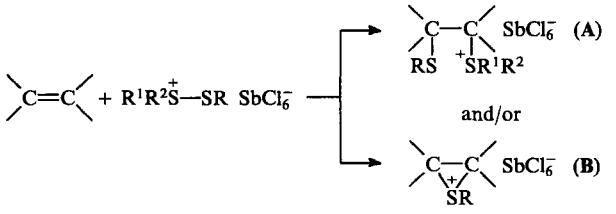
The probable mechanism of the rearrangement of thiolosulfinates on treatment with the anhydrides of trichloro- and trifluoro-acetic acids, described in the literature,[165] also involves the generation of thiosulfonium intermediates.



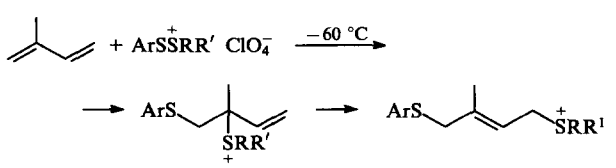
R = Me, $PhCH_2$; X = Cl, F.

b. The applications of alkyl(aryl)thiosulfonium and [dialkyl(aryl)]-alkylthiosulfonium salts in organic synthesis

It has been noted[155,157,158,166] that alkyl(aryl)thiosulfonium salts are effective agents for transferring the RS^+ groups to the double bond in Ad_E reactions with alkenes such as cyclohexene, 1-methylcyclohexene, tetramethylethene, cyclooctene, styrene, isoprene, etc. These reactions take place relatively easily even at −10 to −30 °C and lead to the formation β-alkyl(aryl)-thiosulfonium salts **A**[155,157,158,166] and/or *S*-alkyl(aryl)epi-sulfonium salts **B**.[155–158]



According to Kal'yan et al.,[155] the interaction of alkenes with the salts RR′S^+–SAr $SbCl_6^-$ (R = R′ = Me; Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4, 2,4,6-$Me_3C_6H_2$, 4-$CF_3C_6H_4$, C_6F_5) and RR′S^+SAr $SbCl_6^-$ [R + R′ = $-(CH_2)_4-$, Ar = 4-ClC_6H_4, 2,4,6-$Me_3C_6H_2$] proceeds most unambiguously. In the reactions of these salts with cyclohexene, styrene, and isoprene, the formation of only β-arylthioalkylsulfonium salts **A**, readily isolated in the form of substances fairly stable in the solid state, has been observed. According to ^1H NMR data, the salts obtained under these conditions from isoprene have the structure of 1,4-adducts formed as a result of the rearrangement of the 1,2-adducts.

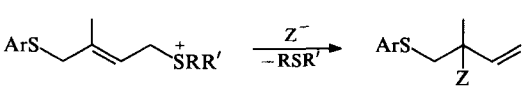


The formation of the episulfonium salt **B** has been observed in the reaction of $(RR'S^+-SC_6H_4Me\text{-}4)\ SbCl_6^-$ (R = Me, R' = C_6H_4Cl-4) with cyclohexene, but, when the methyl group in the *S*-aryl fragment of the initial salt is replaced by CF_3 or Cl, a 1 : 1 mixture of the salts **A** and **B** is obtained. This enabled the authors[155] to postulate the primary formation of the episulfonium salt **B**, the interaction of which with the sulfide present in the reaction mixture leads to the salt **A**. The reactivity of the episulfonium salt **B** is then determined by the nature of the substituents in the *S*-aryl fragment. In terms of their reactivity in relation to nucleophiles, certain salts **A** are close to the episulfonium salt **B**. Thus the reactions of these salts with the acetate anion lead to the corresponding acetoxy-adducts.

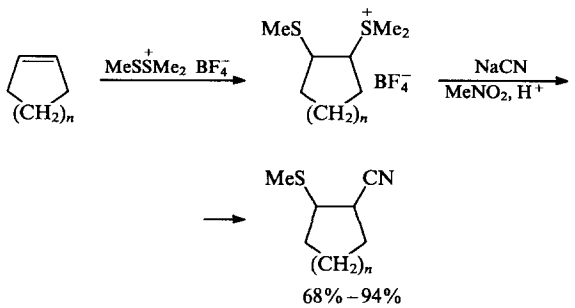


R = Me, Ph; R' = Ph, 4-ClC_6H_4.

