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Fluorine-containing alkyl(aryl) vinyl sulfides

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Abstract. Approaches to the synthesis of fluorine-containing alkyl(aryl) vinyl sulfides, their reactions with electrophilic and nucleophilic reagents and the behaviour in cycloaddition and oxidation reactions are considered systematically. The bibliography includes 136 references.

I. Introduction

The first data concerning fluorine-containing vinyl sulfides appeared in the early 1950s;[1, 2] however, no reviews considering the chemistry of these compounds have been published so far. The interest in this type of compound is due to their high reactivity and the possibility of converting them into biologically active preparations and materials for engineering. In addition, researchers keep an eye on the theoretical aspects of the chemistry of fluorine-containing vinyl sulfides. The presence of the sulfur atom, possessing p electrons and vacant d orbitals, together with a multiple bond within the same molecule stipulates the occurrence of intramolecular pπ-interactions, which have a substantial influence on the properties of vinyl sulfides. Recent studies discuss fundamental problems such as the ability of the sulfur atom to stabilise carbocations, carbanions and radicals and the possibility of migration of substituents in the carbon – carbon – sulfur triad. The influence of the fluorine atoms rich in 2p electrons and the electron-withdrawing polyfluoroalkyl groups on the properties of α,β-unsaturated sulfides are under investigation.

This review covers the most important data on methods of synthesis and chemical properties of alkyl(aryl) vinyl sulfides containing fluorine atoms and/or fluorinated substituents both at the double bond and at the sulfur atom. The scope of consideration includes compounds with several heteroatoms at the double bond having a high preparative value, for example, ketene thioacetals and their O- and N-analogues, whose chemical properties are similar to those of vinyl sulfides.

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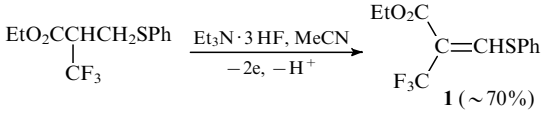
II. Methods of synthesis

Fluorinated α,β-unsaturated sulfides are synthesised by means of electrophilic and nucleophilic substitution, addition, elimination and condensation reactions usual for organic chemistry.

1. α,β-Elimination in fluorine-containing sulfides

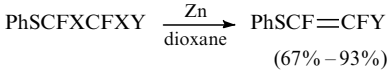
Elimination reactions, first of all, dehydrohalogenation, are employed most widely to prepare fluorine-substituted vinyl sulfides, because sulfides are readily produced upon the addition of thiols to fluoroalkenes. Various organic and inorganic bases are used as dehydrohalogenating agents. Examples of such reactions are listed in Table 1.

Anodic oxidation of ethyl 3,3,3-trifluoro-2-phenylthiomethylpropionate in the presence of $Et_3N \cdot 3\,HF$ in acetonitrile results in β-phenylthio-α-(trifluoromethyl)acrylate **1**.[30]



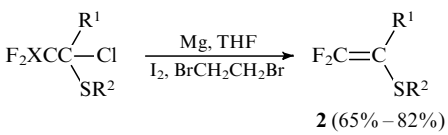
Presumably, this reaction proceeds *via* a radical cation, which reacts with the fluoride ion. The β-fluorinated sulfide formed in the first step is unstable under the reaction conditions and is readily dehydrofluorinated to give sulfide **1**.

Vinyl sulfides can be efficiently purified from saturated sulfides by halogenation of the reaction mixture, separation of the resulting high-boiling dihalides and the subsequent dehalogenation with zinc in dioxane.[5, 6]



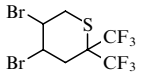
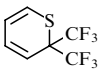
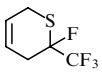
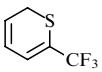
X = Cl, Br; Y = F, Cl, CF_3.

Vinyl sulfides **2** with a terminal difluoromethylidene group were prepared by dehalogenation of the corresponding sulfides on treatment with magnesium in the presence of catalytic amounts of iodine and 1,2-dibromoethane.[31]



R^1 = H, F, Cl, EtS; R^2 = Ph, Et; X = F, Cl.

Table 1. Synthesis of vinyl sulfides by dehydrohalogenation of halogen sulfides.

Starting sulfide	Vinyl sulfide	Reagents and conditions	Yield (%)	Ref.
$RSCF_2CHXY$ (X = F, Y = Cl, R = Me, Et, Bn, Ph; X = Y = Cl, R = Ph; X = F, Y = CF_3, R = Bn, Ph)	$RSCF{=}CXY$	KOH (solid)	~75	1, 3–8
$MeSCF_2CHX_2$ (X = F, Cl)	$MeSCF{=}CX_2$	KOH, DMSO	80–90	9
$RSCH(CF_3)CH_2Cl$	$RSC(CF_3){=}CH_2$	KOH, MeOH	~90	10, 11
$F_3CSCH_2CH_2Cl$	$F_3CSCH{=}CH_2$	KOH, EtOH	97	12
$Cl_2FCCF_2SCH_2CH_2Cl$	$Cl_2FCF_2CSCH{=}CH_2$	KOH, $(EtOCH_2CH_2)_2O$	71	13
$(F_3C)_2CHSEt$	$F_2C{=}C(CF_3)SEt$	KOH, Et_2O	58	14
$F_3CSCH_2CHBrSCF_3$	$F_3CSCH{=}CHSCF_3$	KOH, EtOH	38	12, 15
$PhSCH_2CHBrCF_3$	$PhSCH{=}CHCF_3$	KOH, EtOH	–	16
$PhSCHBrCHBrCF_3$	$PhSCH{=}CBrCF_3$	KOH, EtOH	85	16
$F_3CCH(SPh)_2$	$F_2C{=}C(SPh)_2$	KOH, THF	62	17
$F_2HC(CF_2)_3CH(SR)_2$ (R = Bn, Pr^n, 4-MeC_6H_4)	$F_2HC(CF_2)_2FC{=}C(SR)_2$	NaOH, $C_4H_8O_2$	~77	18
$R_fF_2CCH(SR)_2$ (R_f = F, CF_3, C_2F_5; SR = SEt, $S(CH_2)_3S$)	$R_fFC{=}C(SR)_2$	KOH, H_2O, CH_2Cl_2, Bu_4NBr	80–97	19
$F_3CCH(SPh)_2$	$MeOFC{=}C(SPh)_2$	KF, MeOH	71	17
$F_3CSCH(CH_2Cl)CO_2Me$	$F_3CSC(CO_2Me){=}CH_2$	NEt_3	60	20
$F_3CCH(SR)CH_2Cl$ (R = Alk, Ar)	$F_3CC(SR){=}CH_2$	NEt_3	~90	21–23
$(F_3C)_2CHSMe$	$F_2C{=}C(CF_3)SMe$	$BF_3 \cdot NEt_3$	73	24
$F_3CCH(X)CF_2SR$ (X = CF_3, CO_2Me; R = Bn, Bu^t)	$F_3CC(X){=}CFSR$	$BF_3 \cdot NEt_3$	57–70	3, 25
$F_3CCH(SR^1)XR^2$ (R^1, R^2 = Me, Et, Ph; X = O, S)	$F_2C{=}CXR^2$ (SR^1)	AlkLi	62–70	26, 27
F_3CCH_2SPh	$F_2C{=}CHSPh$	$LiNPr^i_2$	15	28
		KOH	60	29
		in a glass vessel	–	29

Dehalogenation takes place also in the reaction of n-butyl 2,2,3,3,4,4,5,5-octafluoro-1,1-dichloropentyl sulfide (**3**) with triphenylphosphine.[32]

$$F_2HC(CF_2)_3CCl_2SBu^n + Ph_3P \longrightarrow$$

3

$$\longrightarrow [F_2HC(CF_2)_3\overset{-}{C}ClSBu^n\ Ph_3\overset{+}{P}Cl] \xrightarrow{-Ph_3PClF}$$

$$\longrightarrow F_2HC(CF_2)_2CF{=}CClSBu^n$$

(77%)

Distillation of 1,1,1-triethoxy-2,2-bis(trifluoromethylthio)-ethane, prepared by the reaction of trifluoromethanesulfenyl chloride with ethyl orthoacetate, is accompanied by elimination of an ethanol molecule to give 1,1-diethoxy-2,2-bis(trifluoromethylthio)ethylene (**4**).[33]

$$(F_3CS)_2CHC(OEt)_3 \xrightarrow[-EtOH]{\Delta} (F_3CS)_2C{=}C(OEt)_2$$

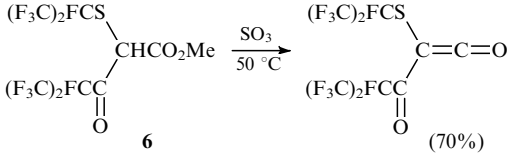
4 (27%)

Dehydration of bis(trifluoromethylthio)acetic acid on heating with P_2O_5 gives bis(trifluoromethylthio)ketene (**5**).[34]

$$(F_3CS)_2CHCO_2H \xrightarrow[80-100\ ^\circ C]{P_2O_5} (F_3CS)_2C{=}C{=}O$$

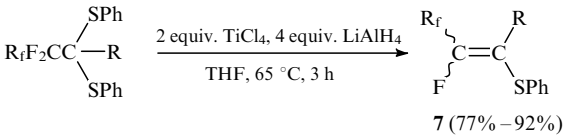
5 (60%)

Perfluorinated isobutyryl(isopropylthio)ketene is formed on heating of the methyl ester **6** in SO_3 at 50 °C.[35]



6 (70%)

An efficient method which allows one to prepare tetrasubstituted phenylthioalkenes **7** in high yields has been developed.[36]

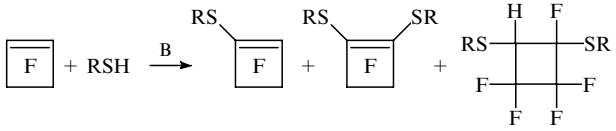


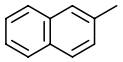
7 (77%–92%)

R = Me, Pr^n, cyclo-C_6H_{11}, Ph; R_f = F, F_3C, F_5C_2.

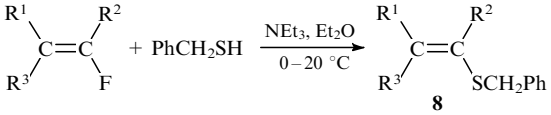
2. The introduction of alkyl(aryl)thio groups into unsaturated compounds using nucleophilic substitution reactions

Fluorinated vinyl sulfides were first prepared [1] by the reaction of perfluorocyclobutene with thiols in the presence of organic bases (NEt_3, Triton B). This gave a mixture of products resulting from replacement of one or two vinylic fluorine atoms.



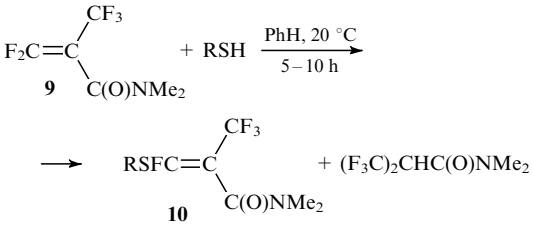
R = Bu^n, HO_2CCH_2, .

Subsequently, this reaction was extended to various fluoroalkenes of both aliphatic and alicyclic series with an internal double bond.[37–39] For example, the reaction of fluoroalkenes with α-toluenethiol in the presence of triethylamine gives vinyl sulfides **8** in 40%–65% yields.[37]



R^1 = R^2 = CF_3, R^3 = Cl; R^1–R^2 = $(CF_2)_3$, R^3 = CF_3;
R^1–R^2 = $(CF_2)_2$, R^3 = F; R^1–R^2 = $(CF_2)_4$, R^3 = Cl;
R^1 = R^2 = CF_3, R^3 = C_2F_5.

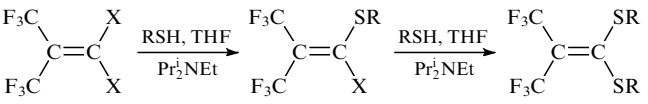
Unlike internal alkenes, fluoroalkenes with a terminal double bond are usually converted into addition products at the C=C bond when they react with thiols in the presence of organic bases; in some cases, the reaction mixtures contain vinylic substitution products as impurities (up to 20%).[3,4,40,41] An exception to this rule is the dimethylamide of perfluoromethacrylic acid (**9**), which reacts with PhSH and $PhCH_2SH$ to give products of replacement of the fluorine atom **10** (as a mixture of *cis*- and *trans*-isomers according to ^{19}F NMR data) apart from hexafluoroisobutyric dimethylamide.[42]



R = Ph, Bn.

