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THE ELEMENT DISPLACEMENT PRINCIPLE: A NEW GUIDE IN p-BLOCK ELEMENT CHEMISTRY[1]

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[1] This review is based on an article published in 1982 entitled "A New Classification Principle: The Periodic System of Functional Groups" [Haas, A., *Chemiker Zeitung* **106**, 239 (1982)] and contains new results supporting this principle.

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I. Introduction

The concept that will be discussed in this article has its origin in the hydride displacement principle published by Grimm (*1*) in 1925. He showed that elements situated up to four places before a noble gas change their properties by taking up 1, 2, 3, or 4 (x) hydrogen atoms so that the resulting radicals behave as pseudoatoms, which resemble the reference elements situated in the periodic system x groups to the right of them, e.g., $CH \mathrel{\hat{=}} N$, $CH_2 \mathrel{\hat{=}} O$, $CH_3 \mathrel{\hat{=}} F$, and so on. The radicals obtained by this procedure are isoelectronic and isoprotonic with the reference elements; they are termed "pseudoelements." So far this principle has been used only on elements of the second period, but it also applies without limitations to all other Group IV–VII elements. An impressive example is found in the following series of oxyacids: H_9InO_6 (as $M_3^I[In(OH)_6] \cdot 2H_2O$; $M = Na^+, K^+$), H_8SnO_6, H_7SbO_6, H_6TeO_6, H_5IO_6, and H_4XeO_6. They can be written as $H_4(InH_5)O_6$, $H_4(SnH_4)O_6$, $H_4(SbH_3)O_6$, $H_4(TeH_2)O_6$, $H_4(JH)O_6$, and $H_4(Xe)O_6$. Their similar chemical properties are due to the pseudoxenon behavior of (IH), (TeH_2), (SbH_3), (SnH_4), and (InH_5).

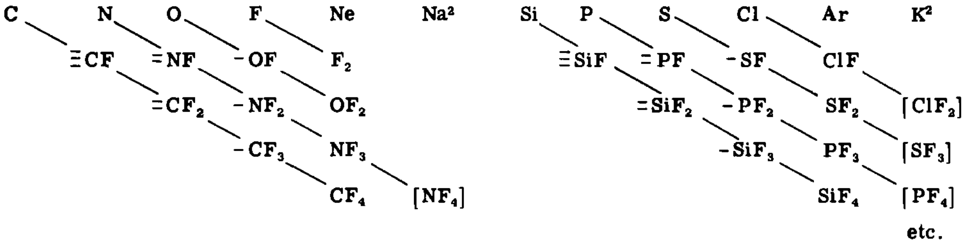
Birkenbach and Kellerman (*2*) reported also in 1925 on monovalent inorganic groups consisting of two or more electronegative atoms with chemical and physical properties partly similar to those of halogens, e.g., CN, SCN, OCN, N_3, NCO, NCS, etc. They were also termed "pseudohalogens," although they are neither isoelectronic nor isoprotonic with the reference halogens. At the beginning of the perfluorohaloorgano chemistry of the elements, Lagowski (*3*) drew attention in 1959 to the halogen-like behavior of the CF_3 and CF_3S radicals for, among other reasons, the fact that their electronegativities were comparable with those of the halogens [CF_3 (3.3) and CF_3S (2.7)]. The latter radicals again are neither isoprotonic nor isoelectronic with the halogens.

Incorporating these pseudoelements into the periodic system, the large differences between the chemical and physical properties of elements of different periods are appreciably alleviated. If, e.g., the electrode potentials (in volts) of pseudohalogens are arranged with those of halogens the following progression is obtained (*4*): F^- (2.3), $(NC)_2N^-$ (2.3), O_2NO^- (2.3), $(NC)_3C^-$ (2.1), Cl^- (2.0), NCO^- (2.0), $(O_2N)_3C^-$ (2.0), Br^- (1.7), NCS^- (1.5), I^- (1.2), $NCSe^-$ (1.1). It should be possible to eliminate sudden changes by incorporating further composite element-like groups into the periodic system, provided that a concept can be found which is able to establish a correlation between "pseudoelements," "pseudohalogens," and CF_3 or CF_3S, and which also allows the existence of new element-like groups to be deduced.

This requirement is met by the concept of *element displacement.*

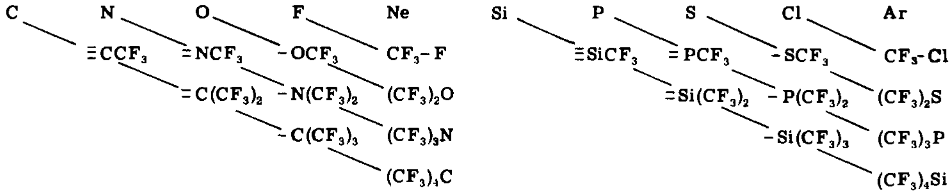
II. The Element Displacement Principle

Coordination of the elements of Groups IV–VII—subsequently termed base elements—with elements or element groups—termed ligands—forming one, two, three, or four covalent bonds results in a shift of one, two, three, or four places to the right (higher atomic number) within a period. This process is termed the *element displacement principle.* In the following, fluorine is used as a representative for all other monovalent ligands. With the fluorine atom, which is isogeometric with the hydrogen atom, as a ligand the following perfluorinated groups are obtained.