Salts of type **A** based on isoprene react in an unusual manner with the acetate anion and other nucleophiles. In this case, the reaction proceeds exclusively in accordance with an S_N2 mechanism with formation of β-acetoxysulfides.

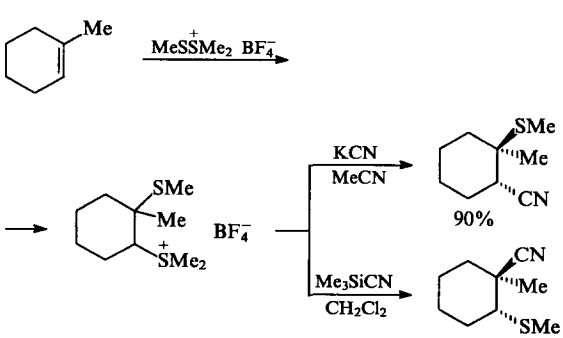


It has been noted[9] that β-alkyl(aryl)thiosubstituted salts **A** are effective electrophiles for the transfer of the β-alkyl(aryl)thioalkyl group in reactions with anionic C-nucleophiles. For example, it has been shown that the adducts of different alkenes with $MeS\overset{+}{S}Me_2\ BF_4^-$ react fairly readily with the cyanide ion, which has made it possible to develop a general method for the cyanosulfenylation of alkenes under mild conditions.

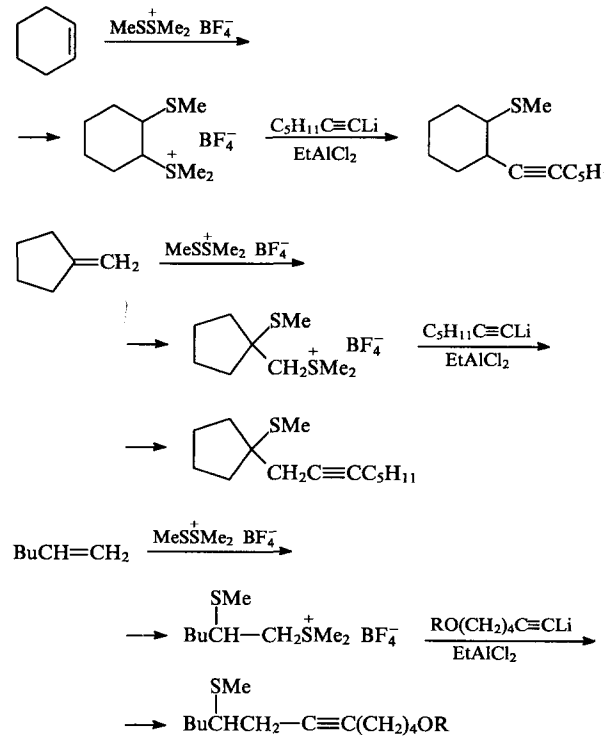


68%–94%

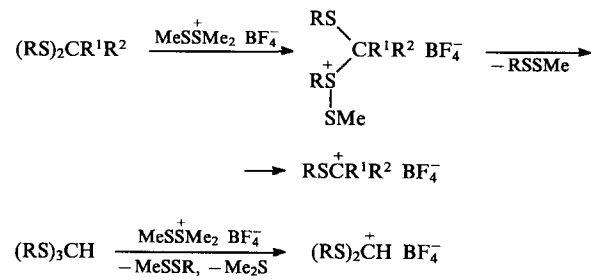
When the reaction conditions are altered, both regioisomers may be obtained.



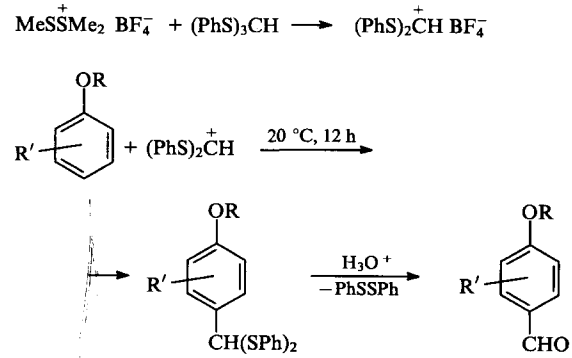
Complexes of acetylides with organoaluminium compounds are also used as the C-nucleophiles.[9]



One of the very important aspects of the use of alkyl(aryl)-thiosulfonium salts in organic synthesis is the generation of α-thio-substituted[167] and α,α-dithio-substituted[168] carbonium ion intermediates.

