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Polyfluoroalkanesulphenyl chlorides

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ABSTRACT. **Data appearing since 1975 are correlated for the methods of synthesis of polyfluoroalkanesulphenyl chlorides, their reactions with O-, S-, N-, P- and C-nucleophiles, with unsaturated aromatic and heteroaromatic compounds, for their behaviour in oxidation and heterocyclisation reactions and in free radical conversions.**

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I. Introduction

The first information on polyfluoroalkanesulphenyl chlorides (PFASC) appeared in the fifties.[1,2] Certain unusual properties of these compounds served as a spur towards a wider study of the chemistry of the fluorine-containing sulphenyl chlorides. By 1975 more than 190 publications had appeared on the synthesis and reactivity of PFASC and have been correlated in a detailed review.[3]

Theoretical interest in the chemistry of these compounds has grown markedly in recent years. As functionally substituted aliphatic compounds of two-coordinate sulphur the PFASC and their numerous conversion products are an interesting subject for studying the dependence of reactivity on intramolecular *pd* interactions. In several unfluorinated analogues these are particularly strongly displayed in C–C–S triads and determine the high reactivity of these compounds towards heterocyclisation and numerous rearrangements through the episulphonium state.[4,5] The appearance of the abundant 2*p* electrons of fluorine atoms at positions 3, 4 and 5 to the sulphur atom does not affect these properties appreciably.

However in the last two decades most attention has been paid to the investigation of the applied chemistry of PFASC. The high electron-accepting properties of polyfluoroalkylthio groups and particularly of their oxidation products,[6] imparting to the molecule a reduced light sensitivity and combustibility, have stimulated syntheses of numerous compounds desirable in practice and materials derived from these compounds. Opportunities for using PFASC as effective precursors of biologically active compounds have been more widely investigated.

The main types of compound studied from this point of view are given below in Tables 1 and 2. They reflect the main trend in the development of the chemistry of biologically active fluorine-containing compounds, viz. a continuation of the study of the highly reactive fluoroalkanesulphenamides, on the basis of which the fungitoxic preparations Euparen and Euparen-M were designed previously and are in use. A second direction has also developed based on the modification, using polyfluoroalkylthio groups, of known natural and synthetic biologically active compounds, their analogues and precursors. The opportunities in this direction are caused by the relatively low stability of the S–R_F bond, which is inclined to ready biodegradation with the elimination of fluoride ion, the appearance of which in the cytosol of cells aids normalisation of cellular hormone metabolism disturbed in numerous pathological states.[7] Information already available in this area enables consideration of various PFASC as efficient synthons for the synthesis of target preparations for medicine and agriculture.

The most important data on the chemistry and application of PFASC appearing during 1975–1991 are correlated in this review. Mainly, attention is paid to a consideration of the features of their methods of formation and reactivity and also to the opportunities for use in syntheses of biologically active compounds.

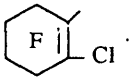
II. Methods of preparation

In the search for methods of obtaining PFASC the usual reactions for the unfluorinated analogues have been studied, such as the chlorination of disulphides, sulphides with labile leaving groups, thiols, thiocarbonyl compounds and thiiranes, the hydrochlorination of sulphenamides, reactions of sulphur chlorides with unsaturated compounds, the functionalisation of compounds with an S–Cl bond and also certain methods specific to fluorine chemistry. The features of the general methods of synthesising PFASC are most frequently displayed under the more forcing conditions of highly selective conversions and in side reactions which do not occur in the chemistry of the unfluorinated analogues.

1. Chlorination of disulphides

Symmetrical bispolyfluoroalkyl disulphides are usually converted unequivocally into PFASC on chlorination.[8–14]

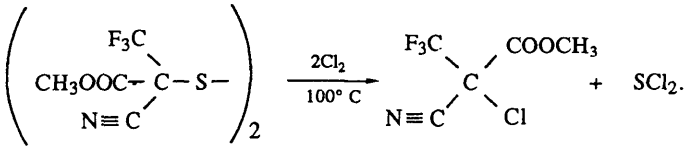
$$R_FSSR_F \xrightarrow{Cl_2} 2R_FSCl,$$

R_F = $ClCH_2-CH(CF_3)$, $CF_3CHClCH_2$, $CF_3OCFClCF_2$, $ClCF_2CF_2$, Cl_2CFCF_2, $CF_3(CF_2)_2$, $CF_3(CF_2)_6$, $(CF_3)_2CFO(CF_2)_2$, $(CF_3)_2CF$, $(CF_3)_3C$, $ClCF_2-C(CF_3)_2$, $CH_3OOC-C(CF_3)_2$, .

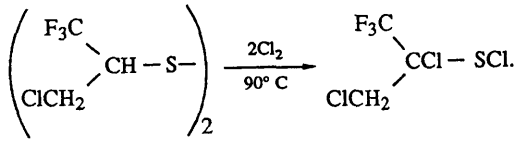
The reaction conditions depend appreciably on the nature of the polyfluoroalkyl group. The introduction of a CF_3 group into the α and β positions of the alkyl group does not show a marked effect on the conditions of chlorolysis of the S–S bond. Thus 2-chloro-1-trifluoromethylethanesulphenyl chloride was obtained in high yield from the corresponding disulphide at 20 °C or on mild cooling.

Disulphides with a CF_2 group on the sulphur atom are chlorinated at 90–110 °C. Replacement of one or two fluorine atoms of the CF_2 group by trifluoromethyl or a methoxycarbonyl group leads to a further reduction of the nucleophilicity of the sulphur atom and an increase in the chlorolysis temperature to 100–130 °C. The chlorolysis of bis(2-chloroperfluoro-1-hexenyl) disulphide occurs at 150 °C. In these reactions the nucleophilicity of the polyfluoroalkyl disulphides is controlled mainly by the efficient three-centre 2*p*3*d* interactions of the fluorine and sulphur atoms and also by the electron-withdrawing effects of the substituents at the α-carbon atom. Chlorolysis of the S–S bond of low reactivity disulphides is facilitated on UV irradiation.[12] The bispolyfluoroalkyl polysulphides undergo chlorolysis into PFASC under the same conditions as the corresponding disulphides.

In sulphides with strongly electron-accepting groups the R_F–S bond as well as the S–S bond may undergo chlorolysis:[13]



When a CH bond is present in the α position to sulphur it is readily chlorinated at increased temperature.[15]



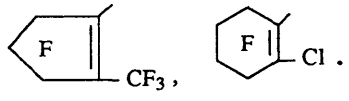
2. Chlorination of sulphides and other polyfluoroalkylthio derivatives

The conditions of forming PFASC from polyfluoroalkyl sulphides are determined mainly by the nature of the readily leaving alkyl group. However the structure of the polyfluoroalkyl group also has some effect.

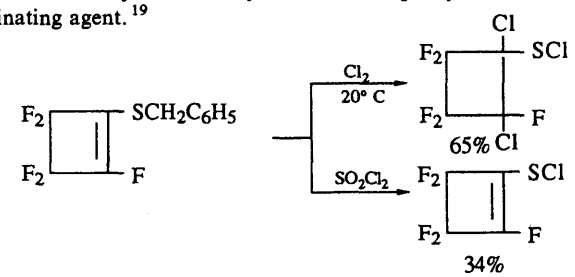
Various polyfluoroalkyl and polyfluoroalkenyl benzyl sulphides are chlorinated to PFASC at 20 °C in polyfluoroalkanes or without a solvent[16–22]

$$R_FSCH_2C_6H_5 \xrightarrow[20^\circ C]{Cl_2} R_FSCl + C_6H_5CH_2Cl,$$

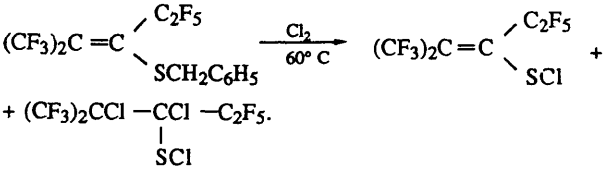
$R_F = CHF_2$, $(CF_3)_2CHCF_2$, CF_3CFCl, $(CF_3)_2CF$, $CHFClCF_2$, $(CF_3)_2C{=}CF$, $(CF_3)_2C{=}C{-}C_2F_5$, $((CF_3)_2CF)_2C{=}C{-}CF_3$,



In some cases chlorination of a multiple bond occurs simultaneously. This is successfully excluded by the use of sulphuryl chloride as the chlorinating agent.[19]

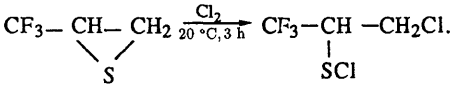


In the case of polyfluoroalkenyl benzyl sulphides the reaction may by accompanied by a chlorotropic conversion of the resulting PFASC. This leads to a mixture of compounds.[22]

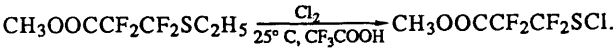


Chlorination of benzyl 2,2,2-trifluoroethyl sulphide occurs initially at the C–H bond of the trifluoroethyl group and fission of the benzyl group occurs after this.[23]

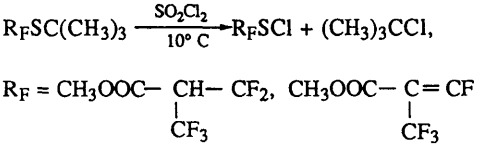
Chlorolysis of cyclic sulphides, for example trifluoromethylthiirane, is a reaction of this type[24]



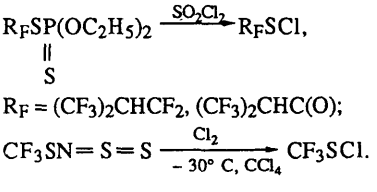
The ethyl group may act as the leaving group on chlorination in trifluoroacetic acid, which enables β-methoxycarbonyltetrafluoroethanesulphenyl chloride to be obtained.[25]



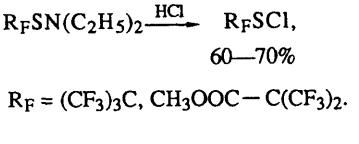
As with the unfluorinated analogues the t-butyl group is eliminated more readily than benzyl. In this case the PFASC are formed in the cold even on chlorination with sulphuryl chloride.[26]



Chlorinating agents split S–P [26] and S–N [27] bonds even more readily.



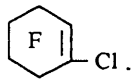
Polyfluoroalkanesulphenamides are converted into PFASC on treatment with dry HCl.[28]



3. Chlorination of thiols and thiocarbonyl compounds

Stable polyfluoroalkenethiols are readily chlorinated to give PFASC at 20 °C.[21,29] However 2-chlorooctafluoro-1-cyclohexenesulphenyl chloride was obtained by this method only at 150 °C,[14]

which indicates the extremely strong *pd* atomic interactions in the four-centre Cl–C=C–S system.

$$R_FSH + Cl_2 \longrightarrow R_FSCl,$$
$$R_F = (CF_3)_2C{=}\ C{-}\ C_2F_5,\ ((CF_3)_2CF)_2C{=}\ C{-}\ CF_3,$$ 

Chlorolysis of 1,1-diphenyltrifluoroethanethiol occurs under mild conditions with sulphuryl chloride.[30]

$$CF_3{-}\ C(C_6H_5)_2SH \xrightarrow{SO_2Cl_2} CF_3\ {-}C(C_6H_5)_2SCl.$$
96%

Many PFASC which are impossible to synthesise by other methods have been obtained by the reaction of highly reactive thiocarbonyl compounds with chlorine and chlorine fluoride under mild conditions.[11,22,31–34]

$$\begin{matrix} X \\ \diagdown \\ C{=}S \\ \diagup \\ Y \end{matrix} \xrightarrow[-80\text{ to }90\ ^\circ C]{Cl_2} XYCCl{-}\ SCl,$$

$X = CF_3$, $Y = F$, Cl, CF_3; $X = CF_3$, $Y = Br$; $X = Y = F$;
$X = C_2F_5$, $Y = (CF_3)_2CH$, $(CF_3)_2CCl$;

$$\begin{matrix} X \\ \diagdown \\ C{=}S \\ \diagup \\ Y \end{matrix} \xrightarrow[-100^\circ C]{ClF} XYCF{-}\ SCl,$$

$X = Y = CF_3$; $X = Y = Br$; $X = CF_3$, $Y = F$, Br; $X = S = C = N$, $Y = F$.