The groups obtained by fluorine displacement are different from Grimm's pseudoelements, being neither isoelectronic nor isoprotonic with their reference atoms and should conceptually be clearly differentiated from them. It is suitable to call these and other radicals obtained similarly *paraelements.*[3]

Each paraelement for its part is then able to function as a ligand. Thus, for example, using the halogen-like CF_3 radical, the *first-order derivative paraelements* shown below are obtained.



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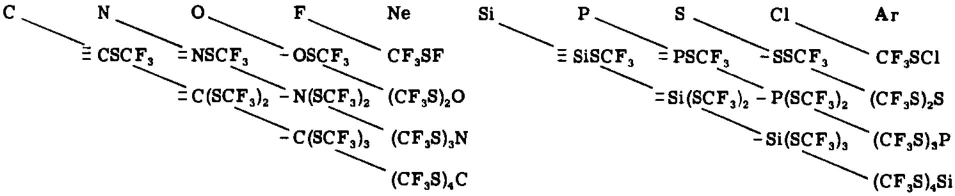
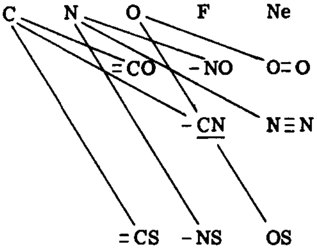
[2] Paraelements of this group are only stable as cations.

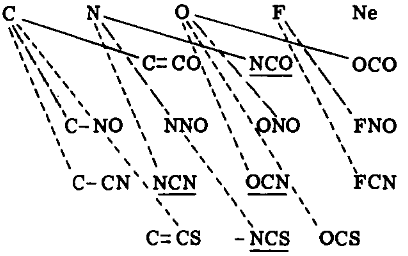
[3] παρα (para): near, secondary.

If first-order derivative paraelements are themselves used as ligands this system of nomenclature leads to second-order derivative paraelements, e.g., using CF_3S. This procedure can be continued in many cases with meaningful results.



Which sort of paraelements do we obtain with ligands like oxygen, sulfur, or nitrogen? When any one of these is used as the ligand a displacement of two or three groups must of course result, as follows:





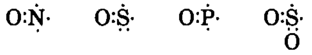
(*4,5*)

These resulting paraelements may also appear as ligands. If, for example, the CO, NO, CN, or CS groups are coordinated above, first-order derivative paraelements are obtained.

All classical pseudohalogens can be deduced in this way. A base element and paraelement have the same number of valence electrons. This means that covalent electron pairs held in common by base atom and ligand are assigned to the base atom, which becomes electronically isovalent with the reference element.

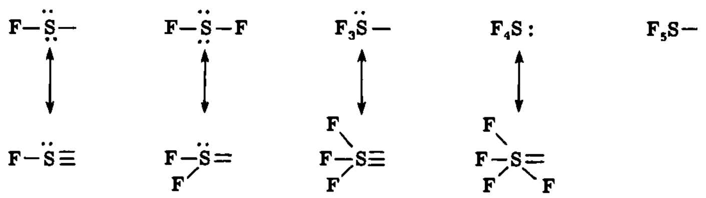
The elements boron, aluminum, gallium, indium, and thallium similarly add ligands forming pseudo- or paraelements which are shifted to the right. Analogously, addition of an electron to an element (equivalent to a covalent bond) forms an ion which is shifted in the same direction, e.g., $Tl^- \triangleq C$ (*6*); $C^- \triangleq N$; Si^-, Ge^-, $Pb^- \triangleq P$; Si^{2-}, $As^- \triangleq Se$; O^-, $S^- \triangleq Cl$ (*7*). A shift to the left side of the periodic system is achieved by loss of electrons, e.g., $N^+ \triangleq C$, $C^+ \triangleq B$, $O^+ \triangleq N$, $Cl^+ \triangleq S$.

The elements of Groups I–III have, with the exception of boron, low ionization potentials and therefore are shifted mainly to the left when forming covalent bonds with a ligand. Covalent electron pairs between base atom and ligand are transferred in the process of heterolytic fission to the ligand, leaving a formal positive charge on the base atom, which is displaced to a reference element of lower atomic number. The elements of Group III therefore can be shifted to the right by acquiring or to the left by losing electrons. Therewith the possibility of paraelement formation is not exhausted, as elements of Groups IV–VII have at their disposal free electron pairs and consequently are able to form coordinate bonds:



The number of unpaired valence electrons on the central atom being unchanged, base and reference element are identical.

Elements of the third to fifth periods are also able to expand their octet shells. New paraelements result in this way which have not so far been mentioned, e.g.,



Thus when fluorine is a ligand sulfur can form the following paraelements:

$F{-}\ddot{S}{\equiv}$ and $(F{-})_3S{\equiv} \longrightarrow$ paranitrogen

$(F{-})_2\ddot{S}{=}$ and $(F{-})_4S{=} \longrightarrow$ paraoxygen

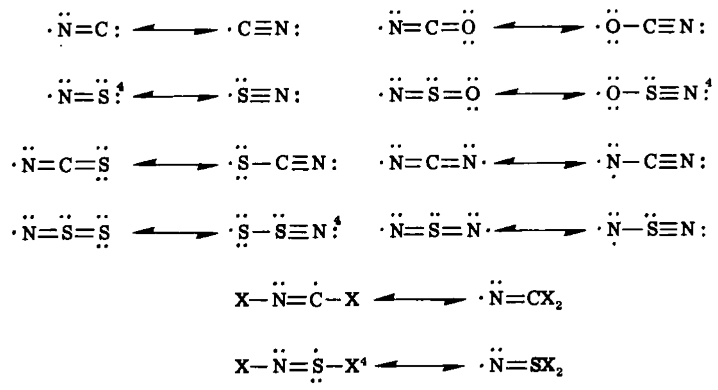
$F{-}\underset{\cdot\cdot}{\ddot{S}}{-}$, $(F{-})_3\ddot{S}{-}$, and $(F{-})_5S{-} \longrightarrow$ parahalogen

An analogous behavior is found for the other elements, e.g., phosphorus, arsenic, selenium, etc. Paraelements of this sort are no longer electronically isovalent with their reference elements; they do, however, remain isovalent with the reference element. Thus the criterion of isovalence is common to all paraelements.