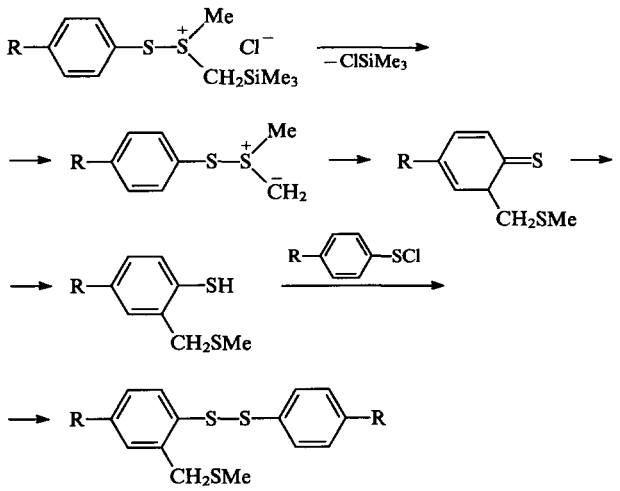


In a regioselective method[169] for the formylation of phenols and naphthols, a α,α-diphenylthio-substituted carbonium ion is generated with the aid of the salt $MeSS^+Me_2\ BF_4^-$.

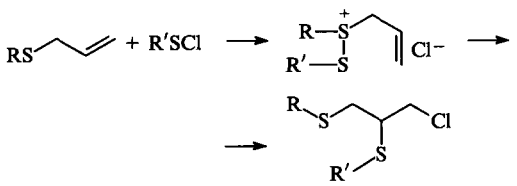


The rearrangements of alkyl(aryl)thiosulfonium salts are frequently employed to synthesise various sulfur-containing compounds. For example,[170] the spontaneous 2,3-sigmatropic rearrangement of the salts $RR'S^+SAr\ Cl^-$ (R = Me; R' = CH_2SiMe_3; Ar = Ph; 4-MeC_6H_4, 4-ClC_6H_4), formed in the

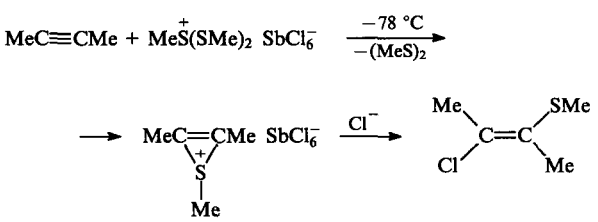
reactions of arenesulfenyl chlorides with methylthiomethyl(trimethyl)silane, has been described.[170] The authors suggest[170] that the rearrangement proceeds via an ylide formation stage.



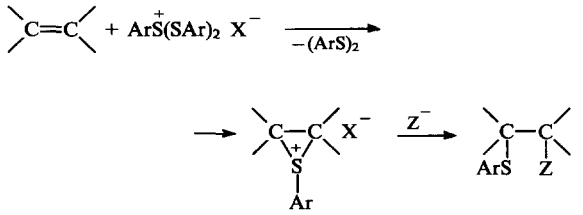
An interesting case of a degenerate 2.3-sigmatropic rearrangement has been observed in the interaction of sulfenyl chloride with allyl sulfides.[54,171]



[Dialkyl(aryl)]alkyl(aryl)thiosulfonium salts are also effective agents for the transfer of the RS^+ group in Ad_E reactions with unsaturated hydrocarbons. The interaction of such salts with ethyne hydrocarbons leads to the formation of thiirenium salts, the reactions of which with nucleophiles involve ring opening and the formation of unsaturated sulfides.[172]



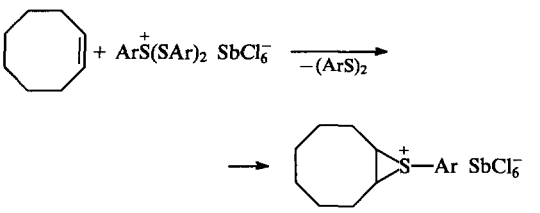
(Diaryl)arylthiosulfonium salts react rapidly with alkenes even at −60 °C, affording the corresponding *S*-arylepisulfonium salts, which are converted into β-substituted aryl sulfides on treatment with nucleophiles.[159–161]



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

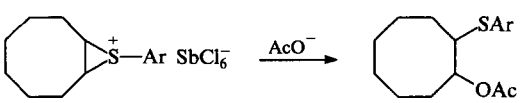
X = $SbCl_6$, SbF_5Cl, Z = OAc.