4. Addition of sulphur chlorides to unsaturated compounds

The thermal reactions of sulphur chlorides with polyfluoroalkenes has been studied widely in the search for methods of synthesising precursors of PFASC such as the bis(2-chloropolyfluoroalkyl) disulphides.[35] Trifluoroethylene, tetrafluoroethylene, chlorotrifluoroethylene, perfluoromethyl vinyl ether and 2H-pentafluoropropene participate in these reactions. Symmetrical and unsymmetrical dichlorodifluoroethylenes, hexafluoropropene and octafluoromethylpropene do not react. The electrophilic addition of SCl_2 on thermolysis always gives a complex mixture of compounds including PFASC, polyfluoroalkylpolythiosulphenyl chlorides, sulphides, polysulphides and products of alkene chlorination. The addition of S_2Cl_2 with the predominant formation of disulphides occurs only under forcing conditions (140–155 °C) with a large excess of polyfluoroalkene, which has made several PFASC available for investigation.

$$\begin{matrix} R \\ \diagdown \\ C{=}\ CF_2 \\ \diagup \\ X \end{matrix} \xrightarrow{S_2Cl_2} \left(\begin{matrix} R \\ \diagdown \\ CCl\ {-}CF_2 \\ \diagup \\ X \end{matrix} \right)_2 S_2 \xrightarrow{Cl_2} \begin{matrix} R \\ \diagdown \\ CCl{-}CF_2SCl, \\ \diagup \\ X \end{matrix}$$

R = H, F, Cl, CF_3, CF_3O; X = H, F.

The preparative value of these reactions is markedly extended by carrying out the process in the presence of catalysts. 1,2-Dichlorodifluoroethylene is converted into 1,2-dichlorotrifluoroethanesulphenyl chloride in the system $SF_4–HF–S_2Cl_2$ under relatively mild conditions.[36] It is considered that ionisation of S_2Cl_2 in the presence of SF_4 and HF facilitates the electrophilic addition of sulphur monochloride cation at the multiple bond and the presence of fluoride ion and the chlorine formed in the reaction mixture enables the unequivocal formation of the sulphenyl chloride.

$$S_2Cl_2 \xrightarrow{HF,\ SF_4} Cl^- + {}^+SSCl,$$
$$SF_4 + 4Cl^- \xrightarrow[-4F^-]{} SCl_4 \longrightarrow SCl_2 + Cl_2,$$
$$CFCl{=}CFCl \xrightarrow{{}^+SSCl} \left[{}^+CFClCFClSSCl \xrightarrow{F^-} \right.$$
$$\left. \longrightarrow CF_2ClCFClSSCl \right] \xrightarrow{Cl_2} CF_2ClCFClSCl.$$

Chlorotrifluoroethylene reacts similarly with S_2Cl_2 under these conditions, however the reaction products proved to be the two possible regioisomers.

$$CF_2{=}\ CFCl \xrightarrow{SF_4-HF-S_2Cl_2} CF_3CFClSCl + CF_2ClCF_2SCl.$$

Hexafluoropropene forms a combined addition product with sulphur dichloride and fluorosulphonic acid (1:3) with elimination of HCl at 40–60 °C.[37,38]

$$CF_3CF{=}\ CF_2 \xrightarrow[-HCl]{SCl_2,\ HSO_3F} CF_3{-}\underset{\displaystyle SCl}{\underset{|}{CF}}\ {-}CF_2OSO_2F.$$
75%

A mixture of chlorosulphonic acid and SCl_2 gives a similar product in 34% yield. In combined reactions of this type S_2Cl_2 gives a mixture of compounds containing thiosulphenyl chlorides and trisulphides in addition to sulphenyl chlorides.

Under conditions of the specific solvation of the S–Cl bond (acetonitrile, benzonitrile, $POCl_3$ and SO_2) sulphur mono- and dichlorides add to hexafluorodimethyl ketene with the formation of sulphenyl and thiosulphenyl chlorides.[39]

$$(CF_3)_2C{=}C{=}O + S_nCl_2 \longrightarrow (CF_3)_2C \begin{matrix} \diagup\ C(O)Cl \\ \diagdown\ S_nCl \end{matrix}.$$
$n = 1, 2.$ 90%

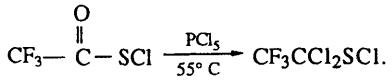
These reactions are effected particularly readily (at negative temperatures) in acetonitrile.

5. Functionalisation of compounds with an S–Cl bond

The C–H bond in the α position to a sulphur atom is readily chlorinated. This enables 1,2-dichloro-1-trifluoromethylethanesulphenyl chloride, which is inaccessible by other methods, to be obtained.[15]

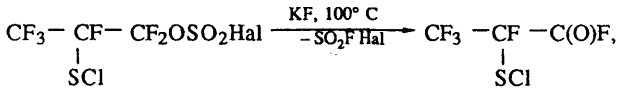
$$\begin{matrix} F_3C \\ \diagdown \\ CH{-}SCl \\ \diagup \\ ClCH_2 \end{matrix} \xrightarrow[90^\circ C]{Cl_2} \begin{matrix} F_3C \\ \diagdown \\ CCl{-}SCl. \\ \diagup \\ ClCH_2 \end{matrix}$$
86%

Trifluoroacetylsulphenyl chloride is converted into 1,1-dichlorotrifluoroethanesulphenyl chloride on reaction with PCl_5.[40]



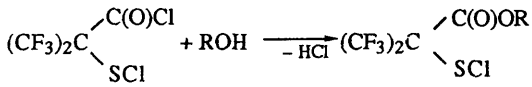
75%

The sulphenyl chloride formed on combined addition of SCl_2 and HSO_3F or HSO_3Cl to hexafluoropropene is converted on heating with KF into the acid fluoride of α-chlorosulphenyltetrafluoropropionic acid.[38]



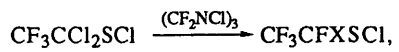
Hal = F, Cl. 74%

The acid chloride of α-chlorosulphenylhexafluoroisobutyric acid reacts under mild conditions with saturated and unsaturated alcohols forming esters in the absence of HCl acceptors.[41] The S–Cl bond is not affected by this.



R = CH_3, CH_2=$CHCH_2$.

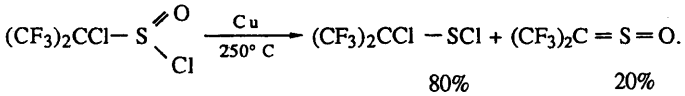
Chloro- and chlorofluoroalkanesulphenyl chlorides react by replacement of chlorine by fluorine exclusively at the C–Cl bond in the position α to the sulphur atom. In these reactions, which were widely studied for trichloromethanesulphenyl chloride previously,[3] HF, FeF_3, HF/CrF_3 and NH_4F have also been studied as fluorinating agents.[42–45] Hexafluorotrichloro-sym-triazine proved to be a new fluorinating agent in principle. Its application enables selective replacement by fluorine of one or two chlorine atoms in 1,1-dichlorotrifluoroethanesulphenyl chloride.[40]



X = Cl, F.

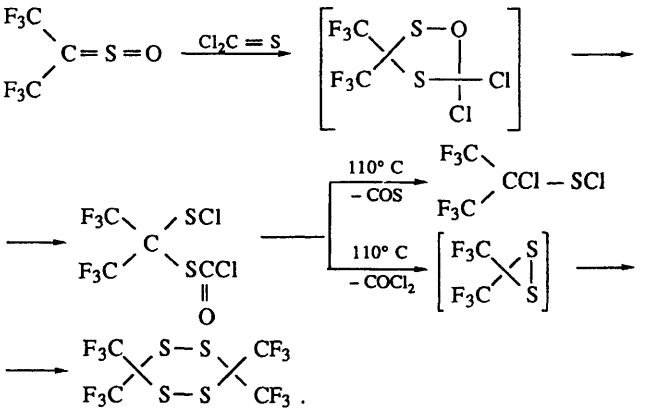
6. Other preparative routes

On heating α-chlorohexafluoroisopropanesulphinyl chloride with activated copper under forcing conditions it undergoes deoxygenation with the formation of a sulphenyl chloride.[46] Only a small portion of the starting material is converted into the dechlorination product bis(trifluoromethyl)methylene sulphoxide.



80% 20%

The (2 + 3) cycloaddition of thiophosgene to bis(trifluoromethyl)methylene sulphoxide leads to α-chloroformylthiohexafluoroisopropanesulphenyl chloride, seemingly through the intermediate dithioxolane.[46] On heating to 110 °C the sulphenyl chloride is decomposed with the elimination of carbonyl sulphide or phosgene with the formation of the corresponding α-chlorohexafluoroisopropanesulphenyl chloride and 3,3,6,6-tetrakis(trifluoromethyl)-1,2,4,5-tetrathiane.



III. Reactivity

The reactivity of PFASC has been studied in the majority of conversions typical of aliphatic sulphenyl chlorides. The polyfluoroalkylthiolation of various nucleophilic reagents, aromatic and heteroaromatic compounds has been widely clarified as has the reaction of PFASC with unsaturated compounds. The information obtained enables PFASC to be considered to be compounds with high reactivity, though appreciably more moderate than their unfluorinated analogues.

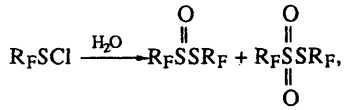
1. Reactions with nucleophilic reagents

The reaction of PFASC with nucleophilic reagents takes place according to the following equation

$$Nu(H) + R_FSCl \rightarrow NuSR_F + Cl^- + (H^+).$$

It is assumed that these reactions occur by an S_N2 mechanism in which the entering and leaving groups are at the vertices of a trigonal bipyramid.[47]

Reaction with O-nucleophiles. The hydrolysis of PFASC was considered in detail in the review[3] using CF_3SCl as example. In addition it was shown that these compounds are stable to water, unlike their unfluorinated analogues. Only on prolonged shaking with water were the final hydrolysis products, sulphides and sulphonic acids, obtained in some cases. The hydrolysis of the chlorofluoromethanesulphenyl chlorides was successfully stopped at the stage of forming thiosulphinates and/or thiosulphonates.[48]



R_F = $CFCl_2$, CF_2Cl.

1,1-Dichlorotrifluoroethanesulphenyl chloride is partially converted after 48 h at 45 °C into chloro(trifluoromethyl)methylene sulphoxide.[23,49]

$$CF_3CCl_2SCl \xrightarrow[45^\circ C]{H_2O} \begin{matrix} CF_3 \\ \diagdown \\ C=S=O \\ \diagup \\ Cl \end{matrix} \quad 28\%$$

α-Chlorohexafluoroisopropanesulphenyl chloride is unchanged under these conditions.[46]

The PFASC are as stable to alcohols as to water. The stable esters of polyfluoroalkanesulphenic acids are obtained under relatively mild conditions in the presence of acceptors of HCl [$N(C_2H_5)_3$, Py] [50,51] and without acceptors only in certain cases on heating.[26]

$$R_FSCl + ROH \rightarrow R_FSOR,$$

$R_F = CF_3$, $R = C_2H_5$, $CH_3OC_6H_4CH_2$, $CF_3SNHCH_2CH(C_6H_5)$;

$R_F = (CF_3)_2CHCF_2$,

$R = C_2H_5$.

The PFASC react more readily with alkoxides and phenoxides of the alkali metals and particularly of mercury.[30,52] Under these conditions the acylsulphenyl chlorides give desulphurisation products.

$$CF_3 - C(C_6H_5)_2SCl + ROH \xrightarrow[20\ ^\circ C, 3\ h]{NaH/THF} CF_3 - C(C_6H_5)_2SOR,$$

$R = (CH_3)_3CCH_2$, $C_6H_5CH_2O(CH_2)_2$, $4\text{-}O_2NC_6H_4$,

$CH_3(CH_2OCH_2)_3CH_2$.

$$(CF_3)_3COHgCl \xrightarrow[0\ ^\circ C,\ 24\ h]{CF_3SCl} (CF_3)_3COSCF_3$$

$$(CF_3)_3COHgCl \xrightarrow[0\ ^\circ C,\ 24\ h]{CF_3CSCl} (CF_3)_3COSCCF_3 \xrightarrow{-S} (CF_3)_3COCCF_3$$

On reacting PFASC with allyl alcohol in the presence of pyridine, equilibrium mixtures are formed of sulphuric acid esters and products of their [2,3]-sigmatropic rearrangement with a significant preponderance of the latter.[53] On heating or on increasing the electron-donating properties of the polyfluoroalkyl group the content of sulphenate in the mixture is increased.

$$R_FSCl + HOCH_2CH=CH_2 \xrightarrow[CH_2Cl_2]{Py} R_FSOCH_2CH=$$

$$= CH_2 \rightleftharpoons R_FSCH_2CH=CH_2,$$

$R_F = CCl_2F$, $CClF_2$, CF_3, $(CF_3)_2CH$, $(CF_3)_2CCl$.