III. Application of the Element Displacement Principle to Recent Chemical Problems

EQUIVALENCE BETWEEN CARBON AND SULFUR(IV)

An interesting relationship between carbon and s^2p^3d hybridized sulfur can be observed in a number of unsaturated functional groups containing carbon and sulfur. In these paraelements carbon and sulfur can be exchanged without altering their chemical properties significantly. The main difference between them is caused by the extra electron pair at the sulfur atom which gives rise to bent or nonplanar structures. While the following carbon-containing paraelements are linear or planar, the corresponding sulfur analogs are bent or nonplanar.



This carbon–sulfur comparability extends only to sp and sp^2 hybridized carbon, meaning only to unsaturated systems. The following series of examples illustrates this.

The imines $(CF_3)_2C{=}NH$ and $(CF_3)_2S{=}NH$ are convincing examples for this carbon–sulfur exchangeability. Reactions of the two imines with RLi, RCl, ClF, as well as photolysis, hydrolysis, and their preparation are similar and take place according to Table I.

Besides these imines there are other compounds contributing evidence for the similarity between carbon and sulfur(IV). The following reactions and the compounds obtained are other conclusive arguments.

$$CF_3N{=}SCl_2 + Ag_2O \longrightarrow CF_3NSO \qquad (13)$$

$$CF_3N{=}CCl_2 + H_2O \longrightarrow CF_3NCO \qquad (14)$$

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[4] Derivatives of these paraelements have not yet been synthesized.

TABLE I

Reaction	$(CF_3)_2C{=}NH$	$(CF_3)_2S{=}NH$
RLi	$(CF_3)_2C{=}NLi$	$(CF_3)_2S{=}NLi$ (*8, 9*)
R′Cl (R′ = Me_3Si, CF_3S—, CF_3CO—)	$(CF_3)_2C{=}NR$ (*23*)	$(CF_3)_2S{=}NR$ (*8, 9*)
ClF	$(CF_3)_2C{=}NCl$ (*11*)	$(CF_3)_2S{=}NCl$ (*10*)
hν	$(CF_3)_2C{=}N{-}N{=}C(CF_3)_2$ (*11*)	$(CF_3)_2S{=}N{-}N{=}S(CF_3)_2$ (*10*)
H_2O	—	$(CF_3)_2S{=}NCl \xrightarrow{H_2O} (CF_3)_2S{=}NH$ (*10*)
H_2O	$(CF_3)_2C{=}NF + KJ + H^+ \longrightarrow (CF_3)_2C{=}NH$	—
Preparation:	$(CF_3)_2C{=}O + NH_3$ (*21*)	$(CF_3)_2SF_2 + NH_3$ (*8, 12*)

$$CF_3SN{=}SF_2 + CF_3SNH_2 \longrightarrow CF_3SN{=}S{=}NSCF_3 \qquad (15)$$

$$RN{=}CCl_2 + RNH_2 \longrightarrow RN{=}C{=}NR \qquad (R = CH_3, C_2H_5) \qquad (16)$$

The reactions of isocyanidedichlorides (—$N{=}CCl_2$) and iminosulfurdihalides (—$N{=}SX_2$) are similar and the products formed show the relationship mentioned before. In recent years it was proved that in some reactions S_2Cl_2, in keeping with its isomeric structure $S{=}SCl_2$, forms with amines $RN{=}S{=}S$ compounds. In its branched form S_2Cl_2 resembles, as expected, $S{=}CCl_2$. Both react with primary amines in a similar way according to

$$RNH_2 + S{=}CCl_2 \longrightarrow RN{=}C{=}S + 2HCl \qquad (17)$$

$$RNH_2 + S{=}SCl_2 \longrightarrow RN{=}S{=}S + 2HCl \qquad (18)$$

$$(R = \text{aryl}{-})$$

In the presence of guinoline CF_3SNH_2 condenses with S_2Cl_2, forming $CF_3SN{=}S{=}S$ (*19*). The corresponding reaction with $S{=}CF_2$ in the presence of NaF leads to $CF_3SN{=}C(F)SSCF_3$ (*20*). The expected CF_3SNCS was not formed and even as an intermediate it was not detected. This is not surprising, as sulfenylisothiocyanates are almost unknown. The only characterized example is $CFCl_2SNCS$, obtained from $FCl_2SN{=}CCl_2$ and P_4S_{10} in boiling xylol in 50% yield (*22*).