The reaction of (diaryl)arylthiosulfonium salts with cyclooctene has been studied in greatest detail. In this case, the authors[161] were able to isolate *S*-arylcyclooctenoepisulfonium hexachloroantimonates in a crystalline state in 100% yield.

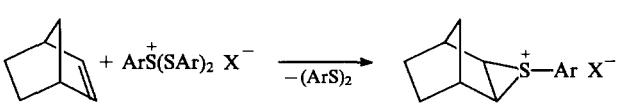


Ar = Ph, 4-ClC_6H_4, 4-MeC_6H_4, 2,4,6-$Me_3C_6H_2$.

The reactions of these salts with the acetate anion lead to the formation of 2-acetoxycyclooctyl aryl sulfides.



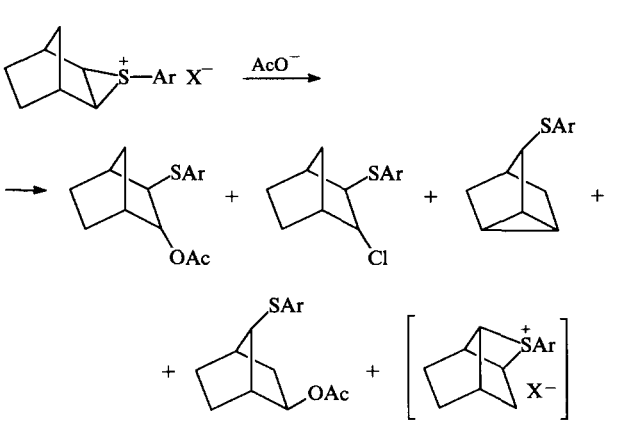
The corresponding *S*-arylnorbornylideneepisulfonium salts have also been isolated in the solid state and characterised.[161]



X = $SbCl_6$; Ar = 4-ClC_6H_4, 4-MeC_6H_4, 2,4,6-$Me_3C_6H_2$.

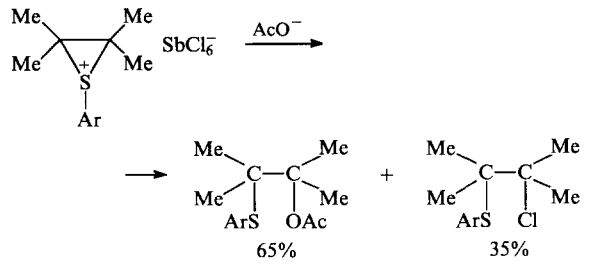
X = SbF_6; Ar = 4-ClC_6H_4, 2,4,6-$Me_3C_6H_2$.

The interaction of these salts with the acetate anion results in the formation of a mixture of several products, which, according to the authors,[161] is due to their instability in solution.

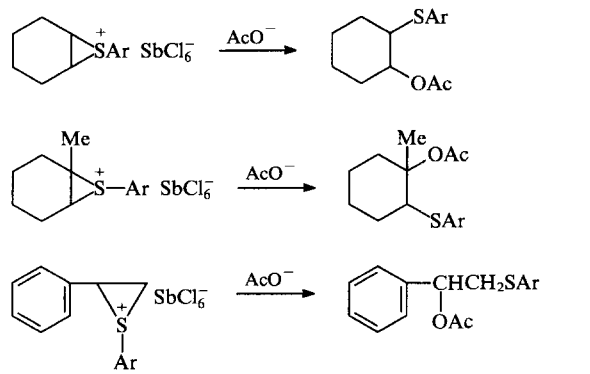


The composition and structure of the final products of this reaction are influenced significantly also by the nature of the initial episulfonium salt. For example, the reaction of the *S*-methylnorbornylideneepisulfonium salt with the acetate anion leads to the formation of only one product—2-acetoxy-3-methylthionorbornane in 95% yield.[161]