The PFASC form mixed anhydrides with salts of carboxylic acids which differ from the unfluorinated analogues in increased stability.[54,55] Their yield was increased with an increase in the number of fluorine atoms at the α-carbon atom.

$$R_FSCl + MOC(O)R \rightarrow R_FSOC(O)R,$$

$R_F = CCl_2F$, $CClF_2$, CF_3; $R = CH_3$, C_2H_5, CF_3, C_2F_5; $M = Na$, Ag.

The mixed anhydrides obtained were more reactive than PFASC in their activity in reactions of electrophilic addition and substitution.[55]

Reactions with S-nucleophiles. Thiolates and thiols react with PFASC in the presence of acceptors of HCl giving unsymmetrical disulphides.[22,24,26,32,56–63] Strong bases aid the symmetrisation of these compounds which may be the reason for the sharp reduction in the yield of the desired products.

$$R_FSCl + RSH \xrightarrow[-HCl]{\ddot{B}} R_FSSR \xrightarrow[RSH]{\ddot{B}} R_FSSR_F + R_2S_2,$$

$R_F = CCl_2F$, CF_3, $FC(O)$, $ClCH_2 - CH(CF_3)$, $(CF_3)_2CHCF_2$, $CF_3 - CCl(CH_2Cl)$, $(CF_3)_2C=C-C_2F_5$, $CF_3C(O)$;

$R = H$, CH_3, $C_6H_5CH_2$, $HOOCCH_2$, CF_3, $C_6H_5NH-C(S)$.

$$2CF_3SCl + \begin{matrix} NaS \\ \diagdown \\ C=S \\ \diagup \\ NaS \end{matrix} \longrightarrow \begin{matrix} CF_3SS \\ \diagdown \\ C=S, \\ \diagup \\ CF_3SS \end{matrix}$$

$$Hg\left(S-C\begin{matrix} N-CF_3 \\ O-CF_3 \end{matrix}\right)_2 \xrightarrow{2CF_3SCl} CF_3SS-C\begin{matrix} N-CF_3 \\ O-CF_3 \end{matrix}$$

$$Hg\left(S-C\begin{matrix} N-CF_3 \\ O-CF_3 \end{matrix}\right)_2 \xrightarrow{ClSCF_2CF_2SCl} \left(CF_2SS-C\begin{matrix} N-CF_3 \\ O-CF_3 \end{matrix}\right)_2$$

Dialkyl disulphides also react analogously. Thus CF_3SCl reacts under mild conditions with dimethylsulphide with the formation of an unsymmetrical disulphide.[64]

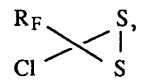
$$CF_3SCl + CH_3SSCH_3 \xrightarrow[-50\ to\ 25\ ^\circ C]{} CF_3SSCH_3 + CH_3SCl.$$

The disulphides formed in reactions of α,α-dichloropolyfluoroalkanesulphenyl chlorides with thioacetic acid are readily split by morpholine with the formation of morpholides of chlorofluorothioacetic acids.[65]

$$R_FCCl_2SCl + \underset{+HSCCH_3}{\overset{O}{\parallel}} \xrightarrow[60^\circ C,\ CCl_4]{} R_FCCl_2SSCCH_3 \xrightarrow{HN\ O} R_FC(S)N\ O,$$

$R_F = CFCl_2$, CF_2Cl.

Initially, decomposition of the disulphide to a dithiirane is proposed



the desulphurisation of which leads to the thioacid chloride $R_FC(S)Cl$ giving the corresponding morpholide with morpholine.

Reaction with N-nucleophiles. The reaction of PFASC with N-nucleophiles with the formation of polyfluoroalkanesulphenamides has been widely studied. Ammonia,[15,30,66] primary [30,51,67–69] and secondary [10,15,19,30,70–74] amines, primary and secondary amides of

carboxylic acids[75–78] and sulphonic acid amides[79] participate in these reactions.

$$R_FSCl + HN\!\!\begin{array}{l}\diagup\\\diagdown\end{array} \xrightarrow[-HCl]{} R_FSN\!\!\begin{array}{l}\diagup\\\diagdown\end{array}.$$

The reaction is usually effected in the presence of HCl acceptors such as trimethyl-, triethylamine, pyridine or an excess of the reacting amine. In certain cases better results are obtained when reacting PFASC with metal amides.

When reacting ammonia and primary amines with an excess of PFASC a second or third polyfluoroalkylthio group is introduced at the nitrogen atom.[3] Tetrafluoroethane-1,2-disulphenyl chloride reacts with primary amines giving 1,3,2-dithiazolidines.[69]

$$ClSCF_2CF_2SCl + H_2NR \longrightarrow \begin{array}{l}CF_2\text{—}S\\ |\quad\quad \diagdown\\ CF_2\text{—}S\quad\quad N\text{—}R\end{array}$$

The polyfluoroalkanesulphenamides are markedly more stable than their unfluorinated analogues. Their thermal and hydrolytic stability is increased with an increase in the electron-accepting properties of the polyfluoroalkyl group and is reduced with an increase in the basicity of the amine. Many of the sulphenamides obtained possess high biological activity. Highly active compounds are found among them which are of interest in agriculture and medicine. Data on the structure and biological activity of the sulphenamides obtained from N-nucleophiles and PFASC are given in Tables 1 and 3.

N-Silylated compounds are sulphenylated by PFASC with elimination of chlorotrimethylsilane. Stable fluorocarbonylated azides and thionylimines are obtained in this way.[59]

$$FC(=O)\text{—}SCl + (CH_3)_3SiX \xrightarrow[-(CH_3)_3SiCl]{} FC(=O)\text{—}SX,$$

$X = N_3, \quad -N{=}S{=}O.$

Trifluoromethylthioazide obtained in a similar way is converted even at 20 °C into tetrakis(trifluoromethylthiazyl).[127]

$$CF_3SCl + (CH_3)_3SiN_3 \xrightarrow[-(CH_3)_3SiCl]{-50 \text{ to } -30\ ^\circ C} CF_3SN_3 \xrightarrow[-N_2]{20\ ^\circ C} (CF_3SN)_4.$$

Sulphodiimides silylated at nitrogen form crystalline 1,3,5-trithia-2,4-diazepines in high yield with 1,2-bis(chlorosulphenyl)-tetrafluoroethane.[128]

$$ClSCF_2CF_2SCl + \begin{array}{l}(CH_3)_3SiN\\(CH_3)_3SiN\end{array}\!\!\begin{array}{l}\diagup\\\diagdown\end{array}\!\!S\!\!\begin{array}{l}\diagup\\\diagdown\end{array}\!\!\begin{array}{l}R\\R\end{array} \xrightarrow[-78 \text{ to } 20\ ^\circ C]{CH_2Cl_2} \begin{array}{l}CF_2\text{—}S\text{—}N\\ |\quad\quad\quad \diagdown\\ CF_2\text{—}S\text{—}N\end{array}\!\!\begin{array}{l}\diagup\\\diagdown\end{array}\!\!S\!\!\begin{array}{l}\diagup\\\diagdown\end{array}\!\!\begin{array}{l}R\\R\end{array}$$

$R = CH_3, C_2H_5.$

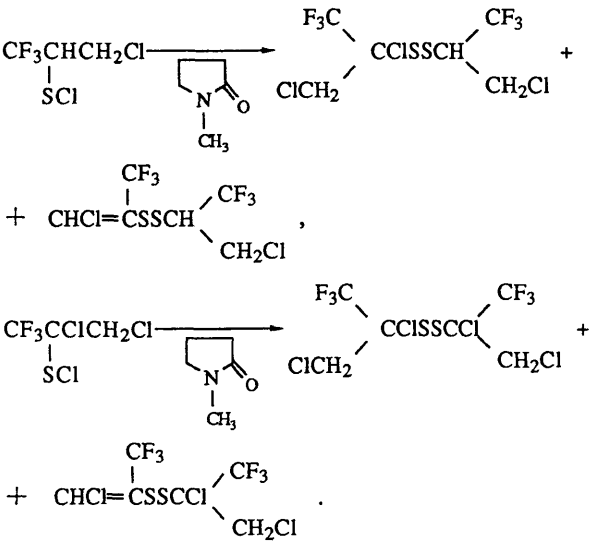
On the other hand hexamethyldisilazane is thiolated by CF_3SCl at the N—H bond. A second molecule of hexamethyldisilazane acts as HCl acceptor in this reaction.[28,51]

Tertiary amines convert PFASC into disulphides.[129] Disulphides are frequently byproducts in reactions where tertiary amines are used as HCl acceptors for this reason.

$$R_FSCl + R_3N \rightarrow R_FSSR_F + [R_3N \cdot Cl_2],$$

$R_F = CF_3, CF_2Cl, CFCl_2.$

2-Chloro-(1-trifluoromethyl)ethanesulphenyl chloride and 1,2-dichloro-(1-trifluoromethyl)ethanesulphenyl chloride are converted in *N*-methylpyrrolidone into the thiocarbonyl compound $CF_3C(S)CH_2Cl$ and the thiirene $CF_3\text{—}C{=}CH$ respectively, which give a mixture of unsymmetrical disulphides with the initial sulphenyl chlorides.[15]



Reactions with P-nucleophiles. The reaction of PFASC with P-nucleophiles has been widely studied in the search for new insecticides. The reaction of trialkyl and diaryl alkyl phosphites with trichloro-, chlorodifluoro-, and dichlorofluoro-, and trifluoromethanesulphenyl chlorides[130,133] occurs under milder conditions than for the unfluorinated alkanesulphenyl chlorides. The main reaction products are the corresponding trihalomethyl thiophosphates. In addition products of the 'anomalous' breakdown of the intermediate phosphorane, viz. trihalomethyl alkyl sulphides, were formed with some contamination by other compounds.

$$(RO)_3P + CCl_{3-n}F_nSCl \rightarrow (RO)_2P(O)SCCl_{3-n}F_n + CCl_{3-n}F_nSR +$$
$$+ (RO)_2P(O)Cl + RCl,$$

$n = 0$ to 3; R = Alk, Ar.

The trihalomethanesulphenyl chlorides react analogously with dialkyl or sodium dialkyl phosphites. Conditions have successfully been found[133] under which diisopropyl and di(trimethylsilyl) phosphites are converted quantitatively into the corresponding trihalomethyl thiophosphates.

$$CCl_{3-n}F_nSCl + (RO)_2P(O)H \rightarrow (RO)_2P(O)SCCl_{3-n}F_n,$$

$n = 1$ to 3; $R = iso\text{-}C_3H_7, (CH_3)_3Si$.

Table 1. Biological activities of sulphenamides obtained by reacting PFASC with primary and secondary amines ($R_FS-NR^1R^2$).