N-(Thiosulfinylamines) are very reactive compounds and decompose to $RN{=}S{=}NR$ and sulfur. Some isothiocyanates behave similarly. In the presence of 2,5-dihydrophosphol-1-oxide they condense to

$RN{=}S{=}NR$, according to

$$2RN{=}S{=}S \longrightarrow RN{=}S{=}NR + \text{“}S{=}S{=}S\text{”}$$

$$[R = \text{aryl } (\mathit{24});\ R = CF_3S\ (\mathit{19})]$$

$$2R'{-}N{=}C{=}S \xrightarrow{\text{catalyst}} R'N{=}C{=}NR' + SCO\ (\mathit{25})$$

As a result of the reaction with the catalyst, SCO, rather than $S{=}C{=}S$ (which is similar to the unstable “$S{=}S{=}S$”), is formed. Equivalency is also observed in the chlorination and in the fluorination reaction, e.g.,

$$R\ddot{N}{=}\ddot{S}{=}\underset{\cdot\cdot}{\ddot{S}} + 2Cl_2 \longrightarrow R\ddot{N}{=}\ddot{S}Cl_2 + SCl_2 \qquad [R = \text{aryl } (\mathit{24})]$$

$$CF_3\ddot{N}{=}C{=}\underset{\cdot\cdot}{\ddot{S}} + 2Cl_2 \longrightarrow CF_3\ddot{N}{=}CCl_2 + SCl_2\ (\mathit{26})$$

$$C_2H_5N{=}C{=}S + HgF_2 \longrightarrow C_2H_5N{=}CF_2 + HgS\ (\mathit{73})$$

$$CF_3SN{=}S{=}S + HgF_2 \longrightarrow CF_3\ddot{S}N{=}\ddot{S}F_2\ (\mathit{74}) + HgS$$

The two isomeric paraelements $—\ddot{N}{=}CX_2$ and $XN{=}C(X)—$ resemble formally the sulfur analogs $—\ddot{N}{=}\ddot{S}X_2$ and $X\ddot{N}{=}\ddot{S}(X)$.

While compounds of the type $R_f\ddot{N}{=}CX_2$, $R_f\ddot{N}{=}\ddot{S}X_2$ and $R_fC(X){=}\ddot{N}X$ are already known, hitherto no substances of the type $R_f\ddot{S}(X){=}\ddot{N}X$ with $R_f \neq X$ (X = halogen) have been described. While the fluorination of $(CF_3CN)_3$ at 240°C leads to $CF_3C(F){=}NF$ (*27*) this reaction cannot be applied for the synthesis of $CF_3\ddot{S}(F){=}NF$, as the corresponding starting material $(CF_3SN)_3$ is not known. The only available compounds are $(CF_3SN)_4$ and $(CF_3SN)_x$ (*28*) but they do not react with halogens at ambient temperatures. The other method, addition of halogen to R_fCN (*29*), is not applicable to $R_f\ddot{S}{\equiv}N{:}$, as such compounds are not available. The successful preparation of $CF_3S(X){=}NX$ was achieved via halogenation of $CF_3SN[Si(CH_3)_3]_2$ according to the equations

$$\begin{aligned} CF_3SN[Si(CH_3)_3]_2 + F_2 &\xrightarrow{-60°C} CF_3{-}\ddot{S}(F){=}\ddot{N}F + 2(CH_3)_3SiF \\ + Cl_2 &\xrightarrow{-40°C} CF_3S(Cl){=}\ddot{N}Si(CH_3)_3 \xrightarrow[-20°C]{Cl_2} \\ &\phantom{\xrightarrow{-40°C}} CF_3S(Cl){=}NCl + 2(CH_3)_3SiCl \\ + Br_2 &\xrightarrow{20°C} 1/x(CF_3SN)_x + 2(CH_3)_3SiBr \\ + ClF &\xrightarrow{-60°C} CF_3S(Cl){=}NCl + [CF_3SCl, CF_3Cl, (CH_3)_3SiF, (CH_3)_3SiCl] \end{aligned}$$

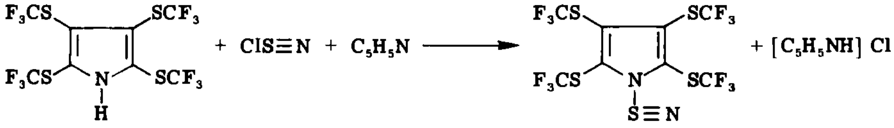
No reaction took place with iodine (*19*).

Another paraelement pair, $—N{=}C{=}N—$ and $—N{=}S{=}N—$, seem to have a lot in common. From both a large number of organic and perfluororganoderivatives are known. The carbodiimide group exists also in an isomeric form as cyanoamide (=N—C≡N). Up to now the corresponding isomer, —N—S≡N:, is not known. The only evidence for such a group to exist is the reaction of secondary amines with $Cl_3S_3N_3$ in boiling CCl_4 in the presence of pyridin according to

$$3R_2NH + Cl_3S_3N_3 \longrightarrow 3RN{=}S{=}NR + 3HCl$$

$$[R = C_6F_5S\ (\mathit{75}),\ CF_3S\ (\mathit{76}),\ CF_3Se\ (\mathit{77})]$$

It is assumed that at elevated temperatures $Cl_3S_3N_3$ pyrolyzes to ClS≡N which condenses with the imine to form $R_2NS{\equiv}N$ as an intermediate. This rearranges immediately to the stable RN=S=NR compound. There might be a chance to isolate a molecule with an N—S≡N group providing a cyclic imine is found with stable element–nitrogen bonds. Tetrakis(trifluoromethylthio)pyrrol might fulfil these requirements and react with $Cl_3S_3N_3$ to give the wanted substances. If rearrangement occurs, ring opening has to take place. When reacting the substituted pyrrole with $Cl_3S_3N_3$ in refluxing CCl_4 in the presence of pyridine, a light yellow substance can be isolated by sublimation *in vacuo.* On standing it changes color continuously, ending with deep purple, without changing its physical properties. On subliming aged material *in vacuo,* light yellow material is recovered almost quantitatively. Analytical and spectroscopic investigations show that the product is the suggested molecule, which is formed according to