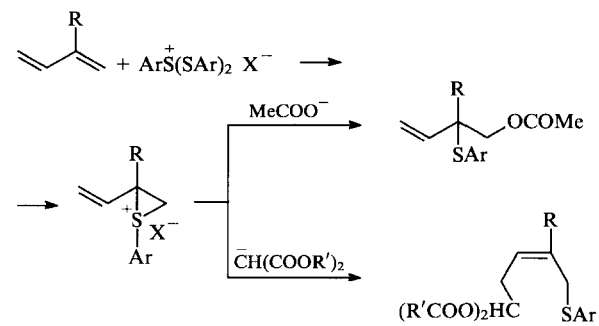
In the reaction of the $ArS^+(SAr)_2$ (Ar = 2,4,6-$Me_3C_6H_2$) salt with tetramethylethene, the authors[161] were able to isolate the episulfonium salt in the crystalline state in 89% yield. The interaction of this salt with the acetate anion leads to the formation of a mixture of two products—2-acetoxy-3-mesitylthio-2,3-dimethylbutane and 2-chloro-3-mesitylthio-2,3-dimethylbutane.



The episulfonium salts formed in the reactions of cyclohexene, 1-methylcyclohexene, and styrene with $ArS^+(SAr)_2\ SbCl_6^-$ (Ar = 2,4,6-$Me_3C_6H_2$) are unstable and it was not possible to isolate them in the crystalline state. Their presence was demonstrated by their reactions with the acetate anion, which resulted in the formation of the corresponding β-acetoxysulfides.



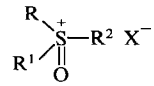
The interaction of (diaryl)arylthiosulfonium salts with butadiene and isoprene[173] afforded the corresponding *S*-aryl-episulfonium salts, which were isolated in a free state. They are hygroscopic crystalline substances stable at temperatures below 0 °C. The reactions of these salts with the acetate anion lead to 1,2-acetoxyarylthio-adducts (yield up to 90%), whilst their interaction with sodiomalonic ester proceeds via a different mechanism and the formation of 1,4-adducts (yield up to 60%).



R = H, Me; R′ = Me, Et; X = BF_4, SbF_6, $SbCl_6$;
Ar = Ph, 4-ClC_6H_4, 4-MeC_6H_4, 2,4,6-$Me_3C_6H_2$, 4-$CF_3C_6H_4$, C_6F_5.

IV. Sulfoxonium (oxosulfonium) reagents

Oxosulfonium salts having the general formula



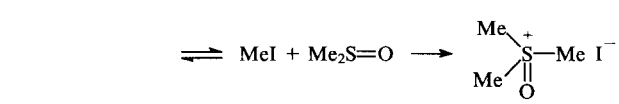
R = Alk, Ar; R^1 = Alk, Ar; R^2 = Alk, Ar, $NAlk_2$;
X = Cl, Br, I, BF_4, etc.;

as well as some of their derivatives are the principal members of the class of oxosulfonium reagents.

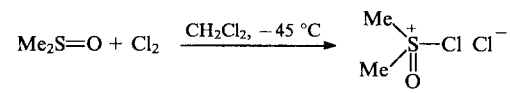
1. Methods for the generation of oxosulfonium salts

a. Generation from sulfoxides

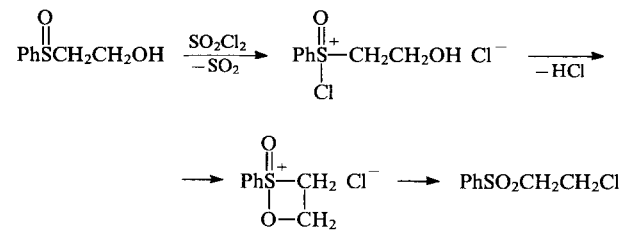
The reaction of dimethyl sulfoxide with methyl iodide results in the formation of dimethylmethoxysulfonium iodide, which is slowly converted into the thermodynamically more stable trimethyloxosulfonium iodide.[2]



Optically active oxosulfonium salts are obtained from optically active sulfoxides by their interaction with the MeI – HgI_2 system.[173] Dimethyl sulfoxide reacts with chlorine in methylene chloride at −45 °C, forming a relatively unstable chlorodimethyloxosulfonium salt.[174]