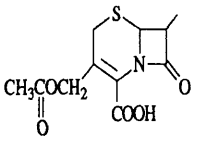
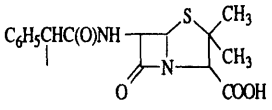
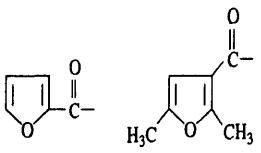
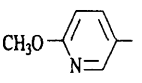
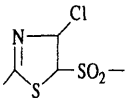
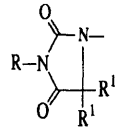
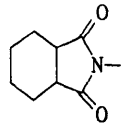
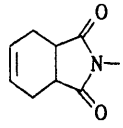
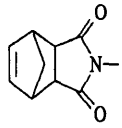
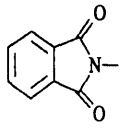
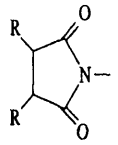
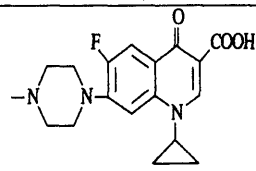
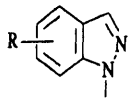
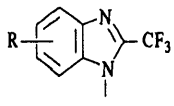
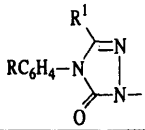
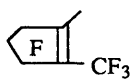
R_F	R^1	R^2	Activity	Ref.
$CFCl_2$, CF_3CCl_2, CF_2ClCCl_2, $CFCl_2CFCl$, $CF_2ClCFCl$, $CFCl_2CCl_2$, CCl_3CF_2	RSO_2—, R = Alk, Ar, $N(CH_3)_2$	Alk, All, $IC{\equiv}CCH_2$, Ar	Herbicides, insecticides, microbiocides, fungicides, antihelminthic agents	[80—88]
$CFCl_2$	R_2N—C(O)C_6H_4—, R = H, Alk, Ar	CF_3	Fungicides, microbiocides	[89—91]
CF_3		H	Antibacterial activity	[92]
CF_3		H	Antibacterial acitivity	[51]
$CFCl_2$, $CFCl_2CCl_2$, $CFCl_2CFCl$	R—C_6H_4—C(O)— R = H, Hal, CF_3, CH_3O	C_6H_5,п-F—C_6H_4	Fungicides, acaricides, antimosquito agents	[93—98]
$CFCl_2CCl_2$, $CFCl_2CFCl$		C_6H_5	Fungicides, acaricides	[99, 100]
$CFCl_2$	X(O)C— X = H, F	Ar	Fungicides, antimicrobial activity	[101—103]
$CFCl_2$	Ar—NH—C(O)—	Ar	Fungicides	[102]
$CFCl_2$	RX—C(O)[illegible]C(O)— X = O, S, N; R = Alk, Ar	Alk, All	Fungicides	[67, 68, 104, 105]
$CFCl_2$, CF_2Cl, CF_3	$(RO)_2P(X)$— R = Alk, Ar X = O, S	Alk	Insecticides	[106, 107]
$CFCl_2CCl_2$	R—N=C(—SC_2H_5)—	Alk, Ar	Herbicides, lepidoptericidal activity	[108]
$CFCl_2CCl_2$			Fungicides	[109]
$CFCl_2$		H, Alk, C_6H_5	Fungicides	[110]
$CFCl_2$, $CFCl_2CCl_2$	$PhCH_2C(O)$	CH_2CN	Fungicides	[111]

Table 2. Biological activity of sulphenamides obtained by reacting PFASC with secondary cyclic amines (R_FS-NR_2).

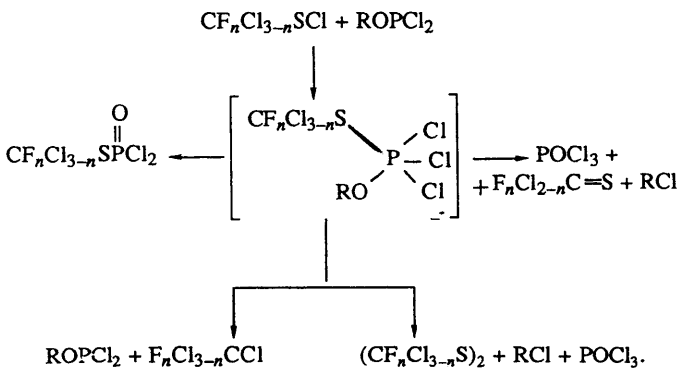
R_F	R_2N-	Activity	Ref.
$CFCl_2$	 R = Alk, Ar, SAlk, R^1 = H, CH_3	Antimicrobial, herbicides, fungicides, insecticides	[112—115]
CF_2ClCCl_2, $CF_2ClCFCl$		Herbicides, insecticides	[84]
$CFCl_2$, $CFCl_2CCl_2$		Antitick action, fungicide	[101, 116]
$CFCl_2$		Antimicrobial activity	[117]
$CFCl_2$, $CFCl_2CCl_2$		Herbicides, insecticides	[83, 84, 118, 119]
$CFCl_2$, $CFCl_2CCl_2$	 R = Alk, Ar	Microbiocides, fungicides	[120, 121]
$CFCl_2$		Antibacterial activity	[122]
CF_3, $CFCl_2$	 R = H, OAlk, SAlk	Plant protection agent	[123]
$CFCl_2$	 R = H, Cl, CF_3, SCF_3	Herbicides	[124]
$CFCl_2$ R = H, Cl, F, Alk; R^1 = H, Alk		Fungicides	[125, 126]

Sulphenyl chlorides with highly electrophilic perfluoroalkenyl groups react with trialkyl phosphites with the exclusive formation of perfluoroalkenyl alkyl sulphides.[19]

$$R_FSCl + P(OC_2H_5)_3 \xrightarrow{-78^\circ C} [(C_2H_5O)_3PCl]^+(SR_F)^- \longrightarrow R_FSC_2H_5,$$

$R_F = (CF_3)_2C{=}CF$, .

The reaction of trihalomethanesulphenyl chlorides with alkyl dichlorophosphites at −30 to 20 °C leads to trihalomethylthio dichlorophosphates in about 50% yield.[134,135] In addition the products were contaminated by many byproducts the relative quantities of which depend appreciably on the number of fluorine atoms in the trihalomethyl group.



Mono-, di- and trithiophosphites with trihalomethyl groups are cleaved by trihalomethanesulphenyl chlorides to a mixture of symmetrical and unsymmetrical disulphides.[135]

$$(R_FS)_xPCl_{3-x} + R'_FSCl \longrightarrow R_FSSR_F + R_FSSR'_F + R'_FSSR'_F + PCl_3$$

$x = 1$ to 3; R_F, $R'_F = CF_nCl_{3-n}$, $n = 1$ to 3.

In contrast, methylthio dichlorophosphite behaves in these reactions as a CH acid.[13]

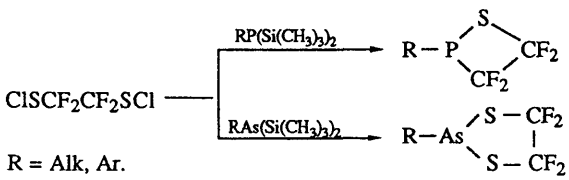
$$CF_3SCl + CH_3SPCl_2 \rightarrow CF_3SCH_2SPCl_2.$$
34%

The trihalomethanesulphenyl chlorides react with white phosphorus under mild conditions (−80 °C) forming mainly dialkyldithiochlorophosphites with contamination by other substances.[135]

$$R_FSCl + P_4 \rightarrow (R_FS)_xPCl_{3-x} + R_FSSR_F + F_mCl_{2-m}C{=}S,$$

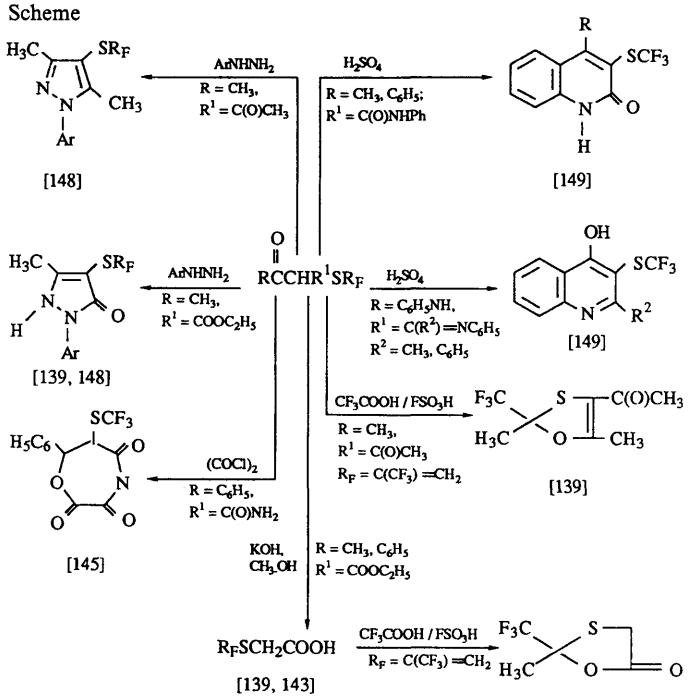
$R_F = CF_nCl_{3-n}$, $n = 1$ to 3, $x = 1$ to 3; $m = 1.2$.

The reaction of 1,2-bis(chlorosulphenyl)tetrafluoroethane with bis(trimethylsilyl) phosphonites and with bis(trimethylsilyl) arsenites leads to thiophosphetanes and dithiarsolanes respectively.[136]



Reactions with C-nucleophiles. Reactions of this type arouse increased interest from the point of view of synthesising numerous polyfluoroalkylthiolated biologically active substances and their precursors. PFASC display a more moderate activity than their unfluorinated analogues when reacting with various C-nucleophiles.

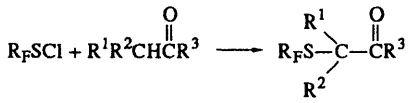
Scheme



Enolising carbonyl compounds, including aldehydes, ketones, α- and β-diketones and various β-ketocarboxylic acid derivatives, are *C*-polyfluoroalkylthiolated most readily and unequivocally in the majority of cases.[16,26,137,147] Actual examples of reactions of this type are given in Table 3. Carbonyl compounds modified by PFASC are widely involved in syntheses of biologically active compounds (see Scheme) and include pyrazoles and pyrazolones,[139,148] oxazepines,[145] quinolinones[149] and 1,3-oxathioles.[139] These are used in the synthesis of cephalosporin antibiotics, polyfluoroalkylthiocarboxylic acids[139,143,150] and 1,3-oxathiolanones.[139]

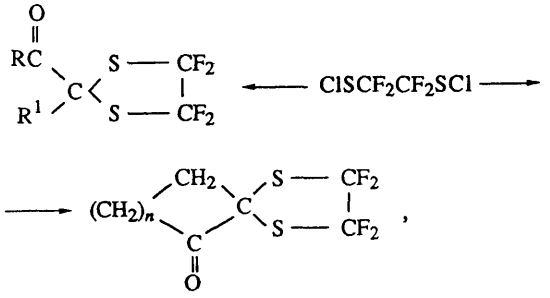
Only products of monosubstitution are formed in the majority of reactions of PFASC with carbonyl compounds,[143,147] however the formation of products of bispolyfluoroalkylthiolation was recorded in the case of acetone and benzoylacetamide.[137,139,145]

Table 3. Reactions of PFASC with carbonium compounds



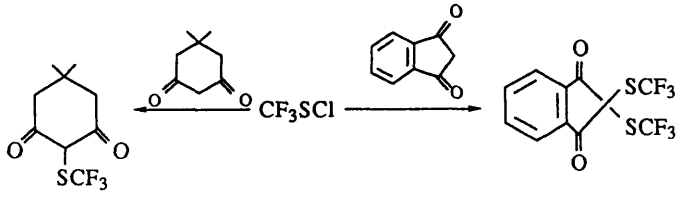
R_F	R^1	R^2	R^3	Ref.
CF_3, $CFCl_2$	CH_3	CH_3	H	[137]
CF_3, $ClCH_2CH(CF_3)$, $CH_3OOC-C(CF_3)=$	H	H	CH_3	[26, 137, 139]
CF_3	CH_3	CH_3	CH_3	[137, 138]
CF_3, CF_2H	H	H	$(CH_3)_3C$	[16]
$ClCH_2CH(CF_3)$	H	H	C_6H_5	[139]
CF_3	H	CH_2CH_2Cl	$X-C_6H_5$	[140, 141]
$ClSCF_2CF_2$	H	H	$CH_3C(O)$	[142]
CF_3, $ClCH_2CH(CF_3)$	H	$COOC_2H_5$	CH_3	[139, 143]
$ClCH_2CH(CF_3)$	H	$CH_3C(O)$	CH_3	[139]
$ClCH_2CH(CF_3)$	CH_3	$COOC_2H_5$	CH_3	[139]
CF_3	$CH_2C(O)CH_2CH_2$	$COOC_2H_5$	CH_3	[144]
CF_3	H	$C(O)NHC_6H_5$	CH_3	[143]
CF_3	H	$C(O)NHC_6H_5$	C_6H_5	[143]
CF_3	H	$C(O)NHC_6H_5$	C_6H_5	[143]
CF_3	H	$C(O)NH_2$	C_6H_5	[145]
CF_3	H	$C(S)NHC_6H_4Br$	CH_3	[145]
CF_3	H	$R-C=N-C_6H_5$, $R = CH_3, C_6H_5$	C_6H_5NH	[143]
CF_3	H	$(R-C=N-CH_2-)_2$, $R = CH_3, C_6H_5$	CH_3, C_6H_5	[146]

1,2-Bis(chlorosulphenyl)tetrafluoroethane forms only heterocyclic disubstitution products with acyclic and cyclic carbonyl compounds.[142,151]

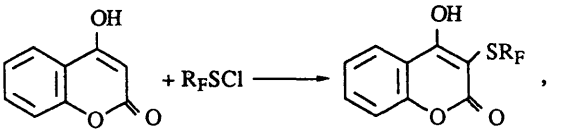


$R = CH_3$, $(CH_3)_3C$; $R^1 = H$, $C(O)CH_3$; $n = 1.2$.