This outcome was explained in the study cited by the noticeable basicity of the dimethylamide group, which can trap the eliminated proton thus preventing its addition to the carbanion centre. As a consequence, the intermediate carbanions are stabilised by giving off a fluoride ion to afford vinyl sulfides.

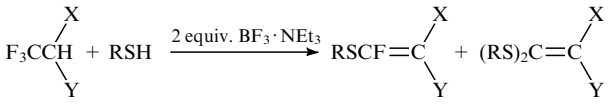
It has been shown recently that perfluoroisobutylene and its chlorinated analogue, *viz.*, 1,1-dichloro-2-trifluoromethyl-3,3,3-trifluoropropene, react with aromatic thiols in THF in the presence of equimolar amounts of diisopropylethylamine giving rise to bis(trifluoromethyl)ketene dithioacetals **11**.[43] When the stoichiometry is strictly maintained, monosubstitution products can also be isolated in these reactions.



11 (62%–78%)

R = Ph, 2-$MeOC_6H_4$, 4-$MeOC_6H_4$; X = F, Cl.

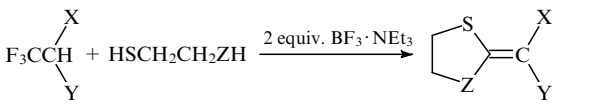
The reactions of thiols with α-trifluoromethyl-substituted CH-acids such as compounds **12a–d** in the presence of $BF_3 \cdot NEt_3$ represent a convenient method for the synthesis of β-functionally substituted vinyl sulfides and ketene dithioacetals.[44]



12a–d

R = Me, Bu^t, Bn, CH_2CO_2Me; X = CF_3: Y = CO_2Me (**a**), CN (**b**); X = Y = CO_2Me (**c**); X = F, Y = CN (**d**).

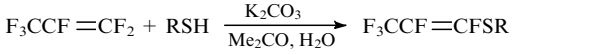
Undoubtedly, the first step of this reaction involves dehydrofluorination of the CH-acid to give fluoroalkene, which is attacked *in situ* by the anion generated upon the action of $BF_3 \cdot NEt_3$ on the thiol. The intermediate thus formed is stabilised through β-elimination of the fluoride ion, which is bound irreversibly by the $BF_3 \cdot NEt_3$ complex. This is why the reaction mixture contains no addition products. The ratio of mono- to di-substituted products depends on the CH-acidity of the substrate, on the reactant ratio, and on the structure of the starting thiol. When sterically hindered 2-methylpropane-2-thiol was used, no even traces of the corresponding ketene dithioacetals were detected in the reaction mixture. By using three equivalents of $BF_3 \cdot NEt_3$ and two equivalents of the thiol, one can deliberately obtain disubstituted products. In particular, bifunctional thiols such as ethane-1,2-dithiol and mercaptoethanol are converted into cyclic thioacetals **13** in high yields.[44]



12a,**b**,**d** **13** (72%–82%)

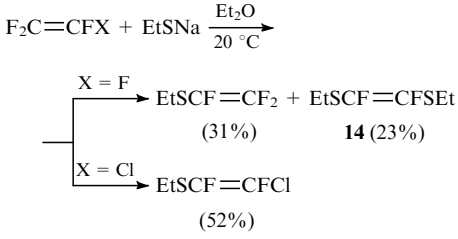
X = F, CF_3; Y = CO_2Me, CN; Z = O, S.

A method for the synthesis of vinyl sulfides by the reaction of perfluoropropylene with thiols in the presence of a solution of potassium carbonate in aqueous acetone has been patented.[45]



R = Alk, Ar.

When fluoroalkenes are made to react with sodium or lithium thiolates, fluorinated vinyl sulfides mixed with the addition products are formed.[5,6,46,47] In some cases, these reactions do not give saturated thioethers.[48,49] In the case of tetrafluoroethylene, further reaction takes place resulting in symmetrical bis(ethylthio)alkene **14**.[48]



The order of mixing of the reactants is significant in the reactions of fluoroalkenes with thiolates. Indeed, the addition of perfluoroisobutylene to a suspension of RSNa in ether gives rise to double substitution products, namely, ketene dithioacetals **11**, whereas the reverse order of reactant mixing results in the predominant formation of monosubstituted compounds **15**.[50,51]

$$(F_3C)_2C{=}CF_2 \xrightarrow[-NaF]{NaSR} (F_3C)_2C{=}C(SR)_2 + (F_3C)_2C{=}CFSR$$

11 (40%–45%) **15** (43%–55%)

R = Et, Bu^n, Ph.

A similar nucleophilic displacement of fluorine on treatment with sodium ethanethiolate takes place for perfluoroalkenyl ethers **16**. The reaction affords mixed ketene acetals **17**.[50]

$$(F_3C)_2C{=}CFOR + NaSEt \longrightarrow (F_3C)_2C{=}C(OR)(SEt)$$

16 **17**

R = Me, Et.

When perfluoroisobutylene reacts with potassium diethyl phosphorodithioate, one fluorine atom is replaced in the first stage to give compound **18**, which cannot be isolated because it spontaneously decomposes. The resulting thioketene **19** dimerises to give dithiacyclobutane derivative **20**.[52]

$$(F_3C)_2C{=}CF_2 + (EtO)_2PSSK \xrightarrow[-KF]{}$$

$$\longrightarrow \left[(F_3C)_2C{=}C(F)\text{–}P(OEt)_2 \,(=S) \xrightarrow[-FPS(OEt)_2]{} (F_3C)_2C{=}C{=}S \right] \xrightarrow{19}$$

18 **19**

$$\longrightarrow (F_3C)_2C{=}C(\text{–}S\text{–})C{=}C(CF_3)_2$$

20 (75%)

The dimer **20** is also formed in the reaction of perfluoroisobutylene with salts of other thiol acids.[52–55]

Heating of copper trifluoromethanethiolate with 1,2-dibromoethylene in *N*-methylpyrrolidone furnishes 1,2-bis(trifluoromethylthio)ethylene (**21**).[56]

$$F_3CSCu + BrHC{=}CHBr \xrightarrow{100\ ^\circ C,\ 48\ h} F_3CSCH{=}CHSCF_3$$

21 (64%)

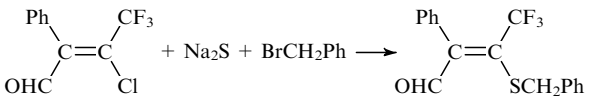
On treatment with the ethanethiolate anion, the chlorine atom in β-functionally substituted α-trifluoromethyl-α-chloroethylenes **22** is substituted. The reaction affords a mixture of *Z* and *E* isomers of vinyl sulfides **23** where the *Z* isomer markedly predominates.[57] Unfortunately, the method of generation of the thiolate anion is not indicated in the study cited.

$$R^1\text{–}C(C(O)R^2){=}CClCF_3 \xrightarrow{EtS^-} R^1\text{–}C(C(O)R^2){=}CCF_3(SEt)$$

22 **23**

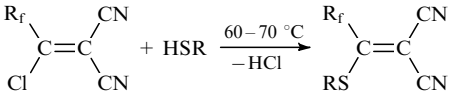
R^1 = H, R^2 = Ph; R^1 = Ph, 4-ClC_6H_4,  ; R^2 = H.

Successive treatment of 3-chloro-2-phenyl-3-trifluoromethylacrolein with sodium sulfide and benzyl bromide yields vinyl sulfide **24** resulting from substitution of the benzylthio group for the chlorine atom.[58]



24 (78%)

1-Chloro-2,2-dicyano-1-polyfluoroalkylethylenes react with thiols on heating in the absence of bases. The reaction can be followed by monitoring the evolution of hydrogen chloride.[59]



(72%–90%)

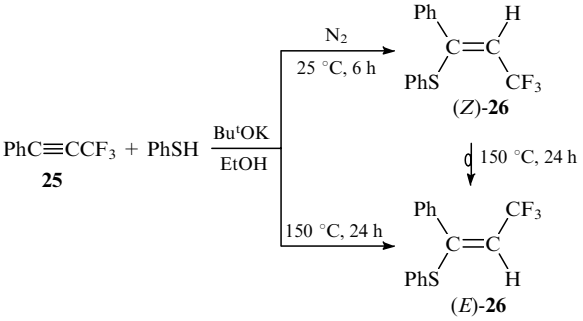
R = Bn, CH_2CO_2Me; R_f = CF_3, C_2F_5.

When bases, for example, triethylamine, are added as HCl acceptors, resinification of the reaction mixture takes place.

3. The addition of sulfur-containing reagents to alkynes and allenes

Nucleophilic and radical addition of sulfur-containing reagents to alkynes, which allows one-step synthesis of vinyl sulfides, has been thoroughly studied.[60] Both fluorine-containing alkynes and fluorinated thiols can be used to prepare fluorine-containing vinyl sulfides.

The addition of PhSH to trifluoromethyl(phenyl)acetylene (**25**) proceeds in the presence of potassium *tert*-butoxide in ethanol; the product yield is nearly quantitative.[61]

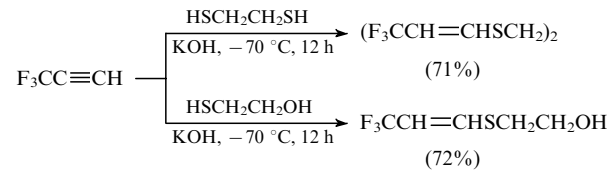


(*Z*)-**26**

(*E*)-**26**

Under kinetically controlled conditions, this reaction gives only *Z* isomer of vinyl sulfide **26**, while under conditions of thermodynamic control, a mixture of products is formed with substantial predominance of the *E* isomer (*Z*:*E* = 23:64). At 150 °C, vinyl sulfide (*Z*)-**26** isomerises to give the *E* isomer. It is noteworthy that the oxygen analogue of sulfide **26** does not tend to undergo such *Z*,*E* isomerisation. The easy isomerisation of vinyl sulfide (*Z*)-**26** was explained by orbital interaction between the sulfur atom and the trifluoromethyl group. A similar situation is observed for the addition of thiols to trifluoromethyl-containing alkynes activated by an aldehyde or a keto group.[62]

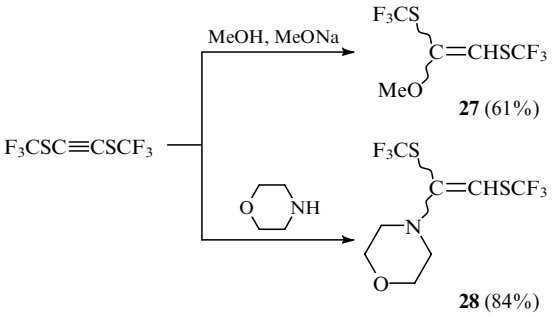
The reaction of 1,1,1-trifluoropropyne with bifunctional thiols proceeds in good yields under mild conditions; in the case, of 2-mercaptoethanol, the reaction proceeds selectively involving the sulfur atom.[63]



(71%)

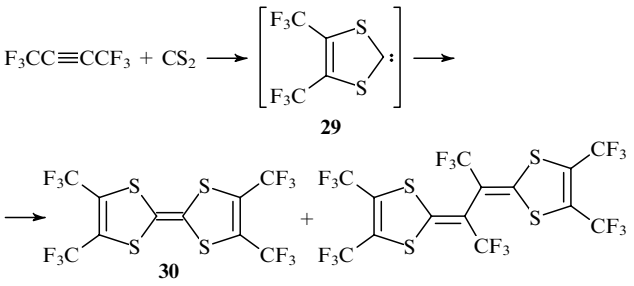
(72%)

Nucleophilic addition of methanol (in the presence of sodium methoxide) or morpholine to bis(trifluoromethylthio)acetylene gives rise to mixtures of *cis*- and *trans*-isomers of the corresponding vinyl sulfides **27**, **28**.[12]

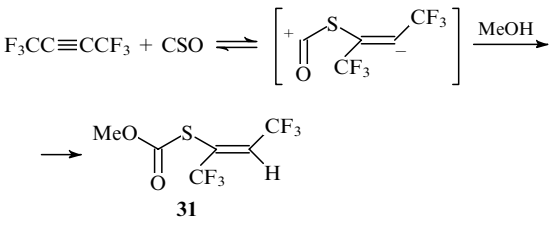


The addition of morpholine to benzylthiopolyfluoroalkylacetylenes also gives products in high yields.[64]

Carbon disulfide reacts with activated alkynes at ~100 °C in methanol to give mixtures of products.[65] The initial stage of the reaction is cycloaddition of the alkyne to carbon disulfide to give intermediate carbene **29**; it can either dimerise to give adduct **30** or participate in other reactions.