According to molecular weight determinations the product is monomeric and shows no tendency to trimerize to a trithiazyl ring. Such cyclizations are observed for FSN (*78*) and ClSN (*79*), which are comparable with FCN and ClCN. This suggests that —S≡N is similar to —C≡N and not to N—O compounds. An unexpected connection can be drawn between F—S—N— and HC compounds starting from $F_4S_4N_4$. If the paranitrogen FS≡ and nitrogen are completely replaced by pseudonitrogen CH, $(FS)_4N_4$ is converted to cyclooctatetraene. Both substances have localized double bonds [d(C=C) = 1.34 Å, d(C—C) = 1.48 Å (*80*) compared with d(S=N) = 1.54 Å, d(S—N) = 1.66 Å]. The bond lengths are of course not equal but the differences between double and single bond (Δ = 0.14, Δ′ = 0.12 Å) are very close. In its boot conformation $(CH)_8$ and the S_4N_4 frame have almost the same structure. The four basic atoms in $F_4S_4N_4$ do not form an ideal square but are a little eclipsed.

IV. Halogen-Like Properties of Parahalogens of Different Derivation

A. EQUIVALENCE BETWEEN CF_3 AND FLUORINE

Impressive similarities between fluorine and a parafluorine are observed with F and CF_3. In a number of reactions this can be demonstrated in a convincing manner.

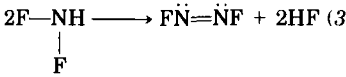
(1) The association of two SF_2 or CF_3SF molecules (*30*), according to

$$2F\text{—}S\text{—}F \rightarrow F_3\text{—}S\text{—}S\text{—}F$$

$$2CF_3\text{—}S\text{—}F \rightarrow CF_3SF_2SCF_3$$

(2) The acid–anhydrofluoride behavior of perfluorinated acids, not dissociating in H_2O

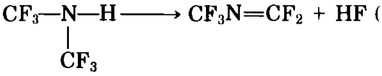
$$2FOH \longrightarrow \ddot{\underset{\cdot\cdot}{O}}=\ddot{\underset{\cdot\cdot}{O}} + 2HF \ (\mathit{31})$$



$$2F\text{—}\underset{\displaystyle F}{\underset{|}{N}}H \longrightarrow F\dot{N}=\dot{N}F + 2HF \ (\mathit{32})$$

$$2Cl\text{—}CF_2H \xrightarrow{600\text{ to }800°C} F_2C=CF_2 + 2HCl \ (\mathit{33})$$

$$CF_3OH \longrightarrow F_2C=O + HF \ (\mathit{34})$$



$$CF_3\text{—}\underset{\displaystyle CF_3}{\underset{|}{N}}\text{—}H \longrightarrow CF_3N=CF_2 + HF \ (\mathit{35})$$

$$(CF_3)_3CH \longrightarrow (CF_3)_2C=CF_2 + HF$$

The generation of CF_2 can also be achieved by hydrolysis of $ClCF_2H$ (*33*). Neither direct conversion of CF_3H to CF_2, and hence $CF_2=CF_2$, nor decomposition of $(CF_3)_3CH$ to $(CF_3)_2C=CF_2$, is observed. Addition of HF in the presence of F^- to $(CF_3)_2C=CF_2$, forming $(CF_3)_3CH$, takes place under normal reaction conditions (*36*). Some of the anhydrofluorides react with metal fluorides (bases in HF) to form saltlike compounds.

TABLE II

PHYSICAL DATA OF CF_3SeF_4X, F_5SeX (X = F, Cl), CF_3SeF_3, AND SeF_4

Substance	D (g/cm³)	mp (°C)	bp (°C)	ΔH (kJ/mol)	ΔS (J/mol K)
CF_3SeF_5	2.0 ± 0.15	−76.5 ± 2	8.5 ± 2	26.5 ± 1.5	94.3 ± 5
SeF_6	1.93 (*62*)	−34.6 (*63*)	−45.7[a] (*62*)	27.6 (*63*)	121.8 (*63*)
CF_3SeF_4Cl	2.5 ± 0.15	−88.0 ± 2	43.5 ± 2	32.5 ± 1.5	102.7 ± 5
SeF_5Cl (*64*)	—	−19.0	4.5	26.0	93.6
CF_3SeF_3	2.7 ± 0.15	26.0 ± 1	103 ± 4[b]	53.5 ± 3[a]	142 ± 10[a]
SeF_4	2.77 (*66*)	− 9.5 (*65*) −38.87 (*115*)	101.0 (*65*)	47.0 (*65*)	125.4 (*65*)

[a] Sublimation value.

[b] Extrapolated from $\ln(p/760\ \text{Torr}) = 17.1 - 6435/T$.

$$MF + CF_2O \longrightarrow MOCF_3 \quad (M = K, Rb, Cs)\ (37)$$

$$HgF_2 + 2CF_3N{=}CF_2 \longrightarrow Hg[N(CF_3)_2]_2\ (38)$$

$$HgF_2 + (CF_3)_2C{=}CF_2 \longrightarrow Hg[C(CF_3)_3]_2\ (39)$$

These equations not only demonstrate the fluorine-like behavior of the parafluorine elements FO—, F_2N—, F_3C, CF_3O, $(CF_3)_2N$, and $(CF_3)_3C$, but a similarity to oxygen of NF, CF_2, CF_3N, and $(CF_3)_2C$.