Monosubstitution products of 1,3-cyclohexadiones are formed with CF_3SCl even with an excess of sulphenyl chloride but in the analogous reaction with indane-1,3-dione only the disubstituted product was obtained.[147]

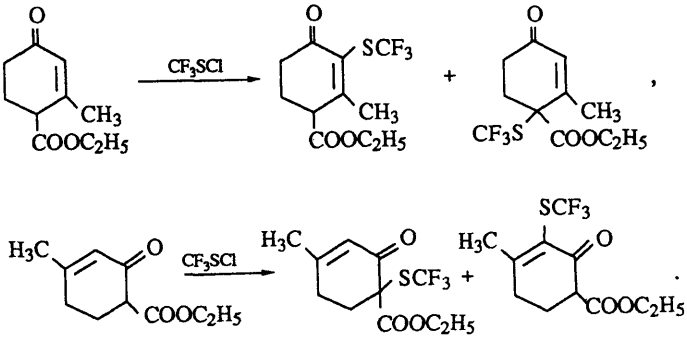


The effect of the PFASC structure on the conditions for thiolating carbonyl compounds has not yet been studied. Only in the example of 4-hydroxycoumarin was it established that the formation of 3-polyfluoroalkylthiolated derivatives was hampered by an increase in the electron-accepting properties of the polyfluoroalkyl group.[52]

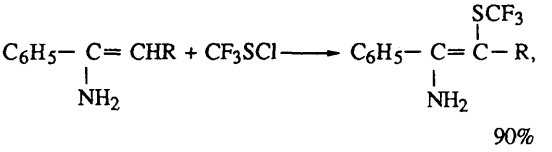


$R_F = ClCH_2-CH(CF_3)$, CCl_2FCF_2, $CH_3OOC-C(CF_3)_2$.

The polyfluoroalkylation reaction is usually effected regiospecifically at the α position to the C=O group. Moreover cyclohexenenonecarboxylic acids, having two CH-acid centres, give a mixture of two products with a predominance of the thiolation product at the more reactive centre.[144]

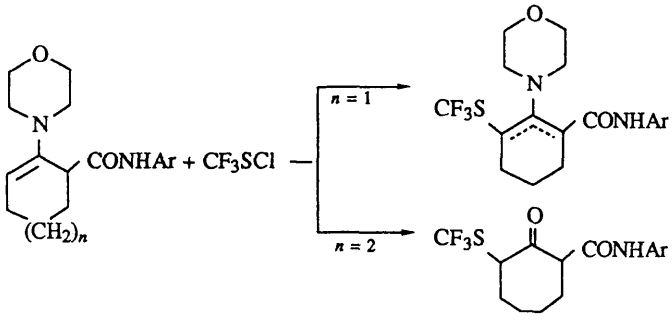


Enamines react with PFASC like the enolised ketones giving monosubstitution products.[145]



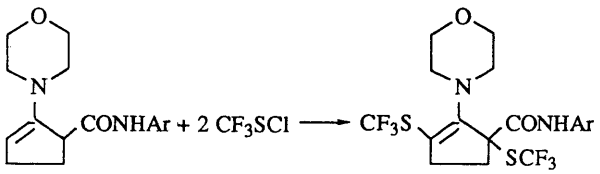
$R = C(O)NH_2$, CN.

Enamines based on derivatives of cyclohexanone- and cycloheptanone-2-carboxylic acids are thiolated in the presence of pyridine only at the unsubstituted 2 position of the ring.[153]



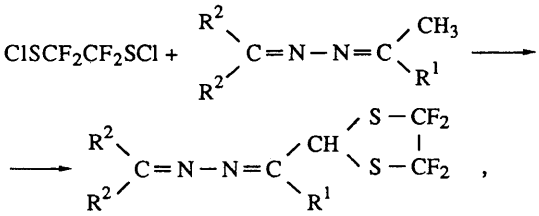
$Ar = C_6H_5$, $4\text{-}ClC_6H_4$.

In contrast, the more strained derivatives of cyclopentanone-2-carboxylic acid are converted by an excess of CF_3SCl into 2,5-dithiolation products.[153]

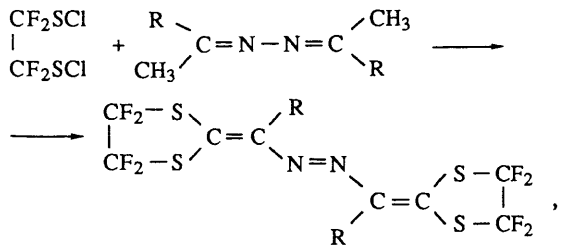


$Ar = C_6H_5$, 4-ClC_6H_4.

1,2-Bis(chlorosulphenyl)tetrafluoroethane readily thiolates azines containing methyl groups. The reaction is accompanied by the evolution of HCl and leads either to dithiolanylazines or to a *trans*-diazene.[154]

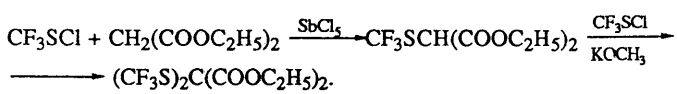


$R^1 = CH_3$, C_6H_5; $R^2 = CF_3$, C_6H_5;

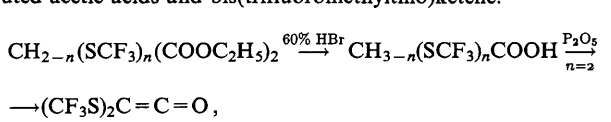


$R = CH_3$, C_2H_5, C_6H_5.

In contrast to ketones, malonic ester reacts with trifluoro- and chlorodifluoromethanesulphenyl chlorides only on heating above 100 °C giving mono- and disubstituted products.[148] Mild trifluoromethylthiolation of malonic ester occurs only on electrophilic catalysis. The monothiolation product reacts further with CF_3SCl in the presence of base.[155]

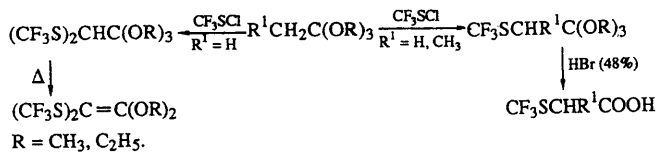


The polyfluoroalkylthiomalonates obtained are converted into substituted acetic acids and bis(trifluoromethylthio)ketene.[155]



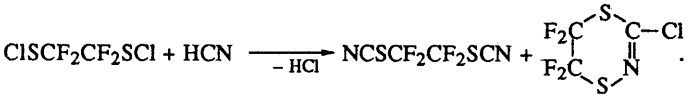
$n = 1, 2$.

Under mild conditions (−5 °C) orthoesters of carboxylic acids form products of mono- and in certain cases ditrifluoromethylthiolation which proved to be good precursors for a series of valuable products.[156]

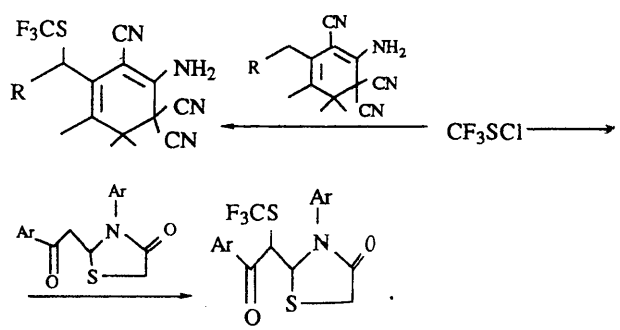


$R = CH_3$, C_2H_5.

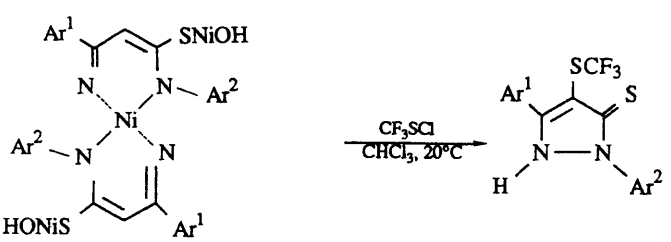
1,2-Dithiocyanotetrafluoroethane, with a 1,4,2-dithiazene as contaminant (4%), is readily formed in the reaction of 1,2-bis-(chlorosulphenyl)tetrafluoroethane with HCN.[157]



Trifluoromethylthiolation occurs fairly readily at the CH-acid centre activated by the cyclohexadiene[158] or thiazolidine[159] rings.



In some cases the trifluoromethylthiolation of compounds is accompanied by heterocyclisation. For example the nickel complex of β-aminothiocinnamic acid anilide is converted into a substituted 3-pyrazoline-5-thione.[160]



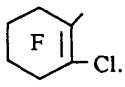
Ar^1, $Ar^2 = C_6H_5$, ClC_6H_4, $CH_3C_6H_4$.

The anilines of the *N*-benzoylamide of benzoylthioacetic acid are converted on trifluoromethylthiolation into 1,3-oxazoline-4-thione and the CF_3S group is lost on heterocyclisation.[145]

Organometallic compounds react readily with PFASC. This enables sulphenylation of lithium alkyl compounds to be carried out with fluorocarbonylsulphenyl chloride,[59] and of various lithium-acetylenes with 1,2-bis(chlorosulphenyl)tetrafluoroethane.[161] The

reaction of perfluoroalkenesulphenyl chlorides with KCN is effected unambiguously under mild conditions.[162] Stable alkenyl thiocyanates are formed by this which indicates the stabilising effects of the *pd* interactions in the F–C–S triad and in the F–C–C–S four-centre systems.

$$R_FSCl + KCN \longrightarrow R_FSCN,$$

$R_F = (CF_3)_2C{=}CF,\ (CF_3)_2C{=}C{-}C_2F_5,$ 

The trifluoromethylthiolation of sodium derivatives of nitromalonic ester is effected less unequivocally,[163] and also the reaction of trihalomethylsulphenyl chlorides with salts of such strong CH-acids as a tetraalkyl methylenediphosphonate.[164]

2. Reactions with aromatic and heteroaromatic compounds

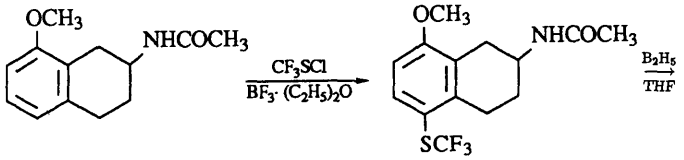
In the last decade interest in polyfluoroalkylthiolated aromatic and heteroaromatic compounds has grown in connection with the prospect of biologically active compounds with valuable properties. The number of studies on the direct thiolation of various types of aromatic and heteroaromatic compounds with PFASC has increased for this reason. Presently this method competes in many cases with the previously widely studied indirect routes of forming polyfluoroalkylthio groups in an aromatic matrix.[6]

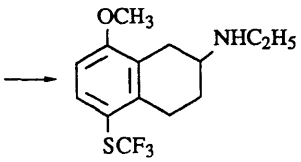
Benzene is thiolated by CF_3SCl on heating (100 °C) in the presence of BF_3 or at 20 °C in the presence of catalytic quantities of CF_3SO_3H.[165]

$$C_6H_6 + CF_3SCl \xrightarrow[[CF_3SO_3H]]{20\ ^\circ C,\ 5\ h} C_6H_5SCF_3 + HCl.$$

Toluene reacts similarly giving a mixture of *ortho* and *para* substitution products but chloro- and bromobenzene in the presence of HF form mixtures of all the possible isomers only at 200 °C.