Carbonyl sulfide reacts with hexafluorobutyne in methanol to give *O*-methyl *S*-vinyl thiocarbonate **31**.[65]



Radical addition of trifluoromethanethiol to methyl propiolate affords a mixture of *cis*- and *trans*-isomers of methyl β-trifluoromethylthioacrylate **32** in good yield.[20] Ester **32** was converted by standard procedures into the corresponding acid, acyl chloride, amide and nitrile.

$$F_3CSH + HC{\equiv}CCO_2Me \xrightarrow{h\nu} F_3CSCH{=}CHCO_2Me$$

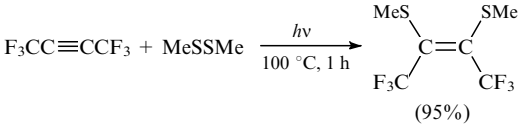
32 (57%)

Under free radical reaction conditions, trifluoromethanethiol or trifluoromethanesulfenyl chloride add to bis(trifluoromethylthio)acetylene.[12]

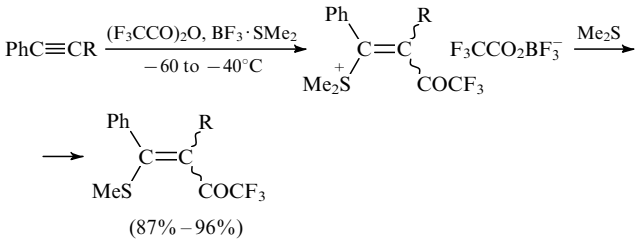
$$F_3CSC{\equiv}CSCF_3 + F_3CSX \xrightarrow{h\nu} (F_3CS)_2C{=}CXSCF_3$$

X = H (39%), Cl (47%).

The reaction of dimethyl disulfide with hexafluorobutyne occurs on irradiation and heating.[66]



When trifluoroacetic anhydride and the dimethyl sulfide – BF_3 complex react with alkynes, conjugate addition of the CF_3CO group and dimethyl sulfide takes place to give sulfonium salts. In the reaction with excess dimethyl sulfide, they are demethylated yielding β-methylthio-substituted α,β-unsaturated trifluoromethyl ketones.[67]



R = H, Me, Et.

Tetrakis(trifluoromethyl)allene reacts with thiols on heating with the formation of α,β-unsaturated sulfides **33a**,**b**.[68]

$$(F_3C)_2C{=}C{=}C(CF_3)_2 + RSH \xrightarrow{140\ ^\circ C} (F_3C)_2CHC(SR){=}C(CF_3)_2$$

33a,**b**

R = Et (**a**, 48%), Ph (**b**, 81%).

The substantially lower yield of compound **33a** is due to the fact that ethanethiol is able to efficiently reduce the multiple bond in the allene, which gives $(F_3C)_2CHCH{=}C(CF_3)_2$ and Et_2S_2.

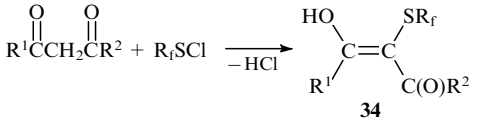
The reaction of 1,1-difluoroallene with α-toluenethiol in the presence of KOH gives initially the addition product; this is followed by vinylic replacement of the fluorine atom in this product.[69]

$$F_2C{=}C{=}CH_2 + PhCH_2SH \xrightarrow[60\ ^\circ C]{KOH,\ THF} PhCH_2SCF{=}CHCH_2SCH_2Ph$$

(61%)

4. C-Sulfenylation involving fluorine-containing sulfenyl chlorides

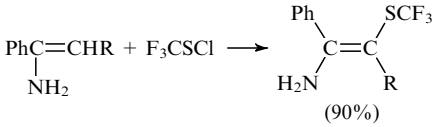
The reactions of β-diketones, β-ketoesters and their anilides with polyfluoroalkanesulfenyl chlorides afford compounds that exist almost completely, according to ^1H NMR spectra of $CDCl_3$ solutions, as enols, *i.e.*, β-hydroxyvinyl sulfides **34**.[21,70–72]



R^1 = Me, Ph; R^2 = Me, Ph, OEt, NH_2, NHPh; R_f = CF_3, $ClCH_2CH(CF_3)$, MeO_2CCF_2, $MeO_2CCF(CF_3)$, $MeO_2CC(CF_3)_2$.

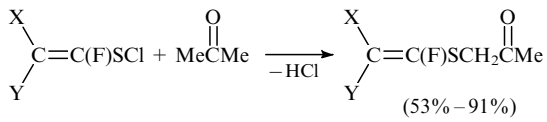
These reactions usually proceed under mild conditions without a solvent and give products in high yields.

Similarly to enolisable ketones, enamines react with polyfluoroalkanesulfenyl chlorides to give monosubstituted products.[73,74]



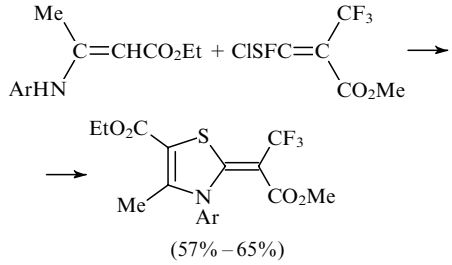
R = $C(O)NH_2$, CN.

α-Fluoro-α,β-unsaturated sulfenyl chlorides easily form C-sulfenylated products with π-donor aromatic and heteroaromatic compounds, various enolisable carbonyl compounds, and some enamines.[25,75–77] For example, the reaction with acetone affords monosulfenylation product.

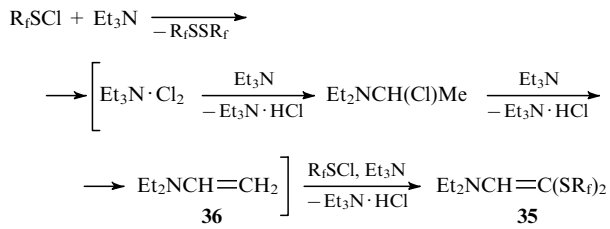


X = CF_3, Y = CF_3, CO_2Me, CN; X = Y = CO_2Me.

The reaction of 1,3,3,3-tetrafluoro-2-methoxycarbonylpropenesulfenyl chloride with esters of 3-(arylamino)crotonic acid takes place under mild conditions. The reaction is accompanied by intramolecular dehydrofluorination and cyclisation giving rise to substituted *N*-aryl-2-(1-methoxycarbonyltrifluoroethylidene)-2,3-dihydrothiazoles.[76]



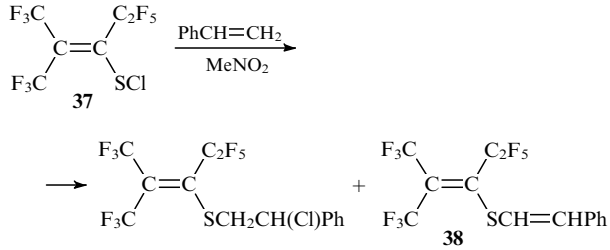
The reactions of chlorofluoromethanesulfenyl chlorides with triethylamine furnish vinyl sulfides **35**. This can be a result of electrophilic replacement of hydrogen in enamine **36**.[78]



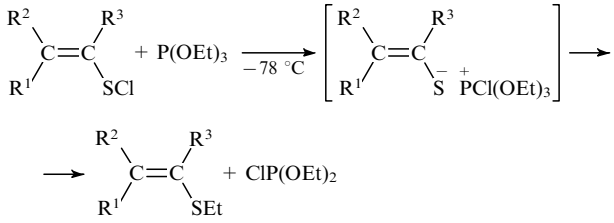
R_f = CF_3, CF_2Cl, $CFCl_2$.

In the first step, sulfenyl chloride acts as a chlorinating agent, as indicated by the presence of disulfide in the reaction mixture. Consecutive chlorination–dehydrochlorination of triethylamine results in enamine **36**, which reacts with two sulfenyl chloride molecules. The reaction with dicyclohexylethylamine proceeds in a similar way.[79]

Aliphatic and alicyclic α,β-unsaturated perfluorosulfenyl chlorides readily enter into electrophilic addition to a double bond; this is a way of introducing fluorine- and sulfur-containing unsaturated fragments into diverse alkenes. When activated alkenes, polar solvents and salt additives are used, replacement of vinylic hydrogen atoms and skeletal rearrangement of alkenes become possible apart from the addition reactions. For example, the reaction of perfluoro-3-chloro-2-methylsulfenylphenylpent-2-ene (**37**) with styrene gives vinylic substitution product **38** in a yield of up to 20%.[80]



The reactions of fluorine-containing α,β-unsaturated sulfenyl chlorides with triethyl phosphite give the corresponding alkenylethyl sulfides.[3]



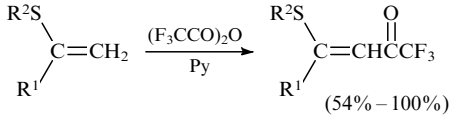
R^1 = R^2 = CF_3, R^3 = F; R^1 = CF_3, R^2–R^3 = $(F_2C)_3$.

Presumably, the attack is directed at the chlorine atom rather than at sulfur (in saturated nonfluorinated sulfenyl chlorides, nucleophiles attack the sulfur atom). As a consequence, the formally positively charged halogen is transferred to the phosphorus atom.

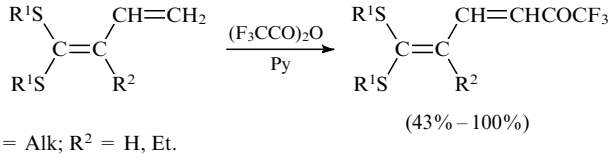
5. Trifluoroacylation of α,β-unsaturated sulfides

Trifluoroacetylation of alkyl(aryl)thioalkenes with trifluoroacetic anhydride at 20 °C or with cooling affords α,β-unsaturated β-alkyl(aryl)thio trifluoromethyl ketones.[81–83] In the presence of pyridine, the yields of reaction products increase. As the sulfur-containing alkenes, one can use vinyl sulfides, ketene dithioacetals and activated dienes such as 1,1-di(alkylthio)alka-1,3-dienes. In the last-mentioned case, the reaction proceeds stereoselectively to give the *E* isomers of enones.

Using ^{1}H NMR spectra and kinetic measurements, it was found that the reaction follows an addition–elimination mechanism.[84] Vinyl sulfides are trifluoroacylated non-stereoselectively.

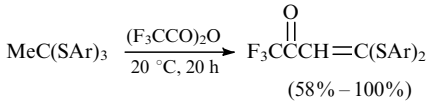


R^1 = H, Alk, Ar, SAlk, SAr; R^2 = Alk, Ar.

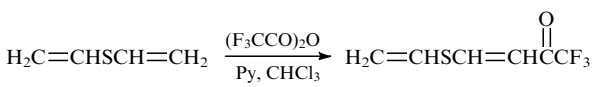


R^1 = Alk; R^2 = H, Et.

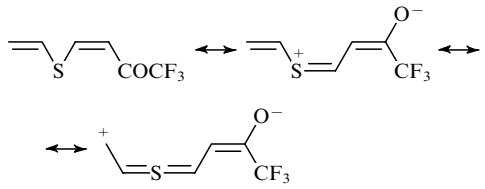
Aryl orthothioacetates react with excess trifluoroacetic anhydride with elimination of aryltrifluorothioacetate to give trifluoromethyl-α,β-enones, which are precursors of the corresponding ketene dithioacetals.[85]



In the case of divinyl sulfide, one vinyl group is trifluoroacylated.[86]

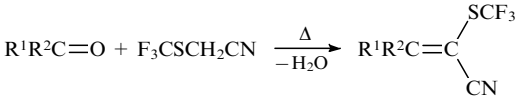


The unexpected reaction selectivity was explained [86] by assuming that the lone electron pair of sulfur occurs in strong p,π-conjugation with the trifluoroacetyl group, which substantially decreases the nucleophilicity of the second vinylthio group.



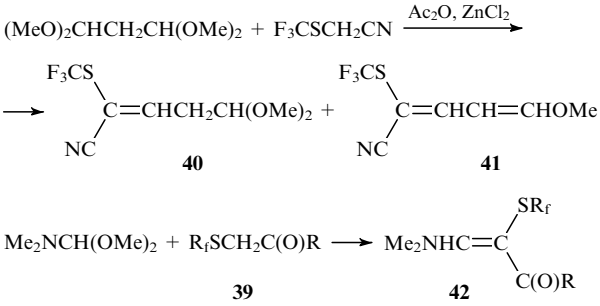
6. Condensation

α-Trifluoromethylthio-substituted acrylonitriles are produced according to the Knoevenagel reaction from trifluoromethylthioacetonitrile and carbonyl compounds.[20] This reaction can be carried out for aliphatic, alicyclic and aromatic aldehydes and ketones.