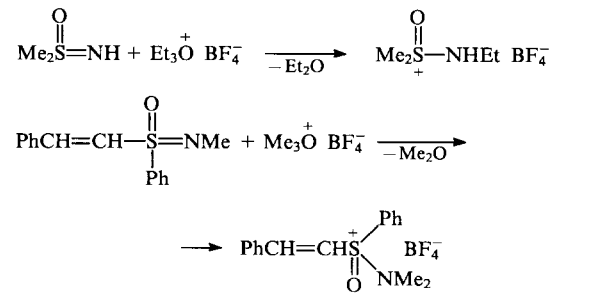


Chlorooxosulfonium salts are also obtained at an intermediate stage in the oxidative chlorination of β-hydroxysulfoxides.[175]



b. Generation from sulfoximides

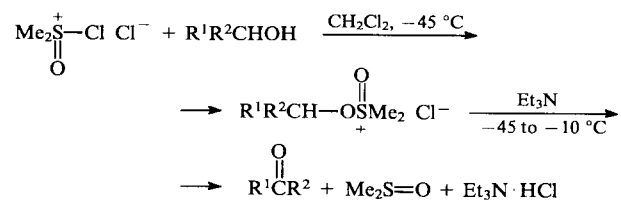
Sulfoximides which are unsubstituted or substituted at the nitrogen atom react relatively easily with trialkyloxonium salts to form oxosulfonium salts.[2]



2. Applications of oxosulfonium salts in organic synthesis

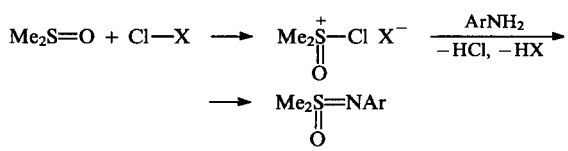
a. Oxidation of alcohols

Chlorodimethyloxosulfonium salts, formed as a result of the chlorination of dimethyl sulfoxide by chlorine, are used to oxidise primary and secondary alcohols to carbonyl compounds.[176]



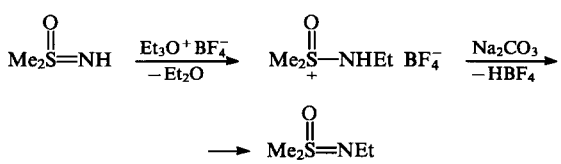
b. Synthesis of sulfoximides

The interaction of chlorooxosulfonium salts with aromatic amine entails the replacement of the chlorine atom at the sulfur atom by the imido-group with formation of sulfoximides.[91]



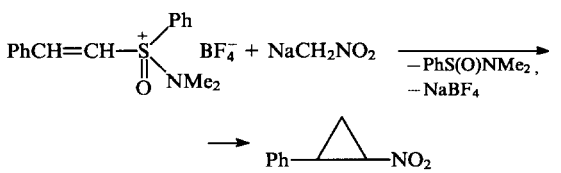
X = Cl, Bu^{t}O.

Sulfoximides are also formed when dialkylaminooxosulfonium salts are treated with bases, which, bearing in mind the ability of unsubstituted sulfoximides to be alkylated by trialkyloxonium salts, may be used to convert unsubstituted sulfoximides into *N*-substituted ones.

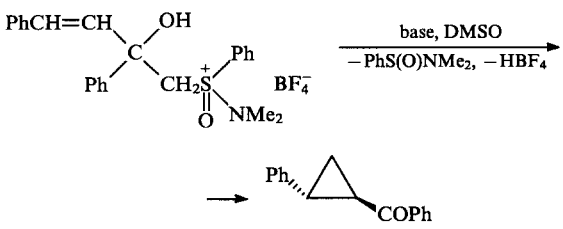


c. Synthesis of cyclopropanes

The interaction of substituted vinyloxosulfonium salts with C-nucleophiles, for example with sodionitromethane, results in the formation of cyclopropanes.[2]

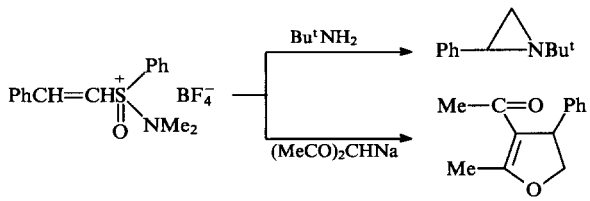


The intramolecular cyclisation of oxosulfonium salts containing an activated double bond also leads to cyclopropanes.[177] It has been suggested that in this case an oxonsulfonium ylide is generated with subsequent transfer of the methylene group to the C=C bond.