(3) Although perfluoroorganosulfur(VI) compounds such as CF_3SF_5, CF_3SF_4Cl, and CF_3SO_3H are well known, corresponding selenium compounds, apart from $C_2F_5SeF_4Cl$ (fully characterized) and $C_2F_5SeF_5$ (*61*) (obtained only in traces), are unknown. This fact is surprising, since SeF_6 and SeF_5Cl are stable substances. One would expect that replacement of F by parafluorine, e.g., CF_3, would lead to stable compounds. Fluorination of CF_3SeF_3 with liquid F_2 at −196°C or more conveniently with AgF_2 at 65–70°C produces a complex mixture out of which CF_3SeF_5 was isolated by codistillation in 3 to 4% yield. Similarly, CF_3SeF_4Cl was made from CF_3SeF_3 and ClF (partial pressure should not exceed 200 mbar) at −105°C (12 hr) in 20% yield. Both compounds decompose at 60°C (1 hr) primarily into CF_4, CF_3Cl, and SeF_4. Physical and spectroscopic data of CF_3SeF_4X, SeF_5X (X = F, Cl), CF_3SeF_3, and SeF_4 are given in Tables II and III. Going from SeF_6 to CF_3SeF_5 or SeF_5Cl to CF_3SeF_4Cl the mp decreases by about 42 or 69°C and the bp increases by 54 or 39°C. These deviations are mainly due to change of the molecular shape differing from a regular octahedron. The other physical data are more or less comparable. The couple SeF_4/CF_3SeF_3 shows a different mp but the other figures are almost equal. Substan-

TABLE III

^{19}F-, ^{77}Se-, AND ^{13}C-NMR-SPECTROSCOPIC DATA OF CF_3SeF_4X, SeF_5X ($X = F, Cl$), CF_3SeF_3, AND SeF_4[a]

	CF_3SeF_5	CF_3SeF_4Cl (−30°C)	SeF_6	SeF_5Cl (*64*)	CF_3SeF_3 (−40°C)	SeF_4 (−140°C) (*70*)
$\delta_F(CF_3)$	−51.2 (quint of d)	−51.9 (quint)	—	—	−65.1 (*71*)	—
$\delta_F[SeF_{4(e)}]$	+29.8 (d of q)	+97.1 (q)		132	−59.7 (*71*)	−37.7
$\delta_F[SeF_{(a)}]$	+63.8 (quint of q)	—	+48 (*67*)	71.3	−21.9 (*71*)	−12.1
$\delta^{77}Se$	+626.8 (quint of d of q)	+650.1 (quint of q)	632.3 (*68*)	?	1072 (*69*)	1114.2 (*68*)
$\delta^{13}C$	+125.3 (q of quint)	+131.0 (q of quint)	—	—	126.6 (*69*)	—
$^{3}J\,CF_3—SeF_{4(e)}$	23.7	25.2	—		—	—
$^{3}J\,CF_3—SeF_{(a)}$	3.1	—	—		—	—
$^{2}J\,SeF_{4(e)}—SeF_{(a)}$	184.1	—	—	213.6	94.4 (*71*)	26
$^{1}J\,{}^{77}Se—SeF_{4(e)}$	1322	1177	—	1258	—	302
$^{1}J\,{}^{77}Se—SeF_{(a)}$	1311	—	1420.9 (*68*)	1352	—	1200
$^{2}J\,{}^{77}Se—CF_3$	381	389	—	—	41 (*69*)	—
$^{2}J\,{}^{13}C—SeF_{4(e)}$	32.9	37.1	—	—	—	—
$^{1}J\,{}^{13}C—CF_3$	352.9	353.4	—	—	346.6 (*69*)	—

[a] External standards: $^{19}F(CFCl_3)$; $^{77}Se(CH_3SeCH_3)$; $^{13}C(SiMe_4)$; δ in parts per million; J in Hertz.

tial differences are observed between Se(VI) and Se(IV) compounds. Comparable values of $\delta(^{77}Se)$ are observed for CF_3SeF_5, CF_3SeF_4Cl, and SeF_6 (that for SeF_5Cl has not been measured). They differ significantly from those of CF_3SeF_3 and SeF_4, which are similar to each other. The coupling constant $J(F_3C—^{77}Se)$ for $CF_3Se(VI)$ compounds is very high compared with values for CF_3Se(I, II, and IV) molecules and therefore characteristic.

Hydrolysis of neither CF_3SeF_5 nor CF_3SeF_4Cl gave CF_3SeO_3H, but oxidation of CF_3SeO_2H with a neutral saturated $KMnO_4$ solution led to good yields of CF_3SeO_3K. Treating the salt with 70 proc. $HClO_4$ in aqueous solution gave the acid CF_3SeO_3H. Attempts to isolate the acid failed. Only concentrations up to 90% were obtained when a solution of CF_3SeO_3H in H_2O was evaporated *in vacuo*. Above this value decomposition to CF_4, COF_2, $2SeO_2$, and H_2O took place. This suggests that $[H_3O]^+[CF_3SeO_3]^-$ is formed but cannot be freed from water. Neutralization reactions of CF_3SeO_3H with Ag_2O or NH_3 resulted in the formation of the salts CF_3SeO_3M (M = Ag, NH_4) (*72*).