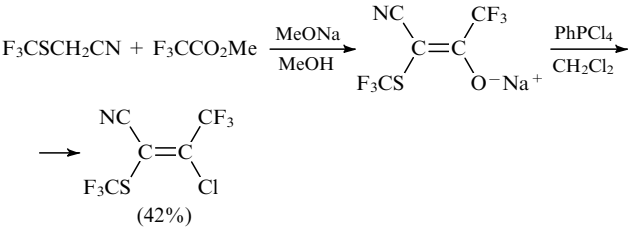
Ethyl(2-trifluoromethylthio)acetate, which has a lower CH-acidity, reacts with aldehydes under similar conditions but does not react with ketones.[87]

In some cases, aldehydes are replaced by their dimethyl acetals in condensations with CH-acids. For example, reactions of malondialdehyde bis(dimethyl acetal) with trifluoromethylthioacetonitrile[88] and *N*,*N*-dimethylformamide dimethylacetal with ketones **39**[89] have resulted in the formation of functionally substituted vinyl sulfides **40**–**42**, which are used in the syntheses of heterocyclic compounds.



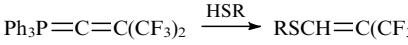
R_f = CF_3, CF_2Cl; R = Me, Pr^n.

Due to the high CH acidity caused by the presence of two electron-withdrawing groups, the nitrile and trifluoromethylthio ones, trifluoromethylthioacetonitrile enters into ester condensation with methyl trifluoroacetate. Chlorination of the resulting enol sodium salt leads to 3-chloro-3-trifluoromethyl-2-trifluoromethylthioacrylonitrile.[90]



7. Syntheses based on phosphonium ylides

Bis(trifluoromethyl)vinyl sulfides were prepared by heating triphenyl-2,2-bis(trifluoromethyl)vinylidenephosphorane with thiols.[91]



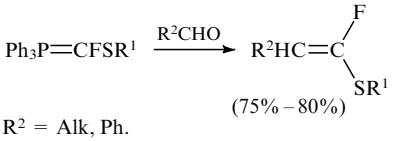
R = Et, C_6Cl_5.

Methods for the synthesis of diverse trisubstituted alkenes containing the alkyl(aryl)sulfenyl group have been developed on the basis of the Wittig reaction. The reaction involves various carbonyl compounds: ketones,[92] aldehydes,[93] esters,[94] and thioesters.[94–96]



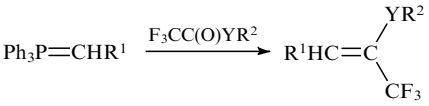
(29%–58%)

R = Me, Bn, Ph.



(75%–80%)

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



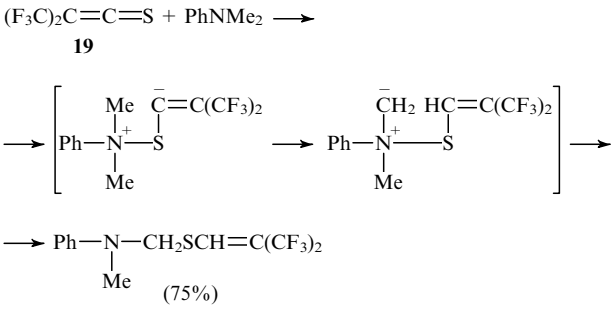
(16%–96%)

R^1 = Alk, Ph, SMe, SPh, CO_2Et, CN; R^2 = Et, C_6H_{13}; Y = S, O.

Butyllithium or sodium hydride is used as the base to generate ylides from the corresponding phosphonium salts.

8. Syntheses based on fluoro-containing thioketenes

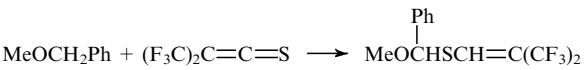
Bis(trifluoromethyl)thioketene (**19**) adds to *N*,*N*-dimethylaniline at 10 °C by attacking one of the methyl groups.[92] The process is interpreted as the electrophilic attack of the nitrogen atom by the sulfur atom followed by proton migration.



(75%)

N,*N*-Dimethyl-*p*-toluidine and *N*,*N*,*N*′,*N*′-tetramethylbenzidine also enter into this reaction (in the latter case, the bisadduct is formed). *N*-Ethyl-*N*-methylaniline and *N*,*N*-dimethyl-1-naphthylamine function as bases catalysing dimerisation of thioketene **19**.

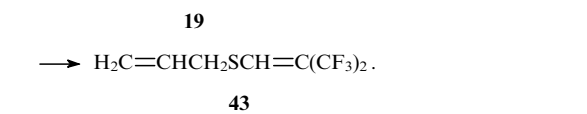
Diethyl ether and methyl benzyl ether react with bis(trifluoromethyl)thioketene (**19**) by a similar mechanism. In the latter case, 3,3,3-trifluoro-2-trifluoromethylpropenyl sulfide is produced.[92]



(60%)

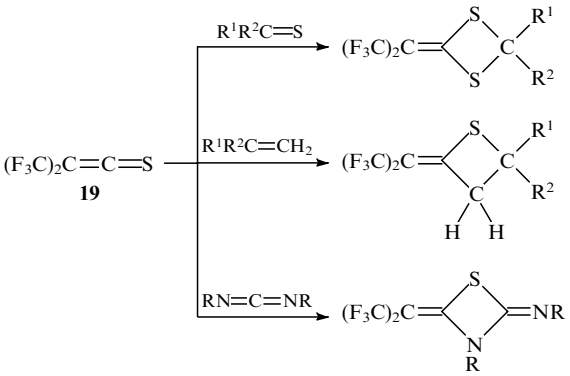
The ability of bis(trifluoromethyl)thioketene (**19**) to enter into ene reactions with some alkenes giving the corresponding propenyl sulfides and with allene and dialkylketenes was demonstrated using a large number of examples.[92]

For example, ketene **19** reacts with propylene to afford compound **43** in 61% yield.

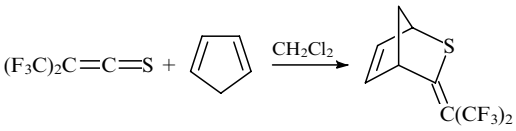


43

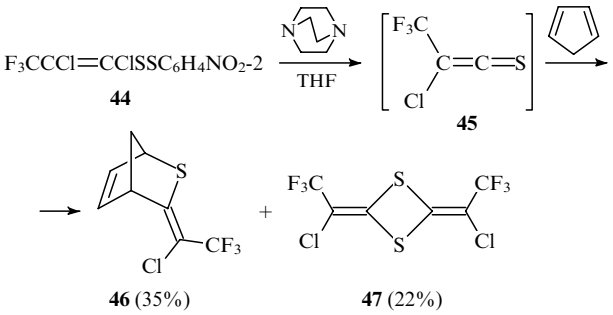
The reactions of bis(trifluoromethyl)thioketene **19** with unsaturated substrates such as thiocarbonyl compounds, alkenes unable to form the products of ene reactions, carbodiimides, *etc.* follow the [2 + 2]-cycloaddition pattern.[97]



When made to react with dienes such as 2,3-dimethylbuta-1,3-diene,[97] cylopentadiene and its derivatives, bis(trifluoromethyl)thioketene (**19**) is converted into [4 + 2]-cycloaddition products.[98] The adduct with cyclopentadiene was obtained in 96% yield.

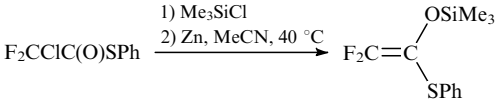


Disulfide **44** reacts with 1,4-diazabicyclo[2.2.2]octane with intermediate formation of chloro(trifluoromethyl)thioketene **45**, which was isolated as the adduct with cyclopentadiene. Along with bicyclic compound **46**, this reaction produces chloro(trifluoromethyl)thioketene **47**.[99]

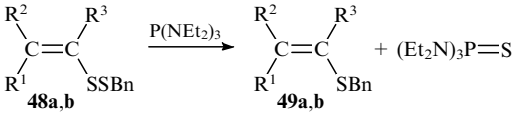


9. Other methods of synthesis

The addition of chlorotrimethylsilane to *S*-phenyl chlorodifluorothioacetate followed by dehydrochlorination on treatment with zinc was used to prepare a mixed acetal of difluoroketene.[100]

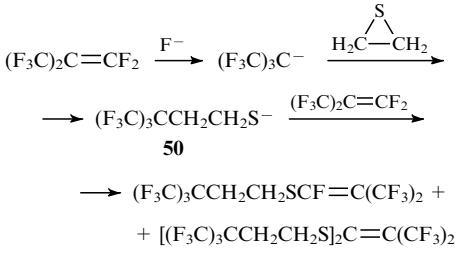


The reaction of benzyl polyfluoroalkenyl disulfides **48a**,**b** with phosphorous hexaethyltriamide is accompanied by desulfurisation and gives vinyl sulfides **49a**,**b**.[101, 102]

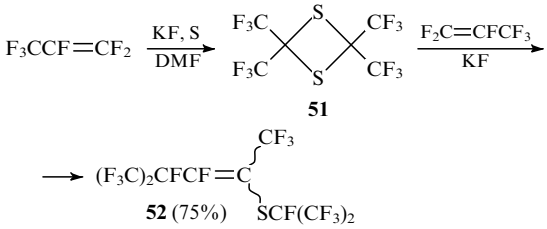


$R^1 = R^2 = CF_3$, $R^3 = C_2F_5$ (**a**, 72%);
$R^1 = R^2 = H$, $R^3 = CF_3$ (**b**, 81%).

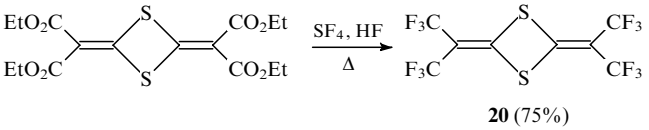
An interesting example of ring opening in ethylene sulfide on treatment with the perfluoro-*tert*-butyl carbanion, which is formed from perfluoroisobutylene in the presence of KF or CsF, has been reported.[103] Nucleophilic substitution of the resulting thiolate anion **50** for one or two fluorine atoms in perfluoroisobutylene results in a mixture of vinyl sulfides.



The reaction of hexafluoropropylene with potassium fluoride and sulfur in dimethylformamide leads to hexafluorothioacetone dimer **51**. The subsequent reaction of compound **51** with hexafluoropropylene leads to a mixture of *E* and *Z* isomers of perfluoro-2,4,6-tris(trifluoromethyl)-5-thiahept-3-ene (**52**).[35]



Heating of tetraethyl 1,3-dithiethanediylidenedimalonate with SF_4 in the presence of HF results in the formation of 2,4-bis[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-dithiethane (**20**), which is the dimer of bis(trifluoromethyl)thioketene **19**.[97]



Depending on the amount of hydrogen fluoride used, it is possible to isolate also the products of transformation of two or three ester groups into trifluoromethyl groups.

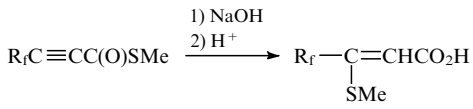
Dimer **20** is also obtained by the reaction of bis(trifluoromethyl)ketene (**19**) with triphenylphosphine sulfide at 200 °C.[104–106]

When reacting with organometallic reagents, esters of perfluoroalkanedithiocarboxylic acids are subjected to a thiophilic attack. The intermediate carbanion is stabilised by elimination of the α-fluorine atom. This reaction yields dithioacetals **53**.[107]

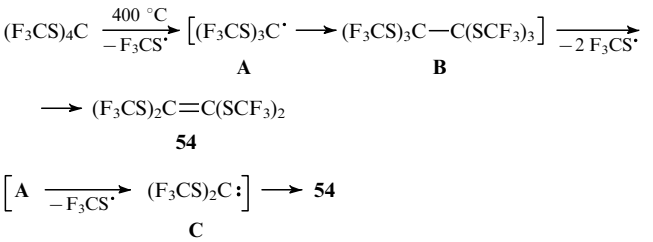


R_f = F, CF_3, $H(CF_2)_3$; R^1 = Et, Pr, Bn; R^2 = Et, Pr, Bu;
M = MgBr, Li.