Trifluoromethanesulphenyl chloride reacts mainly as a chlorinating agent with trifluoromethyl phenyl sulphide in the presence of CF_3SO_3H.[165] A methoxy group in the ring facilitates thiolation and was used in the synthesis of trifluoromethylthiolated compounds with antidepressant activity.[166]



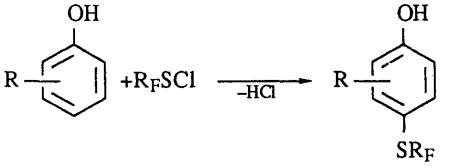


Di- and trimethoxybenzenes are distinguished by an increased ability to polyfluoroalkylthiolate. Both 1,3-di- and 1,3,5-trimethoxybenzenes react without a catalyst.[167,168] It is convenient to use magnesium and mercury derivatives for the thiolation of aromatic compounds with electron-accepting groups, PFASC do not display a marked chlorinating action with these compounds.[168]

$$4\text{-}XC_6H_4HgCl + CF_3SCl \rightarrow 4\text{-}XC_6H_4SCF_3 + 4\text{-}XC_6H_4Cl + C_6H_5X,$$

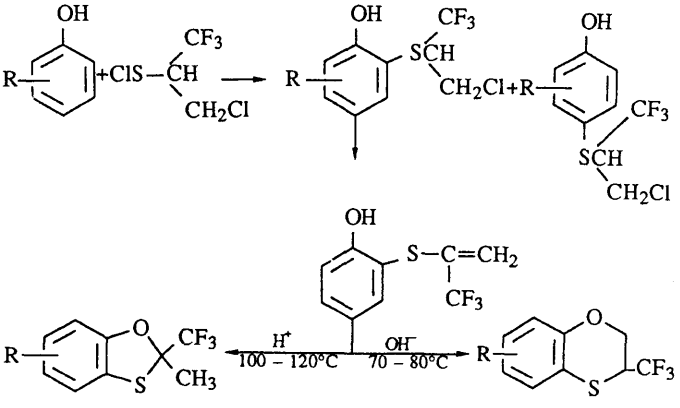
$X = CH_3O,\ CH_3,\ H,\ Cl,\ NO_2.$

Phenol and its derivatives containing electron-donating substituents in the aromatic ring react with PFASC in the absence of catalyst. Reactions are carried out in the presence of pyridine to bind the evolved HCl in the case of the volatile CF_3SCl. Otherwise Lewis acids are used as catalysts to increase the thiolation rate.[3,41,72,167,168,170] Under these conditions *ortho* and *meta* substituted phenols are usually thiolated at the *para* position.



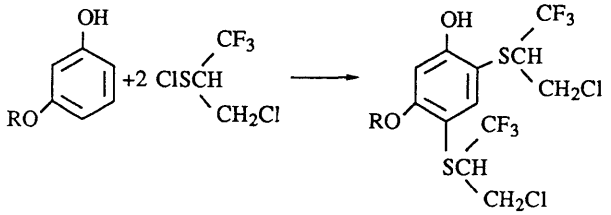
R = H, Alk, Cl, F, OH, OCH_3; $R_F = CF_3,\ C_7F_{15},\ ClCF_2CF_2,$
$Cl_2CFCF_2,\ CH_3OOC{-}C(CF_3)_2,\ AllOOC{-}C(CF_3)_2$

Only particularly reactive PFASC such as $ClCH_2{-}CH(CF_3)SCl$ form *ortho* and *para* substitution products with phenols. The selectivity of the reaction increases in the presence of solvent, the nature of which determines the direction of thiolation to a significant degree.[167] To separate the *ortho*-thiolated phenols it is possible to use their tendency to cyclise.



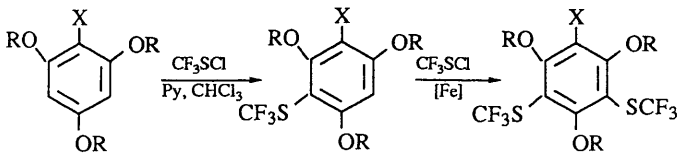
In the absence of a catalyst *para* substituted phenols usually form *ortho* substitution products on heating.[41] Monosubstituted phenols in general are characterised by a marked reduction in the ability to be thiolated by PFASC in the series *meta* > *ortho* ⩾ *para* and electron-donating substituents are arranged in the usual series $CH_3O > CH_3 > F \geqslant Cl$ in inactivating ability. *m*-Methoxyphenol proved to be the most reactive of the studied phenols of this series and gave a mixture of *ortho* and *para* substitution products. Even disubstitution products are formed with an excess of sulphenyl chloride.[167] Dihydroxybenzenes are arranged in the same series as monosubstituted phenols in their reactivity towards PFASC.

Resorcinol is the most reactive and also forms a dithiolation product at 20 °C.



R = H, CH_3 .

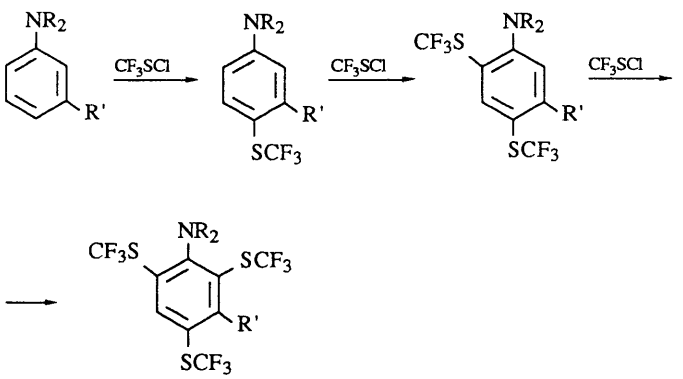
Phenols with electron-withdrawing substituents do not react with PFASC. The only exceptions are derivatives of resorcinol and phloroglucinol which, depending on the conditions, form substitution products with one or two molecules of CF_3SCl.[168]



R = H, CH_3; X = $CH_3(O)C$, CH_3OOC, C(O)H.

The conditions of the reactions under consideration are also determined in many cases by the nature of the PFASC. The polyfluoroalkylthiolation of phenols is appreciably suppressed by an increase in the electron-accepting properties of the polyfluoroalkyl group and the steric effects at the S—Cl group.[41,167]

The *N,N*-dialkylanilines are appreciably more reactive towards CF_3SCl and form *para* substitution products and 2,4-di- and 2,4,6-trisubstitution products when activating OH and CH_3O groups are present.[72]

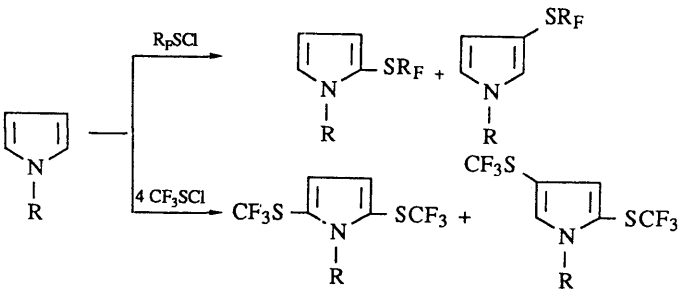


R = CH_3, C_2H_5; R' = H, OH, OCH_2CF_3.

Only *meta*-hydroxy and *meta*-alkoxy derivatives of primary and secondary arylamines give *C*-trifluoromethylthiolation products.[72]

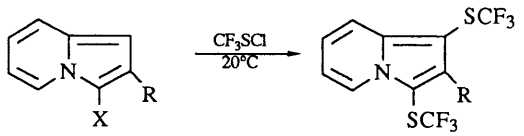
Of the heteroaromatic compounds only compounds with high π-donor properties react with PFASC in the absence of a catalyst.

Pyrrole and *N*-methylpyrrole readily form 2- and 2,5-substitution products in the presence of HCl acceptors. Contamination of 3(4)-substitution compounds as side products has been recorded.[171,172]



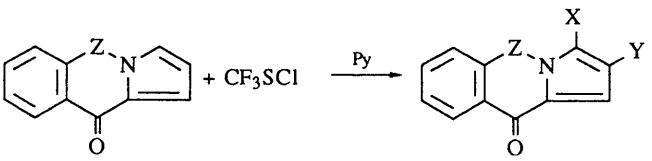
R = H, CH_3; R_F = CF_3, CF_2Cl, $CFCl_2$, CF_3SCFCl, F(O)C, C_7F_{15}.

Indole gives a C(3) thiolation product with CF_3SCl under these conditions.[172] Donating substituents in the pyrrole ring facilitate and accepting substituents hinder thiolation directing it to the 3(4) position.[172] Indolizines react particularly readily with CF_3SCl forming 1,3-disubstituted derivatives even in the case of indolizines acetylated at the 1 position.[173]



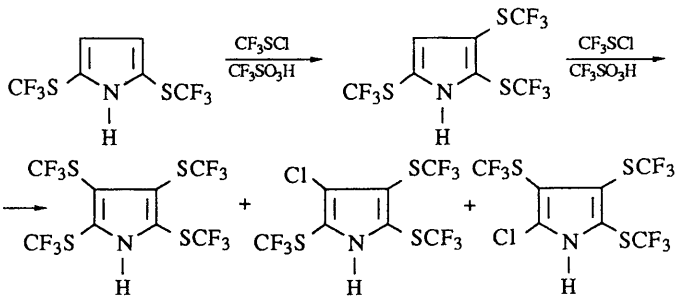
X = H, $C(O)CH_3$; R = H, CH_3, C_6H_5.

The polyfluoroalkylthiolated derivatives of pyrroles possess high biological activity.[174,175] The pyrrolo[2,1-*b*][3]benzazepines with CF_3S substituents in the pyrrole ring are of particular interest, possessing myorelaxant and tranquilising action.[176,177]

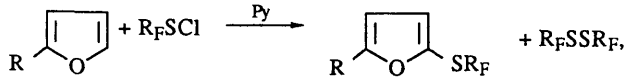


Z = —CH=CH—, X = SCF_3, Y = H; Z = $—CH_2—CH_2$;
X = SCF_3, Y = H; X = H, Y = SCF_3.

The exhaustive trifluoromethylthiolation of the pyrrole ring is of theoretical interest. In the presence of CF_3SO_3H this is accompanied by chlorinating effects of CF_3SCl and 1,2-migration of a trifluoromethylthio group.[178]

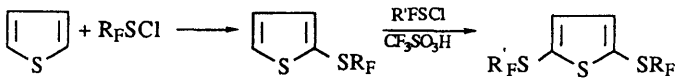


Furan and sylvane (α-methylfuran) react with significantly more difficulty with trihalomethanesulphenyl chlorides in the presence of pyridine. The products are 2- and 5-trihalomethylthio derivatives of furan (sylvane) together with disulphides and polymeric compounds.[171,179] The use of Lewis acids as catalysts or $(C_2H_5)_3N$ as an HCl acceptor proved to be ineffective.



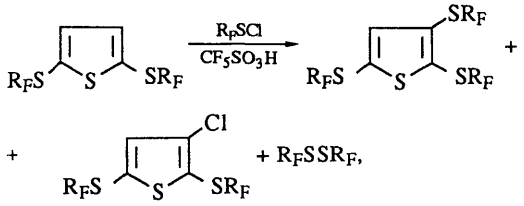
R = H, CH_3; R_F = CF_3, CF_2Cl, $CFCl_2$.

Thiophene reacts with even more difficulty. Monothiolation occurs only on catalysis by $SnCl_4$,[180] in the presence of pyridine under pressure[171] or in CF_3COOH.[181] Disubstitution products were successfully obtained on catalysis by perfluoroalkanesulphonic acids.[180,182]



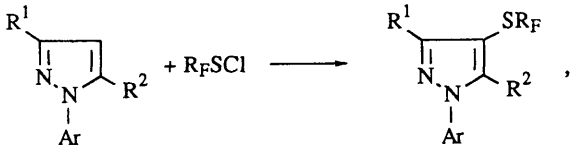
R_F, R_F = CF_3, CF_2Cl, $CFCl_2$.

On further thiolation of thiophene the chlorinating action of R_FSCl is shown.[165]



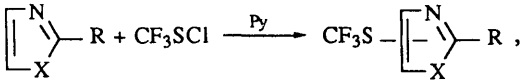
R_F = CF_3, CF_2Cl.