B. EQUIVALENCE BETWEEN $(CF_3S)_2N—$ AND FLUORINE

The bis(trifluoromethylthio)amino radical must be considered as a second-order derivative parafluorine and its high group electronegativity of 3.7 (*47*) supports this classification. The hydrogen derivative $(CF_3S)_2NH$ is a weak acid—pK_D (in dioxan/water) = 9.99 (*48*)—and forms with HgO the compound $Hg[N(SCF_3)_2]_2$ (*49*). Similarly to F_2NNF_2 (*50*), O_2NNO_2 (*51*), and $(CF_3S)_3CC(SCF_3)_3$ (*52*), its dimer $(CF_3S)_2NN(SCF_3)_2$ dissociates at 20°C like a halogen (*53*) according to

$$(CF_2S)_2NN(SCF_3)_2 \rightleftharpoons 2(CF_3S)_2N\cdot$$

In the ^1H-NMR spectrum of $(CF_3S)_2NCH_2N(SCF_3)_2$, prepared from $(CF_3S)_2NH$ and HC(O)H at 0°C (0.5 hr) in the presence of 100% H_2SO_4, $\delta(CH_2) = 5.15$ ppm (*54*) and compares well with $\delta(CH_2) = 5.99$ ppm in CH_2F_2. In boron trihalides $(CF_3S)_2N\cdot$ is able to replace halogens, forming $[(CF_3S)_2N]_nBX_{3-n}$. Only monosubstitution to $[(CF_3S)_2N]BX_2$ is observed when BCl_3 or BBr_3 reacts with $(CF_3S)_2NH$. The corresponding $(CF_3S)_2NBF_2$ can only be made by thermal decomposition of $(CF_3S)_2NB(SCF_3)_2$ at 40°C. It is not very stable and above 60°C gives off BF_3, forming $[(CF_3S)_2N]_2BF$ (*59*). Further substitution of BX_3 (X = Cl, Br) is only achievable in the reaction of stoichiometrical amounts of $(CF_3S)_2NBX_2$ and $Hg[N(SCF_3)_2]_2$, giving $[(CF_3S)_2N]_2BX$. A complete exchange takes place when excess $Hg[N(SCF_3)_2]_2$ reacts with BBr_3, giving $B[N(SCF_3)_2]_3$ in 93% yield. When BCl_3 is used instead of BBr_3 the yield drops to 55% at 80°C. Completely unexpected is the formation of the trisaminoborane from $B(SCF_3)_3$ and the mercurial according to

$$3Hg[N(SCF_3)_2]_2 + 2B(SCF_3)_3 \longrightarrow 2B[N(SCF_3)_2]_3 + 3Hg(SCF_3)_2$$

In order to understand the reactions of $(CF_3S)_2NH$ and $Hg[N(SCF_3)_2]_3$ with BX_3 (X = F, Cl, Br, SCF_3) it is necessary to consider the radicals CF_3S as parachlorine (p-Cl) and $(CF_3S)_2N$ as parafluorine (p-F) according to the element displacement principle. With BF_3 and H(p-F) [= $(CF_3S)_2NH$] and $Hg(p\text{-}F)_2$ ($Hg[N(SCF_3)_2]_2$) no reaction takes place. Similarly no metathetical exchange occurs between BF_3 and HF or HgF_2. But BCl_3 and BBr_3 react with H(p-F) to give monosubstituted boranes in agreement with HF fluorinations of BX_3 (X = Cl, Br). The only difference between $(p\text{-}F)BX_2$ and FBX_2 is that the former are more stable than the mixed boron halides and the reaction with H(p-F) stops after monosubstitution. When $(p\text{-}F)_2Hg$ is used, then, according to reaction conditions, mono-, di-, and trisubstituted boranes are formed with BX_3. In addition, the reaction between $Hg[N(SCF_3)_2]_2$ and $B(SCF_3)_3$ is in agreement with the preparation of BF_3 from BCl_3 and HgF_2, according to

$$2B(p\text{-}Cl)_3 + 3Hg(p\text{-}F)_2 \longrightarrow 2B(p\text{-}F)_3 + 3Hg(p\text{-}Cl)_2$$

$$2BCl_3 + 3HgF_2 \longrightarrow 2BF_3 + 3HgCl_2$$

Decreasing yields going from BBr_3, $B(SCF_3)_3$, to BCl_3 at 25°C are in good agreement with known reactivities of BX_3 and also show that CF_3S (p-Cl) is more reactive than Cl in this metathesis (*60*).

C. EQUIVALENCE BETWEEN CF_3S AND CHLORINE

Besides the similarities between CF_3S and chlorine already given in footnote 1, new examples have been found to substantiate the parachlorine behavior of the CF_3S radical.

1. With the synthesis of $CF_3SP(O)Cl_2$ and $CF_3SP(S)Cl_2$, two new compounds are available which can be derived from the basic substances $OPCl_3$ and $SPCl_3$ by replacing chlorine by the parachlorine CF_3S. This can be confirmed by physical data given in Table IV and chemical reactions.