The electron-withdrawing properties of the polyfluoroalkyl substituent are favourable for the 1,3-shift of the methylthio group in *S*-methyl β-polyfluoroalkylthiopropiolates on treatment with the hydroxide anion.[108] β-Polyfluoroalkyl-β-methylthioacrylic acids containing more than 90% *Z* isomer are formed in these reactions in high yields.



Pyrolysis of tetrakis(trifluoromethylthio)methane at 400 °C and at atmospheric pressure affords tetrakis(trifluoromethylthio)-ethylene **54**.[12]



Presumably,[12] this reaction follows a radical mechanism. Two pathways to the reaction product **54** are possible. The radical **A** formed initially can dimerise to give adduct **B**, which loses two trifluoromethylthiyl radicals being transformed into compound **54**. Radical **A** can be converted into bis(trifluoromethylthio)carbene **C**, which dimerises to give product **54**.

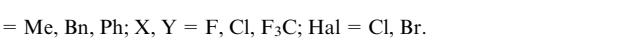
III. Chemical properties

Fluorine-containing vinyl sulfides behave both as alkenes and as sulfides. The reactivity of these compounds depends on the nature and position of substituents. If the fluorinated substituent occurs at the sulfur atom, the double bond differs little in properties from the usual double bond if one takes into account the electron-withdrawing influence of the substituent. Meanwhile, vinyl sulfides with fluorine-containing substituents at the double bond resemble to a larger extent electron-deficient fluoroalkenes, which exhibit a low reactivity toward electrophilic reagents. The behaviour of fluorine-containing vinyl sulfides depends appreciably on a number of factors including the presence of other electron-donating or electron-withdrawing substituents, the positive mesomeric effect of fluorine atoms at the multiple bond, the presence of a good leaving group in the molecule, and the degree of p,π-interaction between the sulfur atom and the double bond, which also depends on the electronic effects of the substituents. The diversity of factors influencing the reactivity of fluorine-containing vinyl sulfides markedly extends the synthetic potential of these compounds. In view of these considerations, the description of chemical properties of fluorinated vinyl sulfides is classified in this review in terms of the nature of the active reagent, irrespective of the reaction route.

1. Reactions with electrophilic reagents

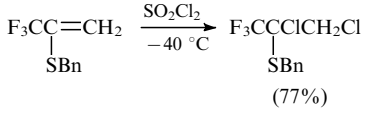
a. Halogenation

Alkyl(aryl)thiochloropolyfluoroethylenes are readily halogenated on treatment with equimolar amounts of chlorine or bromine.[3, 5, 6, 9]

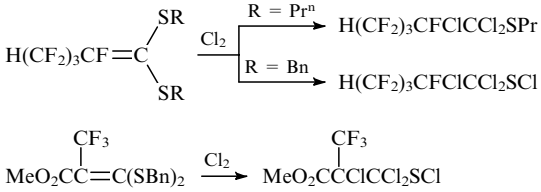


R = Me, Bn, Ph; X, Y = F, Cl, F_3C; Hal = Cl, Br.

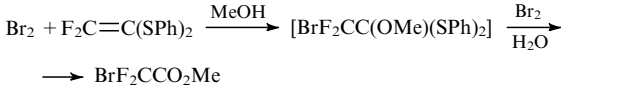
The use of sulfuryl chloride in this reaction gave a mixture of products, although SO_2Cl_2 chlorinates the double bond in benzyltrifluoroisopropenyl sulfide under very mild conditions.[101]



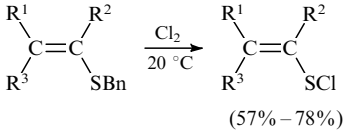
On treatment with excess chlorine, dithioacetals of fluorine-containing ketenes are chlorinated at the double bond with simultaneous replacement of one alkylthio group.[18] In the case where the sulfur atom carries a good leaving group, for example, a benzyl group, chlorolysis proceeds further to give sulfenyl chlorides.[18, 77]



Bromination of 2,2-difluoro-1,1-diphenylthioethylene in methanol is accompanied by conjugate electrophilic addition, as indicated by the formation of methyl bromodifluoroacetate after hydrolysis of the intermediate compound formed.[109]



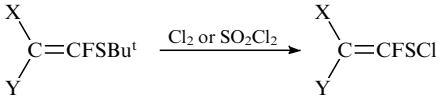
Some perfluoroalkenyl and perfluorocycloalkenyl benzyl sulfides having an electron-deficient multiple bond undergo chlorolysis at the S–Bn bond with retention of the vinyl fragment.[3]



(57%–78%)

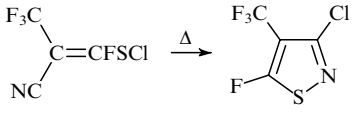
$R^1–R^2 = (CF_2)_4$, $R^3 = Cl$; $R^1–R^2 = (CF_2)_3$, $R^3 = CF_3$;
$R^1 = R^3 = CF_3$, $R^2 = F$.

A number of β-functionally substituted polyfluoroalkenesulfenyl chlorides have been prepared by chlorolysis of *tert*-butyl sulfides by chlorine [77] or sulfuryl chloride.[25]

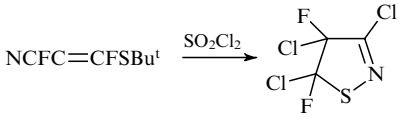


X = CF_3, Y = CO_2Me, CN; X = Y = CO_2Me.

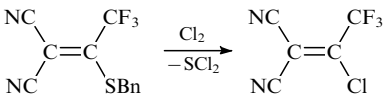
2-Cyano-1,3,3,3-tetrafluoropropenesulfenyl chloride synthesised in this reaction is a labile compound; on heating, it undergoes intramolecular cyclisation involving the nitrile group to give isothiazole.[77]



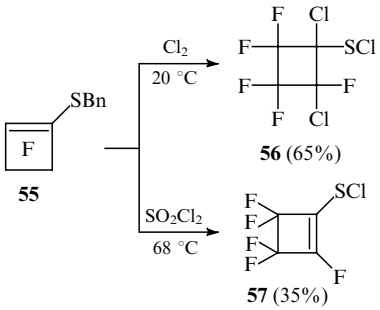
A similar intramolecular cyclisation of the intermediate sulfenyl chloride involving the nitrile group is observed in the chlorolysis of *tert*-butyl (2-cyano-1,2-difluorovinyl) sulfide.[77] Simultaneously, the double bond is chlorinated.



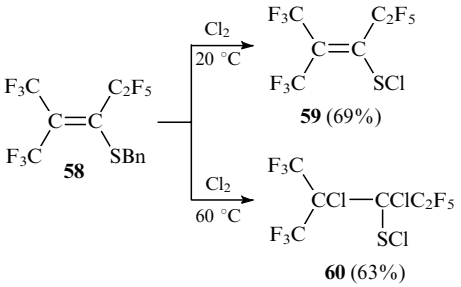
Chlorination of 1-benzylthio-2,2-dicyano-1-trifluoromethylethylene does not yield the expected sulfenyl chloride because both C–S bonds are immediately cleaved to give sulfur disulfide and 1-chloro-2,2-dicyano-1-trifluoromethylethylene.[77]



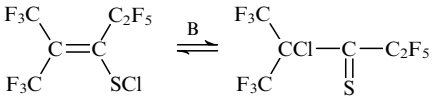
When 1-benzylthioperfluorocyclobutene (**55**) reacts with molecular chlorine, the replacement of the benzyl group is accompanied by chlorination of the double bond; as a result, saturated sulfenyl chloride **56** is formed as the final reaction product. Perfluorocyclobut-1-enesulfenyl chloride (**57**) was prepared by the reaction of benzyl sulfide **55** with SO_2Cl_2.[3]



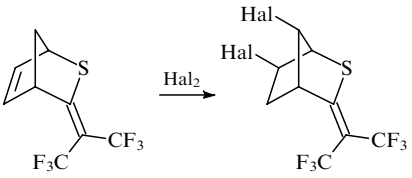
Vinyl sulfide **58** reacts with chlorine at 20 °C to give the corresponding unsaturated sulfenyl chloride **59**,[102] while at higher temperature, the product of further chlorination **60** was obtained together with sulfenyl chloride.



The formation of compound **60** was interpreted[102] as being due to chlorotropy in the carbon–carbon–sulfur triad.



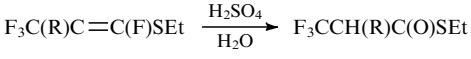
3-(Hexafluoroisopropylidene)-2-thiabicyclo[2.2.1]hept-5-ene and its derivatives are halogenated at the endocyclic double bond giving rise to the Wagner–Meerwein rearrangement products. The exocyclic double bond is not halogenated in this reaction.[98]



Hal = Cl, Br.

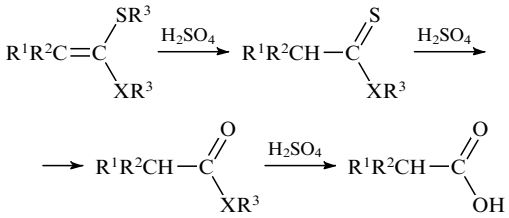
b. Acid hydrolysis

Acid hydrolysis of alkyl perfluorovinyl sulfide carried out under mild conditions affords *S*-esters of α-*H*-thiocarboxylic acids.[110]



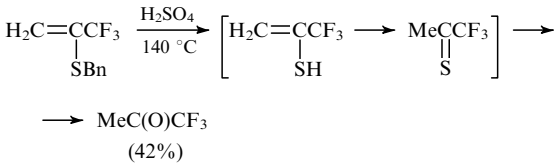
R = F, CF_3.

On treatment of *S,S*- or *S,O*-acetals of fluorine-containing ketenes with sulfuric acid, esters of dithiocarboxylic acids or thiocarboxylic *O*-acids, and esters of thiocarboxylic *O*-acids or carboxylic acids are formed successively, depending on temperature. Fluorine-containing carboxylic acids are the final reaction products.[18,26,27,110,111]



$R^1 = CF_3$, F, CHF_2; R^2 = F, CF_3, H, Alk, OMe;
R^3 = Alk, Ar; X = O, S.

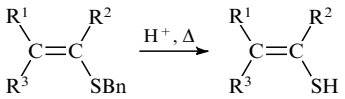
1,1,1-Trifluoroacetone was obtained by acid hydrolysis of benzyl 1,1,1-trifluoroisopropenyl sulfide.[101]



(42%)

This reaction is assumed to give first enethiol, which isomerises to give a thioketone and is subsequently oxidised to a ketone.

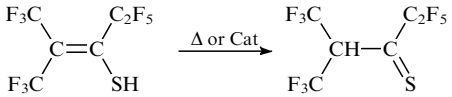
A general method for the synthesis of polyfluorinated enethiols **61** of the aliphatic and alicyclic series has been described.[37] Polyfluoroalkenyl(cycloalkenyl) benzyl sulfides are heated under conditions of kinetic control in the presence of fluorosulfonic acid or concentrated sulfuric acid with simultaneous removal of volatile products by evaporation.



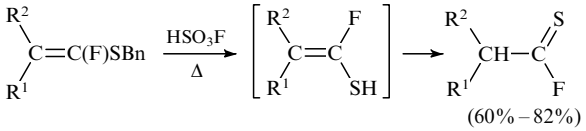
61 (30%–70%)

$R^1 = R^2 = CF_3$, R^3 = Cl; $R^1 = R^3 = CF_3$, $R^2 = C_2F_5$;
$R^1 = R^3 = (F_3C)_2CF$, $R^2 = CF_3$; $R^1–R^2 = (CF_2)_2$, R^3 = F;
$R^1–R^2 = (CF_2)_3$, $R^3 = CF_3$; $R^1–R^2 = (CF_2)_4$, R^3 = Cl.

Enethiols **61** are colourless liquids stable on storage; they do not isomerise spontaneously into the corresponding thioketones. The enethiol to thioketone isomerisation was accomplished only for perfluoro-2-methylpent-2-ene-3-thiol on heating (150 °C, 20 h) or in the presence of catalysts (HSO_3F, Et_2O, $BF_3 \cdot NEt_3$). The back transformation of the thioketone into enethiol does not take place.



In the case where the α-position with respect to the sulfur atom is occupied by a fluorine atom instead of the perfluoroalkyl group, the acid-induced cleavage of the corresponding perhaloalkenyl benzyl sulfides gives fluorides of fluorine-containing α-hydrothionic acids rather than enethiols as the final products.[4]

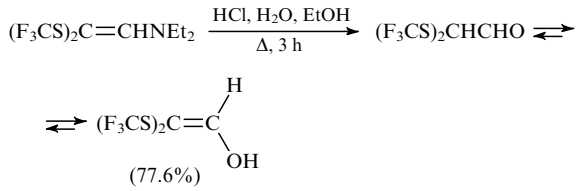


(60%–82%)

$R^1 = R^2 = CF_3$; $R^1 = CF_3$, R^2 = F; R^1 = F, R^2 = Cl.