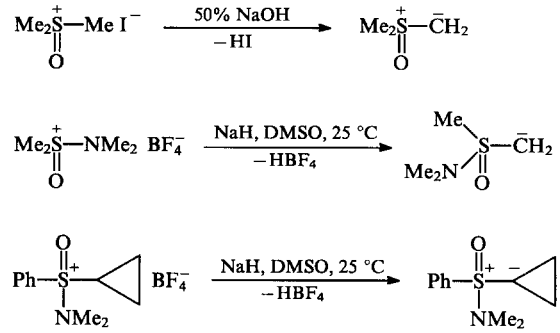
d. Synthesis of heterocyclic compounds

On interaction with primary amines, substituted vinyloxosulfonium salts afford aziridines, whilst their interaction with the sodium salt of acetylacetone leads to dihydrofuran derivatives.[178]

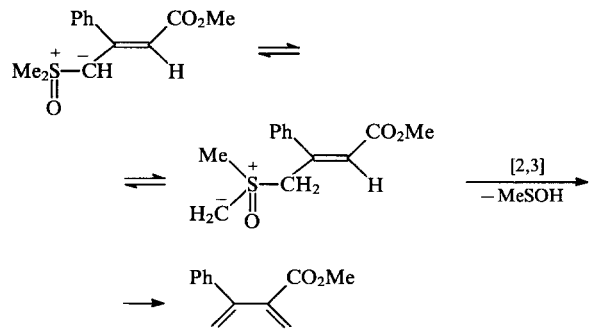


e. Generation of oxosulfonium ylides

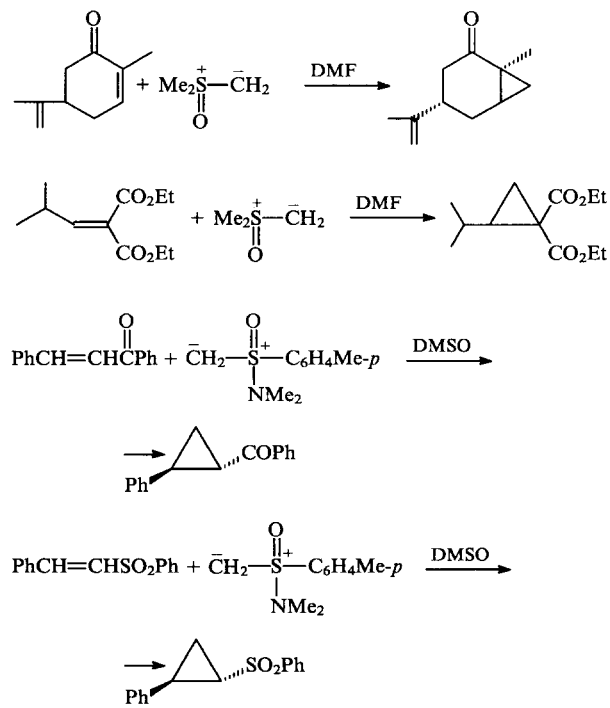
Treatment of dialkyloxosulfonium salts with deprotonating agents leads to the formation of oxosulfonium ylides,[36] which are more stable than dialkylsulfonium ylides.



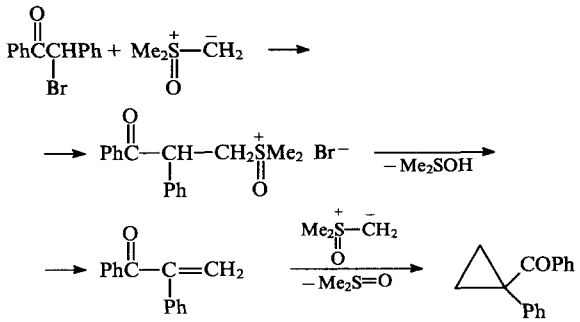
Together with oxosulfonium salts, oxosulfonium ylides have found extensive application in the synthesis of dienes, cycloalkanes, epoxy-compounds, spiro-compounds, and other products of fine organic synthesis. For example, the thermal rearrangement of certain alkenyloxosulfonium ylides is used in the synthesis of dienes.[2]



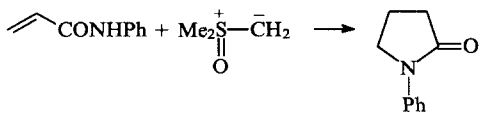
Oxosulfonium ylides are selective agents for the transfer of the methylene group to the electrophilic double bond. As a rule, these reactions lead to the formation of cyclopropanes. In the case of α,β-unsaturated carbonyl compounds, the methylene group adds not to the carbonyl group but to the C=C bond.