Selophene reacts with CF_3SCl like thiophene.[179] Five-membered heteroaromatic compounds with two heteroatoms react with PFASC only in the presence of electron-supplying substituents. Thus *N*-arylpyrazoles with an OH or NH_2 group in the 5 position are thiolated by trihalomethanesulphenyl chlorides at the C(4) atom. The compounds obtained and also their sulphoxides and sulphones display high insecticidal, acaricidal and nematocidal activity.[183–189]



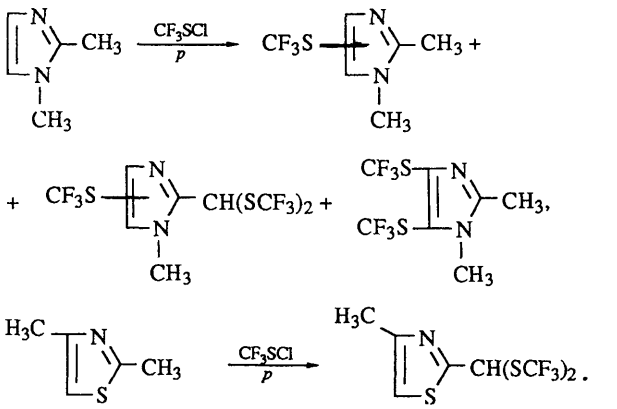
R_F = CF_3, CF_2Cl, $CFCl_2$; R^1 = H, Alk; R^2 = OH, NH_2.

Imidazoles and thiazoles activated by substituents display similar properties. The course of thiolation in this case has not been established precisely.[171,190]

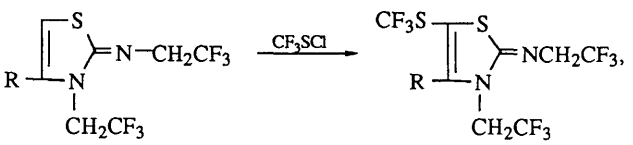


X = S, R = $NHSO_2CH_3$, $NHSO_2CF_3$, $NHCOCH_3$,
X = NCH_3, R = SCH_3, SCH_2CF_3.

The trifluoromethylthiolation of the 1,2-dimethylimidazole ring under pressure is accompanied by the side thiolation of the CH_3 group in the 2 position but in the analogous reaction of 2,4-dimethylimidazole the thiolation of the 2-CH_3 group is the sole course of the reaction.

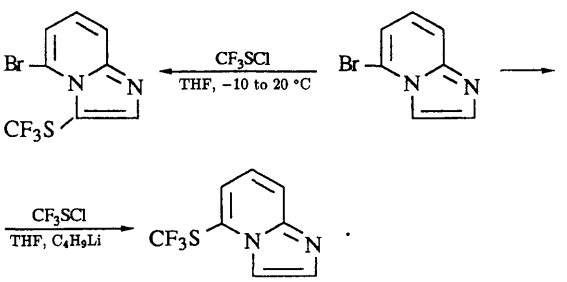


On the other hand derivatives of 2-aminothiazole are readily trifluoromethylthiolated at the C(5) atom.[171]



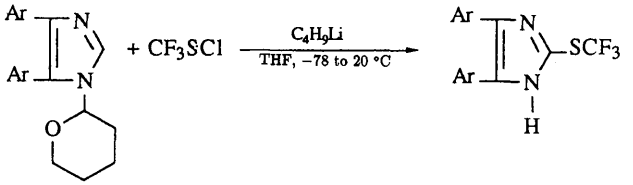
R = H, CH_3.

The reaction of CF_3SCl with 5-bromoimidazo[1,2-a]pyridine under mild conditions is effected in the imidazole ring after generation of a carbanionic centre with butyllithium in the pyridine ring.[191,192]

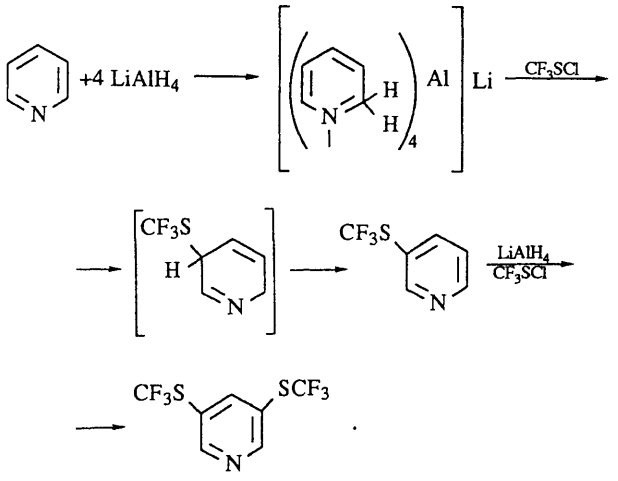


The compounds obtained possess a hypotensive action.

Butyllithium is widely used to generate anions of aromatic[193] and heterocyclic[186,194] compounds which are reactive towards PFASC. A series of active blood pressure regulators was obtained by this route among the 2-trifluoromethylthio-4,5-diarylimidazoles.[194]

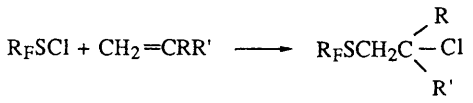


The trifluoromethylthiolation of pyridine was successfully effected only after reducing it to a dihydropyridine derivative.[179,195] The main reaction product is that of 3 substitution together with contamination by the 3,5-bisthiolated compound.



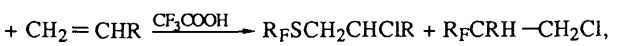
3. Reactions with unsaturated compounds

Features of the electrophilic properties of PFASC are most clearly displayed in their reactions with alkenes.[10,13,36,39,142,196–203] Only 2-chloro-1-trifluoromethylethanesulphenyl chloride reacts with ethylene and its homologues at 20 °C. With the appearance of fluorine atoms or CF_3 and other electron-withdrawing groups in the α position to the S–Cl bond the reaction temperature is abruptly increased (to 100–150 °C). Under relatively mild conditions such compounds add to ethylene only in polar solvents such as CH_3CN. Sterically hindered PFASC generally do not react in the absence of CH_3CN.[10,13,196,198] The addition of PFASC to a terminal ethylene occurs exclusively according to the Markownikov rule with the formation of products under thermodynamic reaction control.



R, R' = H, Alk, Cl, OC_4H_9, $OC(O)CH_3$; R_F = $ClCH_2CH(CF_3)$, $ClCF_2CF_2$, Cl_2CFCF_2, $CH_3OOC-C(CF_3)_2$.

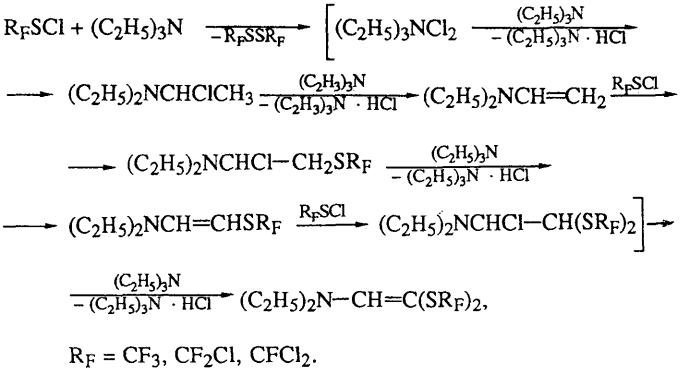
The formation of both regioisomers was observed only on carrying out the reaction in the presence of CF_3COOH which increases the reaction rate markedly.[197]



R = C_4H_9, $BrCH_2$, Br; R_F = CF_3, CF_2Cl, $CFCl_2$.

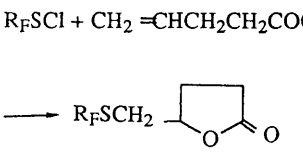
An important feature of the products formed under kinetic control is their stability on storage and fractionation which indicates the significant difficulties in this case of forming an episulphonium ion.

Of the functionally substituted ethylenes only vinyl alkyl ethers and vinyl acetate react readily with PFASC.[198] Seemingly enamines react even more readily as is indicated by the results of the mild reaction or perhalomethanesulphenyl chlorides with triethylamine.[129]



R_F = CF_3, CF_2Cl, $CFCl_2$.

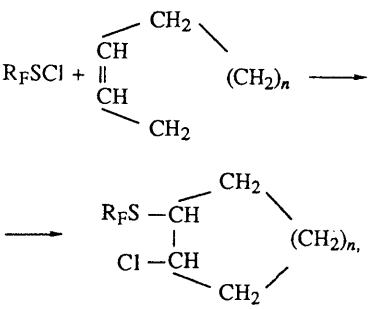
γ,δ-Unsaturated acids and their esters react under unusually mild conditions (−30 to 0 °C) with PFASC forming lactones.[200]



R_F = $ClCH_2-CH(CF_3)$, $ClCF_2CF_2$.

On the other hand β,γ-unsaturated acids and their esters react with PFASC as with other ethylenic compounds giving a mixture of regioisomers.[200] Evidently nucleophilic cooperation in the transition state by the carboxyl or carbalkoxyl groups favours a mild reaction of these compounds with the β,γ-unsaturated acids and their esters.

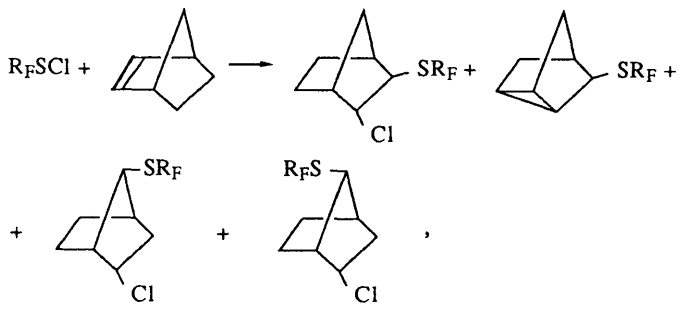
The PFASC, like their unhalogenated analogues, react more readily with strained cycloalkenes than with ethylene homologues. Thus cyclopentene and cycloheptene, differing in the higher strain and lower steric hindrance at the multiple bond, are more reactive in these reactions.[10,13,36,39,196,197]



R_F = CF_3, CF_2Cl, $CFCl_2$, Cl_2CFCF_2, $CF_3OCFClCF_2$, $ClSCF_2CF_2$, $CF_2ClCFCl$, $(CF_3)_3C$, $CH_3OOC-C(CF_3)_2$, $Cl(O)C-C(CF_3)_2$; n = 1, 2, 3.

The addition is effected *trans*-stereospecifically, including when CF_3COOH is present.[197]

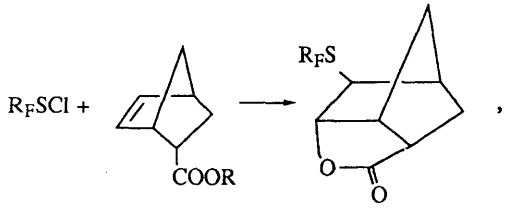
The more strained norbornene molecule reacts vigorously with chlorofluoro-containing methanesulphenyl chlorides in the absence of solvent giving products of *trans*-addition and Wagner–Meerwein rearrangement.[201]



$R_F = CF_3, CF_2Cl, CFCl_2$.

Trifluoromethanesulphenyl chloride is particularly reactive in this reaction and forms all four products even at −40 °C. This indicates an episulphonium mechanism for the reaction. The CF_3 group is capable of transforming the primary episulphonium ion into a norbornyl carbonium ion to a greater extent than a $ClCF_2$ or a Cl_2CF group.

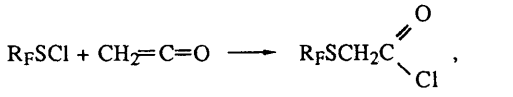
In contrast to norbornene, norbornene-5-carboxylic acid and its esters are lactonised unequivocally like acyclic γ,δ-unsaturated acids.[199]



R = H, CH_3; $R_F = ClCH_2-CH(CF_3)$, $ClCF_2CF_2$, Cl_2CFCF_2, $ClCH_2CCl(CF_3)$, $CH_3OOC-C(CF_3)_2$.