It is reasonable to assume that this transformation involves the intermediate formation of enethiols, which are unstable under the reaction conditions (due to the substantial positive mesomeric effect of the vinylic fluorine atom) and isomerise to thermodynamically more stable forms.

Hydrolysis of the enamine, prepared from trifluoromethanesulfenyl chloride and triethylamine, furnishes bis(trifluoromethylthio)acetaldehyde, which mainly exists as the enol form.[112]

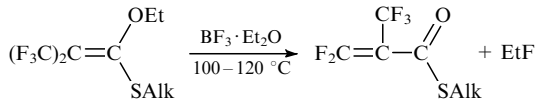


(77.6%)

A similar reaction carried out for β-alkyl(aryl)thio-α-polyfluoroalkyl-containing enamines readily gives the corresponding ketones.[64, 74]

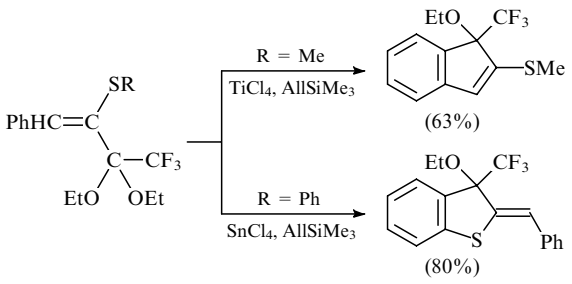
c. Other reactions

Electrophilic elimination of ethyl fluoride from bis(trifluoromethyl)ketene *O*-ethyl-*S*-alkyl acetals takes place on heating with boron trifluoride etherate.[113]

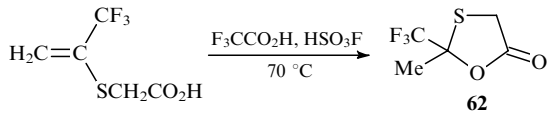


The reaction mechanism is similar to the mechanism of elimination of alkyl fluorides from bis(trifluoromethyl)ketene *O*,*O*-di- and *O*,*N*,*N*-trialkyl acetals in the presence of Lewis acids. On treatment with the Lewis acid, the allylic fluorine atom is eliminated from alkoxyalkene to give the mesomeric carbenium ion.[114] A similar reaction for *S*,*S*-dialkyl dithioacetals of bis(trifluoromethyl)ketene could not be performed.[113]

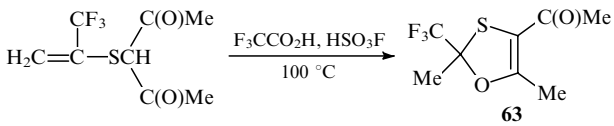
Acetals of α,β-unsaturated trifluoromethyl ketones containing an α-methylthio or α-phenylthio group do not undergo Lewis acid-catalysed intermolecular allylation. The products of intramolecular cyclisation are formed instead.[115]



Some trifluoroisopropenyl sulfides enter into acid-catalysed intramolecular cyclisation. Thus heating of 2-(1-trifluoromethylvinylthio)acetic acid in F_3CCO_2H in the presence of fluorosulfonic acid as the catalyst is accompanied by lactonisation giving thialactone **62** in a preparative yield.[21]

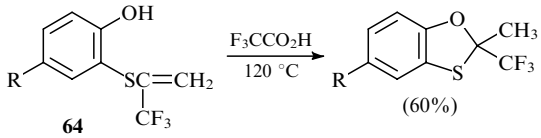


The intramolecular cyclisation of 3-(1-trifluoromethylvinylthio)pentane-2,4-dione occurs under more rigorous conditions.[21] The reaction is accompanied by resinification, the yield of compound **63** being not higher than 30%.



63

Cyclisation of *o*-(1-trifluoromethylvinylthio)phenols **64** occurs when this compound is heated to 120 °C in trifluoroacetic acid in a sealed tube.[116]

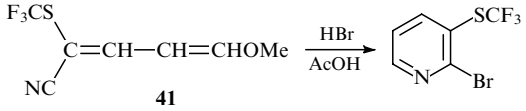


64

(60%)

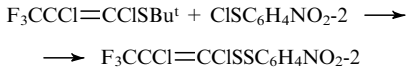
R = H, Me, Et.

The intramolecular cyclisation of 5-methoxy-2-trifluoromethylthiopenta-2,4-dienonitrile (**41**) induced by HBr and AcOH involves the nitrile group. This reaction was patented as a method of synthesis of 3-trifluoromethylthio-substituted pyridines.[117]

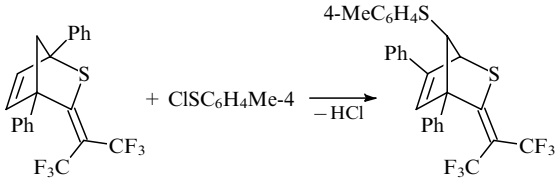


41

In the reaction of *tert*-butyl 2-trifluoromethyl-1,2-dichlorovinyl sulfide with *o*-nitrophenylsulfenyl chloride, the *tert*-butyl group at the sulfur atom is replaced, which results in an asymmetric disulfide.[99]

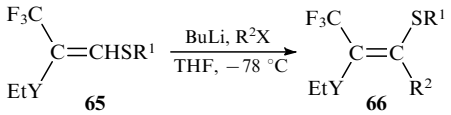


The reaction of 3-(hexafluoroisopropylidene)-1,4-diphenyl-2-thiabicyclo[2.2.1]hept-5-ene with *p*-methylbenzenesulfenyl chloride yields the Wagner – Meerwein rearrangement product, which is spontaneously dehydrochlorinated.[98]



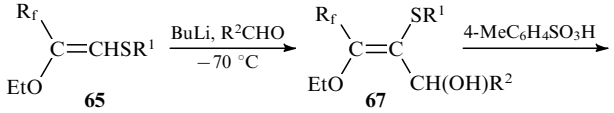
An important feature of sulfur compounds is the ability to stabilise both carbanionic and carbocationic centres.

The ability of sulfur atoms to stabilise α-carbanions has been used in the alkylation of β-polyfluoroalkyl-α-hydrovinyl sulfides **65**. Successive treatment of compounds **65** with butyllithium and alkyl halides [94] or with non-ionisable aldehydes leads to alkylation products **66** and **67**.[115]

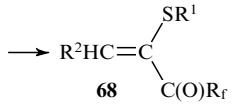


65 **66**

R^1 = Me, Ph; R^2 = Me, All, Bn; X = Br, I; Y = O, S.



65 **67**



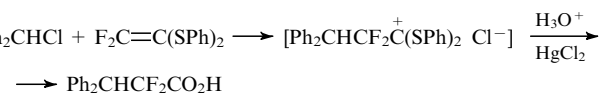
68

$R_f = CF_3, C_2F_5$; R^1 = Me, Ph;

R^2 = Ph, Bu^t, PhCH=CH, PhC≡C, Bu^{t}C≡C, 2-furyl.

The adducts **67**, formed in the reactions with aldehydes, are converted into α,β-unsaturated perfluoroalkylvinyl ketones **68** on treatment with *p*-toluenesulfonic acid. This reaction is stereoselective, giving rise to *Z* isomers of alkenes **68**.

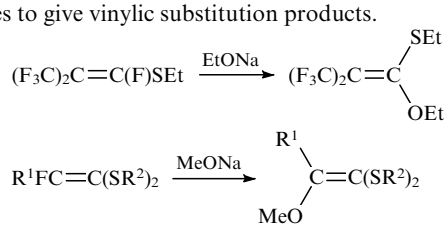
The electrophilic addition of chlorodiphenylmethane to 1,1-difluoro-2,2-di(phenylthio)ethylene involves the difluoromethylene fragment; thus, the sulfur atom stabilises a positive charge more efficiently than a fluorine atom.[109]



2. Reactions with nucleophilic reagents

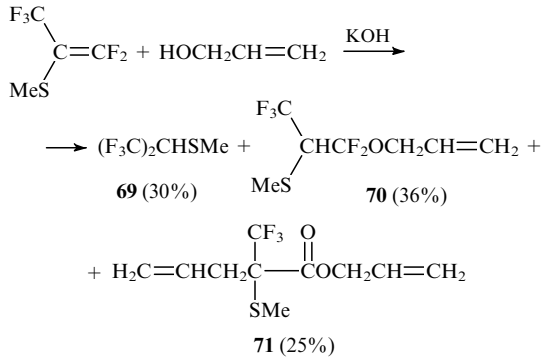
a. Reactions with O-nucleophiles

Vinyl sulfides[32,52] and ketene *S*,*S*-acetals[18,26] with a fluorine atom at a multiple bond are prone to react with aliphatic alcoholates to give vinylic substitution products.



R^1 = F, H$(F_2C)_3$; R^2 = Alk.

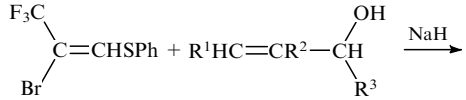
The exothermal reaction of 2-(methylthio)pentafluoropropene with allyl alcohol in the presence of a catalytic amount of KOH produces a mixture of three products, namely, sulfide **69**, allyl ether **70**, and allyl 2-methylthio-2-trifluoromethylpent-4-enoate (**71**), the last compound being the product of a [3,3]-sigmatropic rearrangement.[24]

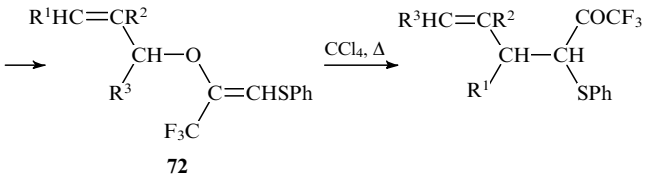


69 (30%) **70** (36%)

71 (25%)

The reaction of 2-bromo-1,1,1-trifluoro-3-phenylthiopropene with substituted allylic alcohols in the presence of sodium hydride leads to the products of bromine replacement.[118] The intermediate formation of 1,1,1-trifluoro-3-phenylthiopropyne was assumed for these reactions.



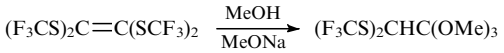


72

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

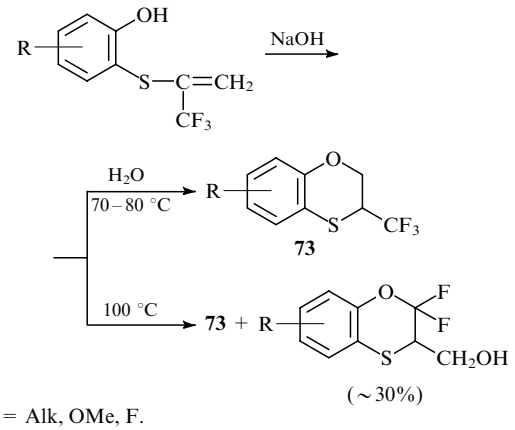
Unsaturated ethers **72** have been used in the Claisen rearrangement for stereocontrolled synthesis of trifluoromethyl ketones.

The final product formed in the reaction of tetrakis(trifluoromethylthio)ethylene with methanol in the presence of sodium methoxide is trimethyl bis(trifluoromethylthio)orthoacetate. This reaction is assumed to occur in several steps that include successive addition of the methoxy anion and elimination of the trifluoromethoxy anion.[12]



(64%)

On heating to 70–80 °C with an aqueous solution of sodium hydroxide, *o*-(1-trifluoromethylvinylthio)phenols are converted into 3-trifluoromethylbenzo-1,4-oxathianes **73** upon an intramolecular cyclisation.[116] When this reaction is carried out under more rigorous conditions with excess NaOH, 2,2-difluoro-3-hydroxymethylbenzo-1,4-oxathianes are formed along with 1,4-oxathianes.[119]

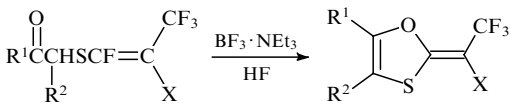


(~30%)

R = Alk, OMe, F.

Apparently, the reaction mechanism includes the attack of the hydroxide anion on the C=C bond of the initial compound, stabilisation of the resulting carbanion due to elimination of the fluoride ion and cyclisation of the intermediate difluoromethylene compound.