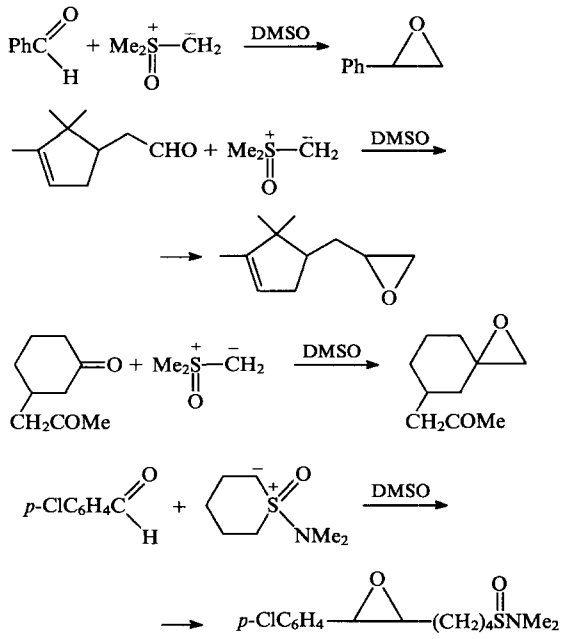
In the interaction of oxosulfonium ylides with α-bromoketones or esters, cyclopropanes are formed as a result of a sequence of alkylation, elimination, and methylene group transfer reactions.



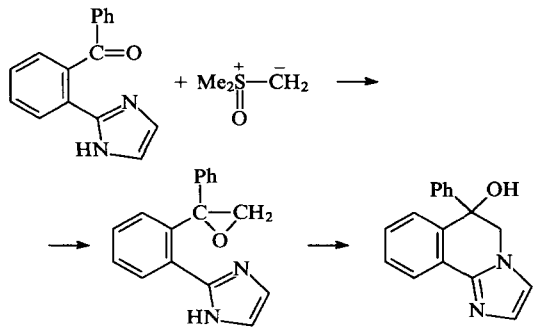
The transfer of the methylene group to the double bond in *N*-substituted amides of α,β-unsaturated carboxylic acids is accompanied by a prototropic shift and subsequent cyclisation with formation of γ-lactams.[2]



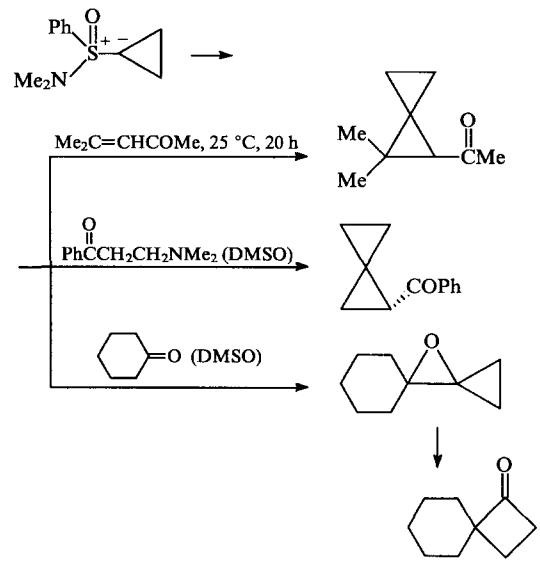
The addition of the methylene group to the C=O bond in aldehydes and ketones has found extensive application in the synthesis of epoxy-compounds with a wide variety of structures.[36]



In those cases where the epoxide molecule contains other reaction centres as well as the oxygen atom, there is a possibility of structural isomerisation.



The transfer of the cyclopropylidene group to the C=C and C=O bonds with the aid of cyclopropyloxosulfonium ylides is to a large extent analogous to the effect of diphenylsulfonium cyclopropylide (see above) and is used in the synthesis of spiro-compounds.[28]



* * *

It is seen from the present review that the application of S-cationoid reagents in fine organic synthesis has become very common during the last 10–15 years. It is based on the ability of such reagents to participate in the transfer of thiyl, methylene, and other functional groups and also on their involvement in the generation of radical-cations and ylides, in the selective oxidation of alcohols, and in other very important processes. This property is used widely in the syntheses of sulfides, cyclopropanes, epoxides, carbonyl compounds, spiro-compounds, sulfimides, sulfoximides, derivatives of iminosulfinic acids, and other important products of fine organic synthesis with functional group substituents.

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