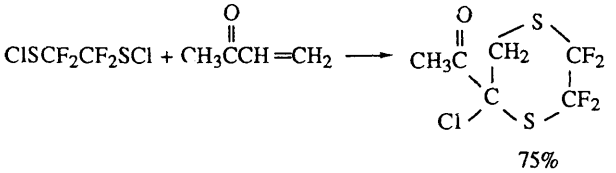
Under more forcing conditions the regioisomeric *trans*-addition products are formed in addition to the lactones. The acid chloride and nitrile of this acid react under more forcing conditions and give only a mixture of the products of *endo* and *exo* addition.

Under mild conditions at −20 to 20 °C PFASC add to ketene giving acid chloride of *S*-polyfluoralkylthioglycolic acid although this is more difficult than with the unfluorinated sulphenyl chlorides.[202,203]



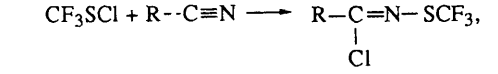
$R_F = CF_3, ClCH_2-CH(CF_3), ClCF_2CF_2, Cl_2CFCF_2$.

1,2-Bis(chlorosulphenyl)tetrafluoroethane reacts with methyl vinyl ketone at 20 °C.[142] The primary addition product cyclises into a 1,4-dithiane with elimination of HCl.



75%

Highly electrophilic unsaturated compounds usually do not react with PFASC. However hexafluorodimethylketene forms an adduct with the highly reactive 2-chloro-1-trifluoromethylethanesulphenyl chloride in acetonitrile.[39] Under forcing conditions (150 °C) fluoro-olefins are predominantly chlorinated by PFASC. Addition products are also isolated in 20% yield.[39,196] On heating, in the presence of catalysts or on UV irradiation trifluoromethanesulphenyl chloride adds at the C≡N bond activated by electron-withdrawing substituents.[204–206]



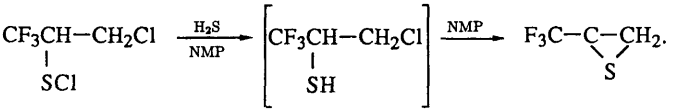
R = CF_3, Cl, $F_2S{=}N$, $F_2S(O){=}N$.

Products of combined trifluoromethylthiolation and fluorination of the C≡N bond were obtained on carrying out this reaction with ClCN, CF_3CN and CCl_3CN in the presence of HgF_2, i.e. $CF_3N(SCF_3)_2$, $CF_3CF{=}NSCF_3$ and $CCl_3CF{=}NSCF_3$ respectively.[207]

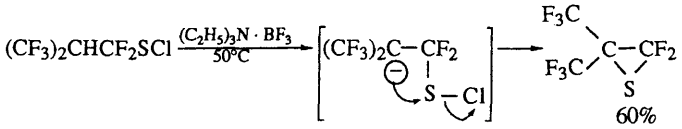
The above information enables it to be assumed that PFASC, like their unfluorinated analogues, react with unsaturated compounds by an Ad_E2 mechanism through an episulphonium transition state. The features of these reactions are determined by the reduction in the energy of formation and stability of the transition states connected with the efficient intramolecular $2p3d$-interactions of the F and S atoms, particularly in the F–C–S triad, and also the high electron-withdrawing ability of the polyfluoroalkyl groups.

4. Cyclisation reactions

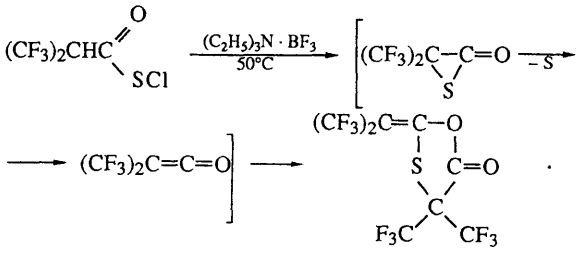
The ability of PFASC to form rings is linked primarily with anionotropic conversions in three-centre C–C–S systems. Thus 2-chloro-1-trifluoromethylethanesulphenyl chloride reacts with H_2S in *N*-methylpyrrolidone (NMP) with the formation of trifluoromethylthiirane. 2-Chloro-1-trifluoromethylethanethiol is an intermediate reaction products.[24]



2-Hydrooctafluoroisobutanesulphenyl chloride is smoothly dehydrochlorinated on heating with the $(C_2H_5)_3N.BF_3$ complex with the formation of perfluoroisobutene episulphide.[26]

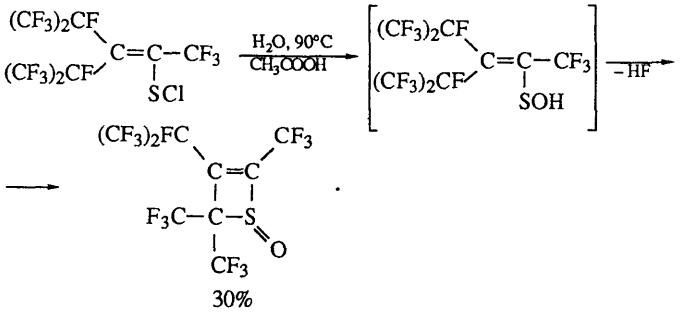


2-Hydrohexafluoroisobutyrylsulphenyl chloride also reacts in this way. However the intermediate thiiranone is desulphurised under the reaction conditions and the resulting bis(trifluoromethyl)ketene undergoes a (3 + 2) cycloaddition with the thiiranone.[26]



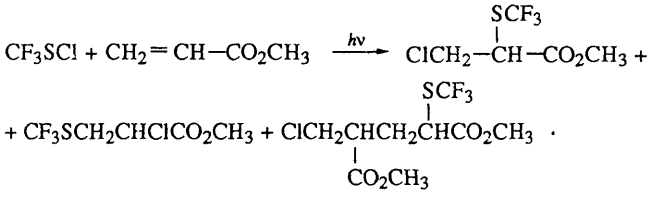
This reaction scheme was confirmed by the positive effect of bis(trifluoromethyl)ketene on the yield of final product.

Mild formation of a thietene ring, which is unusual for sulphur compounds, was observed on acid hydrolysis of the α,β-unsaturated sulphenyl chloride perfluoro-3-isopropyl-4-methyl-2-pentene-2-sulphenyl chloride. In the authors' opinion[137] an unstable sulphenic acid is the intermediate product.



5. Free radical reactions

PFASC undergo free radical conversions on UV or X irradiation and on catalysis by azo compounds. The addition of PFASC to olefins, including fluorine-containing olefins, initiated by UV light leads to both possible isomers and several byproducts.[3] For example CF_3SCl adds to methyl acrylate with the formation of a mixture of three main products,[203] from which CF_3S-containing acrylates are obtained by dehydrochlorination.



Irradiation with UV light initiates a reaction between PFASC and hydrocarbons. Depending on the structure of the sulphenyl chloride and the hydrocarbon the reaction leads to the predominant formation of four types of organic compound.[11,208–210]

$$R_FSCl + RH \rightarrow R_FSH + R_FSR + R_FSSR_F + RCl + HCl.$$

The mechanism of their formation is as follows:

$$R_FSCl \longrightarrow R_FS^{\cdot} + Cl^{\cdot}, \quad (1)$$

$$Cl^{\cdot} + RH \longrightarrow R^{\cdot} + HCl, \quad (2)$$

$$R_FS^{\cdot} + RH \longrightarrow R^{\cdot} + R_FSH, \quad (3)$$

$$R_FSCl + R_FSH \longrightarrow R_FSSR_F + HCl, \quad (4)$$

$$R^{\cdot} + R_FSCl \longrightarrow RCl + R_FS^{\cdot}, \quad (5)$$

$$R^{\cdot} + R_FSCl \longrightarrow R_FSR + Cl^{\cdot}, \quad (6)$$

$$R^{\cdot} + R_FSSR_F \longrightarrow R_FSR + R_FS^{\cdot}. \quad (7)$$

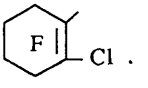
The chief factors determining the composition of the product mixture in these reactions are steric effects at the reaction centres of the sulphenyl chloride and the hydrocarbon. In a series of R_FSCl where R_F was $CF_3 < HCF_2CF_2 < n\text{-}C_3H_7 < (CF_3)_2CF < (CF_3)_3C$ and also in the series $CF_3 < ClCF_2 < Cl_2CF$ the yield of sulphide is significantly reduced. Sulphide was not detected in the reaction mixture in the case of perfluoro-t-butanesulphenyl chloride and stage (4) of the process did not occur for steric reasons. Consequently perfluoro-t-butanethiol and a chlorohydrocarbon are formed exclusively in the free radical reaction of $(CF_3)_3CSCl$ with hydrocarbons. Similarly the ratio of sulphide to chlorohydrocarbon is reduced in the series benzyl < butyl < sec-butyl < cyclohexyl with increasing bulk of the alkyl groups.

6. Oxidation reactions

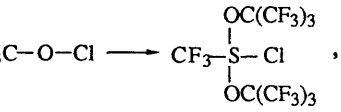
The possibility of obtaining polyfluoroalkanesulphonyl chlorides by the oxidation of PFASC with chlorine in water or hydrochloric acid has been shown in several cases.[12,14,25,196]

$$R_FSCl \xrightarrow[H_2O]{Cl_2} R_FSO_2Cl,$$

$R_F = (CF_3)_2CFOCF_2CF_2$, $CH_3OOCCF_2CF_2$,

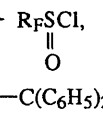
$ClCH_2\text{–}CH(CF_3)$, .

Perfluoroalkyl hypochlorites react with CF_3SCl giving either sulphuranes of S(IV) fluorides.[211]



$$CF_3SCl + CF_3OCl \longrightarrow CF_3SF_3.$$

The PFASC are oxidised by peracids under controlled conditions to polyfluoroalkanesulphinyl chlorides.[23,30,46]



$R_F = CF_3CCl_2$, $CF_3\text{–}C(C_6H_5)_2$, $(CF_3)_2CCl$.

On oxidising $ClSCF_2CF_2SCl$ with 30% hydrogen peroxide di-(2-chlorosulphonyltetrafluoroethyl) disulphide is formed in addition to oxidation to the sulphonyl chloride.[212]

$$ClSCF_2CF_2SCl \xrightarrow{H_2O_2} ClSO_2CF_2CF_2SSCF_2CF_2SO_2Cl.$$

Various fluorinating agents (ClF_3, AgF_2, BrF_3/HgF_2) convert PFASC to a mixture of different products including organic fluorides of tetra- and hexavalent sulphur,[213,214] such as

$$ClCF_2SCl \xrightarrow[60-70°C]{AgF_2} ClCF_2SF_3 + CF_3SF_3 + CF_3SF_5.$$

The information discussed above show that the chemistry of PFASC and of their unfluorinated analogues are mainly similar. In addition, important features of the fluorine-containing sulphenyl chlorides may also be noted. They are more difficult to form, they possess higher stability and markedly less reactivity and their reactions usually occur by thermodynamically controlled routes. The R_FS group of perfluoroalkanesulphenyl chlorides has a clearly expressed 'pseudo-halogen' character as the PFASC display chlorinating properties and the perfluoroalkanethiol group frequently acts as a leaving group in rearrangements and heterocyclisations.

All these features are undoubtedly linked with the effective intramolecular $2p3d$-interactions of the F and S atoms which leave an imprint on the properties of the products of the numerous conversions of PFASC. The stabilising effects of these interactions determine the unusually high static and kinetic stability of the new type of compound, viz. the α-polyfluoroalkenesulphenyl chlorides.

From a practical point of view the PFASC are more convenient reagents for organic synthesis than the functionally unsubstituted alkanesulphenyl chlorides. They store well and are not afraid of moisture. Their reactions are sensitive to solvent effects which enables processes to be controlled reliably. In spite of the somewhat reduced reactivity the PFASC possess a wide spectrum of properties and are efficient precursors of fluorine-containing compounds of numerous types.

Up to the present completely halogenated fluorine-containing methane- and ethanesulphenyl chlorides have been predominantly studied to obtain fluorine-containing analogues of first and second generation pesticides in the synthesis of biologically active compounds for agriculture. The corresponding derivatives of hormonal preparations are practically uninvestigated. In medicine only trifluoromethylthiolated derivatives of neuroregulators of hormone metabolism have been investigated. However the result of even these few investigations indicate that the time has now arrived for an intensive development of the chemistry of PFASC as potential precursors of biologically active compounds for various purposes.

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