The products of sulfenylation of enolysing carbonyl compounds with α-fluoro-α,β-unsaturated sulfenyl chlorides in the presence of the $BF_3 \cdot NEt_3$ complex are prone to undergo intramolecular cyclisation with elimination of HF and the formation of alkyliden-1,3-oxathioles.[120]

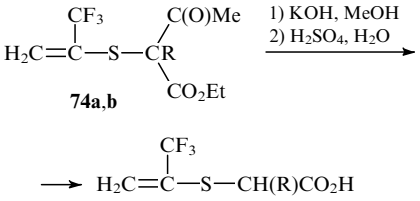


R^1 = Alk, Ar; R^2 = H, CO_2Et, C(O)Me, C(O)CF_3;
X = CF_3, CO_2Me, CN.

The reaction conditions are determined by the ability of the carbonyl compound to undergo enolisation. In the case of β-dicarbonyl compounds, cyclisation takes place even in the

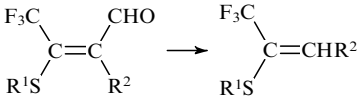
absence of $BF_3 \cdot NEt_3$ on moderate heating. A similar reaction is also typical of *o*-sulfenylated phenols.[75]

When reacting with potassium hydroxide, ethyl 2-(1-trifluoromethylvinylthio)acetoacetates **74a**,**b** are deacetylated to give the corresponding acids.[21] The vinylthio group does not participate in the reaction.



R = H (**a**, 57%), Me (**b**, 52%).

The decarbonylation of vinyl sulfides containing an aldehyde group at the multiple bond takes place on treatment with KOH in dichloromethane [57] or potassium *tert*-butoxide in toluene.[96]

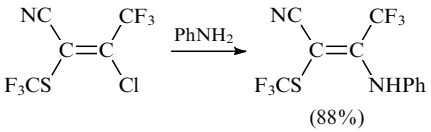


R^1 = Et, Ph; R^2 = Ph, 4-ClC_6H_4, .

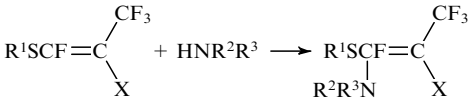
The *Z* isomer markedly predominates in the reaction products, the *Z* to *E* isomer ratio being changed with respect to the initial compounds in favour of the *Z* isomer.

b. Reactions with N-nucleophiles

In reactions with N-nucleophiles, the replacement of various good leaving groups at the multiple bond is most typical of fluorinated vinyl sulfides containing strong electron-withdrawing substituents (including functional ones). For instance, the chlorine atom in 2-chloro-1-cyano-2-trifluoromethyl-1-trifluoromethylthioethylene can be easily replaced by a phenylamino group.[90]



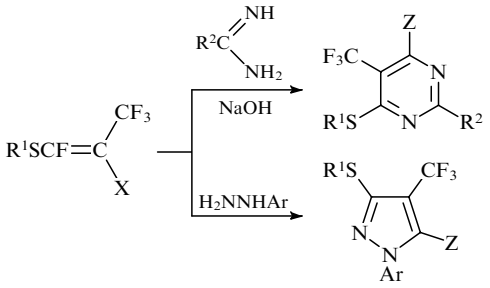
The replacement of the vinylic fluorine atom in β-alkylthio derivatives of perfluoromethacrylic acid on treatment with ammonia and primary or secondary amines proceeds equally smoothly.[121]



R^1 = Bu^t, Bn; R^2, R^3 = H, Alk, Ar; X = CO_2Me, CN.

Meanwhile, 3-benzylthio-2,3-difluoroacrylonitrile not activated by the trifluoromethyl group does not react with primary arylamines even on heating.

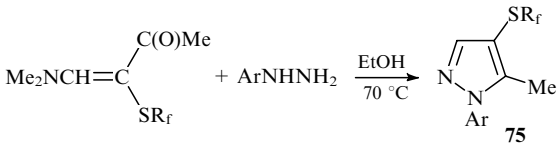
β-Functionalised alkyl(aryl)polyfluoroalkenyl sulfides react with acid amidines and arylhydrazines to form substituted pyrimidines and pyrazoles. Intramolecular cyclisation involves the functional group in the products of replacement of the fluorine atom formed initially.[121]



R^1 = Bu^t, Bn, Ar, Het; R^2 = Me, Ph; X = CO_2Me, Z = OH; X = CN, Z = NH_2.

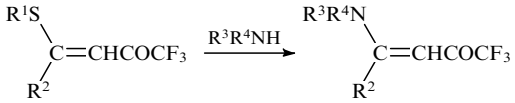
2-Chloro-1-cyano-2-trifluoromethyl-1-trifluoromethylthioethylene [122] and 3-benzylthio-2,3-difluoroacrylonitrile [121] enter into analogous reactions with acid amidines to give aminopyrimidines.

The reaction of 1-polyfluoroalkylthio-2-dimethylaminovinyl methyl ketones with arylhydrazines is also accompanied by heterocyclisation. 4-Polyfluoroalkylthiopyrazoles **75** thus formed have been patented as pesticides.[89]



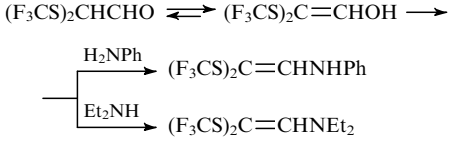
75

The alkylthio group in β-alkylthio-α,β-unsaturated trifluoromethyl ketones is easily substituted by amines. This affords enamines in yields of 56% to 100%.[123]

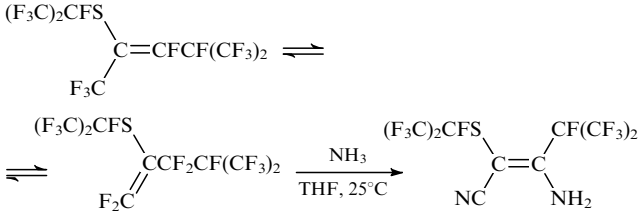


R^1 = Me, Et; R^2 = H, Me, Ph; R^3, R^4 = H, Me, Et, Bn.

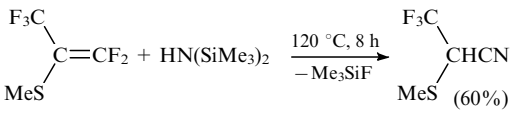
Bis(trifluoromethylthio)acetaldehyde, which mainly exists as the corresponding enol, reacts with amines to give the products of replacement of the hydroxy group.[112]



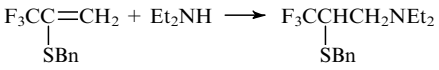
The reaction of perfluoro-2-isopropylthio-4-methylpent-2-ene, which isomerises to the terminal fluoroalkene, with anhydrous ammonia affords cyano-containing enamine.[124]



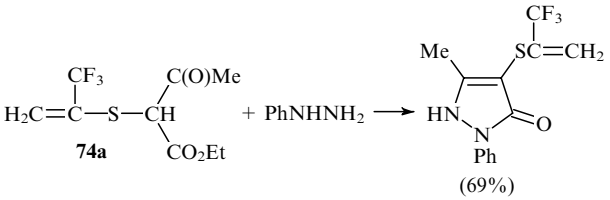
Hexamethyldisilazane adds to 2-methylthiopentafluoropropene under rigorous conditions. The reaction is accompanied by elimination of trimethylfluorosilane to give 2-methylthio-3,3,3-trifluoropropionitrile.[24]



The double bond in 2-benzylthio-1,1,1-trifluoropropene exhibits diphilic properties being able to add both electrophilic (for example, Cl_2) and nucleophilic reagents. The reaction with diethylamine proceeds with a yield of 66%.[101]



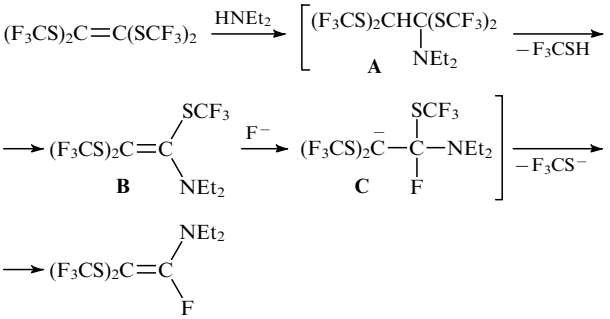
However, the reaction of ethyl 2-(1-trifluoromethylvinylthio)acetoacetate **74a** with phenylhydrazine leads to substituted pyrazoline, the vinylthio group remaining intact.[21]



The reaction of 2,2,2-trifluoroethyl phenyl sulfide with lithium diisopropylamide (LDA) affords (phenylthio)ynamine.[26] The first step involves dehydrofluorination to give 2,2-difluorovinyl phenyl sulfide.



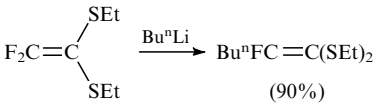
Unexpectedly, 2-diethylamino-2-fluoro-1,1-bis(trifluoromethylthio)ethylene was found to be the major product in the reaction of tetrakis(trifluoromethylthio)ethylene with excess diethylamine.[12]



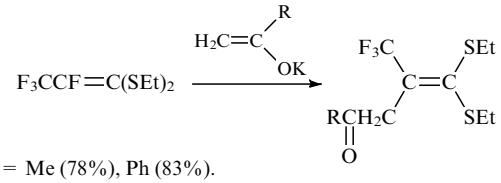
The reaction mechanism proposed in the study [12] includes the addition of diethylamine to the double bond and elimination of trifluoromethanethiol from adduct **A** yielding the product of replacement of one trifluoromethylthio group **B**. Compound **B** reacts with the fluoride ion, which is produced in the reaction mixture upon decomposition of the trifluoromethylthio anion, and is stabilised due to elimination of the second trifluoromethylthio group from intermediate **C**.

c. Reactions with C-nucleophiles

Difluoroketene *S*,*S*- and *S*,*O*-acetals react with C-nucleophiles such as organolithium compounds or Grignard reagents to give products of replacement of the fluorine atom.[17, 26, 27]

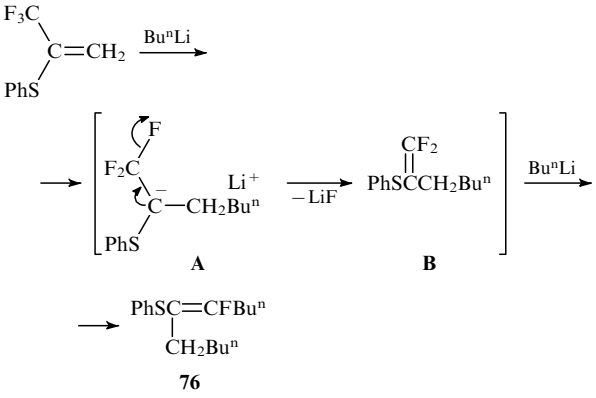


In reactions with enolates, generated by treatment of methyl ketones with potassium hydride, fluoro(trifluoromethyl)ketene diethyl dithioacetal also forms the products of replacement of the vinylic fluorine atom.[125]

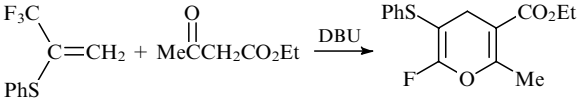


R = Me (78%), Ph (83%).

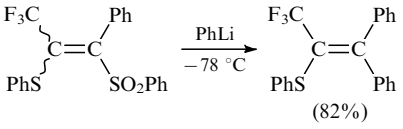
1,1,1-Trifluoroisopropenyl phenyl sulfide adds butyllithium at the double bond.[10] The carbanion **A** thus produced is stabilised by elimination of a fluoride ion being converted into difluoromethylidene compound **B**. This reacts subsequently with BuLi leading to monofluorine-containing vinyl sulfide **76**.



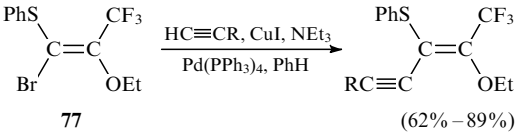
The reaction of the same 1,1,1-trifluoroisopropenyl phenyl sulfide with the anion generated from ethylacetoacetate on treatment with diazabicycloundecene (DBU) proceeds by a similar mechanism. Heterocyclisation takes place to give substituted 4*H*-pyran.[10]



The replacement of the phenylsulfo group in phenyl vinyl sulfone takes place in the presence of phenyllithium.[49]

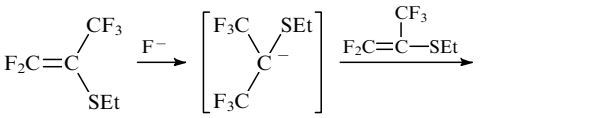


Sulfides containing conjugated double and triple bonds have been prepared by reactions of α-bromovinyl sulfide **77** with alkynes catalysed by palladium complexes.[126]



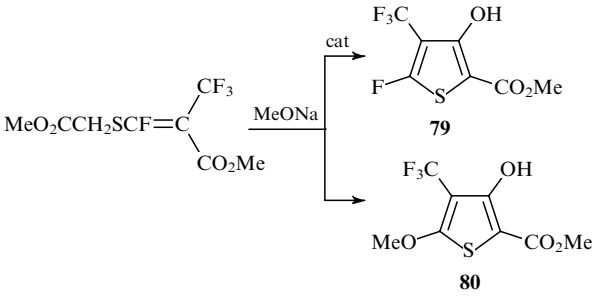
R = Bu, Bu^t, Ph, $SiMe_3$, CH_2OH.

Treatment of 2-ethylthiopentafluoropropene with caesium fluoride results in a carbanion, which reacts with a second molecule of the initial vinyl sulfide to give dimer **78** and other products.[14]



78

Alkoxycarbonylmethyl polyfluoroalkenyl sulfides containing a functional group in the β-position readily cyclise to thiophenes under the action of bases.[59, 127, 128] Thus on treatment with sodium methoxide, methoxycarbonylmethyl 1,3,3,3-tetrafluoro-2-methoxycarbonylpropenyl sulfide generates a carbanion with participation of the methylene group and undergoes intramolecular cyclisation, which affords 5-fluoro-3-hydroxythiophene **79**. The vinylic fluorine atom remains intact. When an excess of sodium methoxide is used, the vinylic fluorine atom in the cyclic structure **79** is substituted by the methoxy group, which yields 3-hydroxy-5-methoxythiophene **80**.[59]



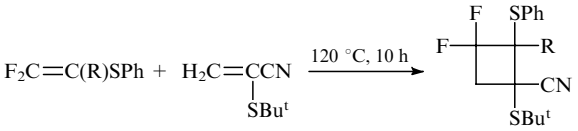
79

80

3-(Methoxycarbonylmethylthio)acrylates with different structures readily enter into a similar reaction. In this case, substituted acrylonitriles are converted into 3-aminothiophenes. The reaction is catalysed more efficiently by triethylamine. With this catalyst, the yields of the reaction products are nearly quantitative.[59]

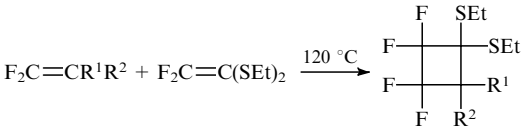
3. Cycloaddition

Published data on cycloaddition involving fluorine-containing vinyl sulfides are scarce. For example, [2 + 2]-cycloaddition of 2,2-difluorovinyl phenyl sulfide and its 1-halogenated analogues to α-*tert*-butylthioacrylonitrile has been reported.[129]



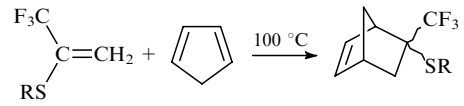
R = H (47%), F (57%), Cl (88%).

α-Substituted acrylic acid derivatives react with difluoroketene *S*,*S*-diethyl acetal to give cyclobutanes in up to 100% yields.[129]



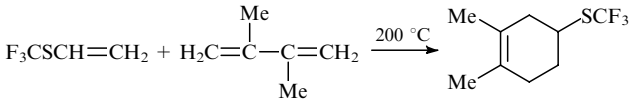
R^1 = CN, CO_2Me; R^2 = OMe, SePh, SBu^t, SPh, .

1,1,1-Trifluoroisopropenyl sulfides enter into the Diels–Alder reaction with cyclopentadiene on heating to 100 °C being thus converted into mixtures of *endo*- and *exo*-adducts.[21, 130]



R = CH_2CH_2Cl, $CH_2C(O)Me$.

Cycloaddition of trifluoromethylthioethylene to 2,3-dimethylbuta-1,3-diene occurs under drastic conditions.[62]



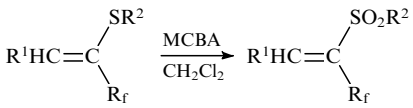
4. Oxidation

Hydrogen peroxide in acetic acid was the first reagent to be used to oxidise vinyl sulfides to α,β-unsaturated sulfones.[5, 6, 8, 16, 67]



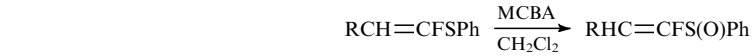
R = Et, Pr^i, Ph; X, Y = F, Cl, F_3C, SPh.

However, lately, organic oxidants have been used most often. For example, 2 equivalents of *m*-chloroperbenzoic acid (MCBA) in dichloromethane ensure oxidation of fluorine-containing vinyl sulfides to sulfones at 20 °C.[49, 93, 96, 126, 131, 132]



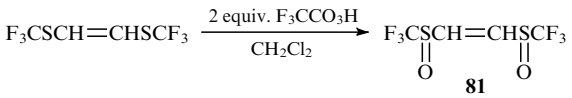
R^1 = Alk, Ar, CO_2Et, CN; R^2 = Et, C_6H_{13}, Ph; R_f = F, CF_3, C_2F_5

When 1 equivalent of MCBA is used, the reactions normally produce mixtures of oxidation products; however, in the case of α-fluorovinyl sulfides, selective preparation of sulfoxides in 79% – 83% yields is possible.[93]



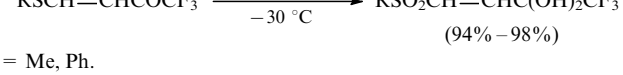
R = Alk, Ar.

By oxidation of n-butyl 1-chloro-2,3,3,4,4,5,5-heptafluoropent-1-enyl sulfide with excess trifluoroperacetic acid at 20 °C, the corresponding sulfoxide was obtained in 70% yield.[32] On treatment of a mixture of *cis*- and *trans*-1,2-di(trifluoromethylthio)ethylenes with trifluoroperacetic acid in dichloromethane at 20 °C, a mixture of disulfoxide **81** isomers was obtained in a high yield. The racemic modification of the *trans*-isomer was isolated from this mixture in 8% yield.[15]



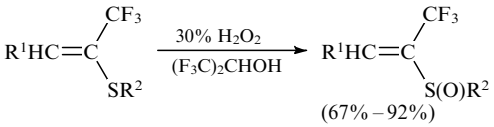
81

The reaction of β-trifluoroacetylated vinyl sulfides with H_2O_2 in CF_3CO_2H involves not only oxidation of the sulfur atom but also transformation of the carbonyl group, giving rise to diols stable up to 40 °C.[133]



R = Me, Ph.

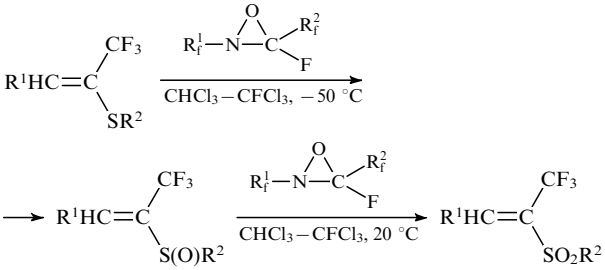
An efficient method for selective oxidation of 1-trifluoromethylvinyl sulfides to sulfoxides consists of treatment of the compounds with 30% hydrogen peroxide in hexafluoroisopropyl alcohol.[134]



R^1 = Bu^i, Ph, CO_2Et, HC=CHPh, CH_2CH_2Ph; R^2 = Et, C_7H_{15}.

The selective formation of sulfoxides in this reaction is due to the effect of the solvent, *i.e.*, hexafluoroisopropyl alcohol (pK_a = 9.3), which activates H_2O_2 through the formation of a hydrogen bond. Simultaneously, hexafluoroisopropyl alcohol forms a hydrogen bond with the oxygen atom of the sulfoxide obtained in the reaction; this markedly changes the nucleophilicity of the sulfur atom and prevents oxidation to sulfone. With a more basic solvent, trifluoroethanol (pK_a = 12.8), the reaction is very slow.

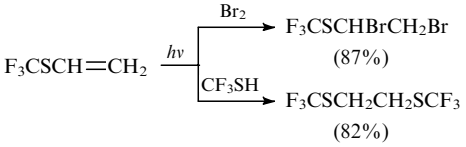
Vinyl sulfides can be oxidised using perfluoro-*cis*-2,3-dialkyloxaziridines. They oxidise α-trifluoromethylvinyl sulfides to the corresponding sulfoxides in the $CHCl_3-CFCl_3$ solvent system at −50 °C.[131] Further oxidation of sulfoxides at 20 °C leads to sulfones.



R^1 = Alk, Ar, CO_2Et; R^2 = Et, C_6H_{13}; R_f^1, R_f^2 = C_4F_9, C_3F_7, C_6F_{13}, C_5F_{11}.

5. Other reactions

On exposure to UV radiation, trifluoromethylthioethylene reacts with bromine and trifluoromethanethiol by a free radical mechanism.[12]

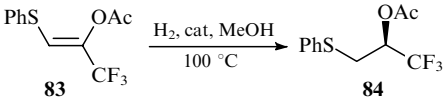


Meanwhile, the radical addition of trifluoromethanesulfenyl chloride to trifluoromethylthioethylene affords several products.[12] The major product is 2-chloro-1,1-bis(trifluoromethylthio)ethane (**82**).

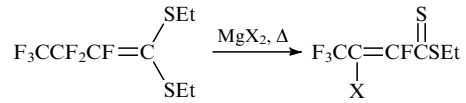
$$F_3CSCH{=}CH_2 + F_3CSCl \xrightarrow{h\nu} (F_3CS)_2CHCH_2Cl + \mathbf{82}\ (43\%)$$

$$+ F_3CSCHClCH_2Cl + (F_3CS)_2CHCH_2SCF_3 + F_3CSSCF_3$$

Enantioselective hydrogenation of vinyl sulfide **83** in the presence of catalytic amounts of ruthenium complexes gives saturated sulfide **84** in 83% yield and with an enantiomeric purity of 89%.[135]

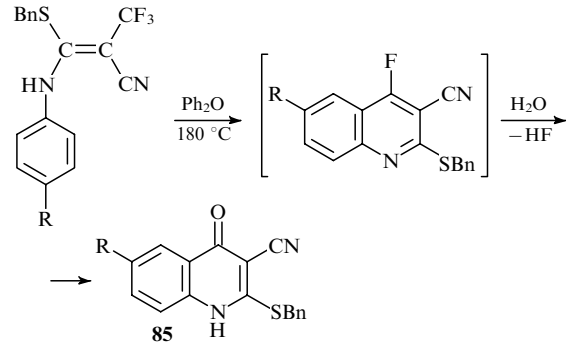


Esters of β-bromo- and β-chloro-perfluorodithiocrotonic acid have been prepared in high yields by heating fluoro(pentafluoroethyl)ketene with anhydrous magnesium halides.[136]



X = Cl, Br.

Cyclisation involving the trifluoromethyl group occurs on heating of cyano(trifluoromethyl)ketene *N*,*S*-acetals in diphenyl oxide. At 180 °C, the reaction was found to be accompanied by evolution of hydrogen fluoride and intramolecular cyclisation to form an aromatic nucleus.[121]



R = H, F, Me, PhO.

Evidently, the first step of the reaction is proton migration from the nitrogen atom to the α-carbon atom and thermal dehydrofluorination of the CH-acid thus formed. On alkaline hydrolysis of the reaction products, 3-cyanoquinolin-4-ones **85** were obtained and characterised.

* * *

To summarise the information covered in this review, one can state that fluorine-containing alkyl(aryl) vinyl sulfides are fairly reactive compounds with great synthetic potential. Numerous convenient methods for the synthesis of fluorinated vinyl sulfides based on readily available starting compounds have now been developed. Therefore, the problems of synthetic applications of these compounds come to the forefront, because until recently, they have been mainly used in reactions where the alkyl(aryl)thio group functioned as a leaving fragment. However, lately, the reactions with retention of the sulfur atom in the molecule as well as regio- and stereo-selective processes have attracted increasing attention.

The preparative accessibility of fluorine-containing alkyl(aryl) vinyl sulfides in combination with high reactivity creates prerequisites for the use of these compounds in the synthesis of diverse organic and heterocyclic products that present both theoretical and practical interest.

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[e] — *Chem. Heterocycl. Compd. (Engl. Transl.)*