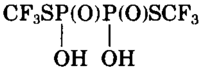
Partial hydrolysis of $CF_3SP(O)Cl_2$ with stoichiometric amounts of H_2O in CH_3CN leads to $CF_3SP(O)(OH)_2$, which on standing or with-

TABLE IV

PHYSICAL DATA OF $CF_3SP(X)Cl_2$ AND $ClP(X)Cl_2$ (X = O, S)

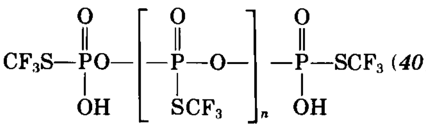
Substance	Properties	D (g/cm³); (°C)	bp (°C)	δ(P) (ppm)	n_D (°C)	mp (°C)	ΔHv (kJ/mol)	Trouton constant (J/kmol)
$CF_3SP(O)Cl_2$	Colorless, highly refracting	1.72 (20)	122	14.27	1.4322 (20) 1.4309 (25)	−65 to −63	49.99	114.22
$ClP(O)Cl_2$ (*5*)	Colorless, highly refracting	1.73 (20) 1.645 (25)	105.1	2.2	1.460 (25)	1.25	33.7	80.1
$CF_3SP(S)Cl_2$	Colorless	1.933 (25)	135	33.38	1.5009 (20)	−68 to −65	40.69	99.8
$ClP(S)Cl_2$ (*6*)	Colorless	1.6271 (25)	125	28.8	1.563 (20)	−35	32.70	82.13

drawing of the solvent condenses to



$$\underset{OH}{CF_3SP(O)}\underset{OH}{P(O)SCF_3}$$

and then to oligomers of the formula



$$CF_3S-\underset{OH}{\overset{O}{\overset{\|}{P}}}O-\left[-\underset{SCF_3}{\overset{O}{\overset{\|}{P}}}-O-\right]_n-\underset{OH}{\overset{O}{\overset{\|}{P}}}-SCF_3$$ (*40*)

Hydrolysis of $OPCl_3$ with 1 mol H_2O gives $HOP(O)Cl_2$, which can be isolated in 90% purity. At 300°C/12 Torr it condenses to $Cl_2P(O)OP(O)Cl_2$, which forms at 100°C/760 Torr $P_3Cl_6O_3$ (*41*). Like $SPCl_3$, $CF_3SP(S)Cl_2$ is stable toward excess H_2O and does not react with it in a homogeneous phase at 20°C during 1 hr (*40*).

2. The hydrolysis of per(fluorohalogeno)organosulfenylchlorides is still an unresolved problem and is also a good example for an element–paraelement comparison.

With the series $CF_nCl_{3-n}SCl$ (n = 0, 1, 2, 3) there are compounds available, from which we know that, e.g., the CF_3S group behaves very similarly to chlorine (footnote 1). Its hydrolysis was studied in 1955 by Haszeldine and Kidd (*42*) and found to take place according to

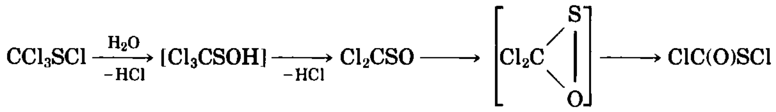
$$CF_3SCl \xrightarrow[-HCl]{H_2O} [CF_3SOH] \longrightarrow CF_3SSCF_3 + CF_3SO_2SCF_3$$

The postulated intermediate CF_3SOH was not detected.

With the preparation of $CF_3S(O)SCF_3$ by controlled hydrolysis of $CF_3SF_2SCF_3$ and its characterization, it was possible to detect $CF_3S(O)SCF_3$ as an intermediate in the reaction of CF_3SCl and water (*43*). So the reaction scheme is now more complete:

$$CF_3SCl \xrightarrow[-HCl]{H_2O} [CF_3SOH] \xrightarrow[-HCl]{CF_3SCl} CF_3S(O)SCF_3 \longrightarrow CF_3SSCF_3 + CF_3SO_2SCF_3$$

The other product of the series, CCl_3SCl, hydrolyzes in a completely different manner, forming $ClC(O)SCl$ according to



The relatively stable intermediate $Cl_2C{=}S{=}O$ was isolated (*44*). The main difference between these two reactions is the HCl elimination from the postulated X_3CSOH. If X = F an intermolecular reaction takes place and for X = Cl an intramolecular elimination occurs.

In this connection it was interesting to study the hydrolysis of CF_2ClSCl and $CFCl_2SCl$. Since both sulfenylchlorides are insoluble in water, hydrolysis was always a two-phase reaction. The following substances are obtained at 20°C:

$$F_2ClCSCl \xrightarrow{H_2O} F_2ClCS(O)SCF_2Cl + F_2ClCSO_2SCF_2Cl$$

$$FCl_2CSCl \xrightarrow{H_2O} FCl_2CS(O)SCFCl_2 + FCl_2CSO_2SCFCl_2$$

The volatile products consisted of HCl, H_2S, CO_2, and COS and the aqueous phase contained HCl, HF, and H_2SO_4. No $CF_nCl_{3-n}SSCF_nCl_{3-n}$ ($n = 1, 2$) is formed in the first 15 hr; but later formation of some disulfide is observed. The products of the hydrolysis were identified by ^{19}F- and ^{13}C-NMR-spectroscopy (see Table V). Neither F_2CSO nor FClCSO appeared, so intramolecular HCl elimination can be excluded. This proves that $F_nCl_{3-n}CSCl$ ($n = 1, 2$) resembles in this respect CF_3SCl and not CCl_3SCl. Two surprising observations can be made here. They are (1) the relative stability of $CF_nCl_{3-n}S(O)SCF_nCl_{3-n}$ ($n = 1, 2$) and (2) the absence of the corresponding disulfides.

For a better understanding of the reaction paths the observed products $CF_nCl_{3-n}S(O)SCF_nCl_{3-n}$ and $CF_nCl_{3-n}SO_2SCF_nCl_{3-n}$ ($n = 1, 2$)

TABLE V

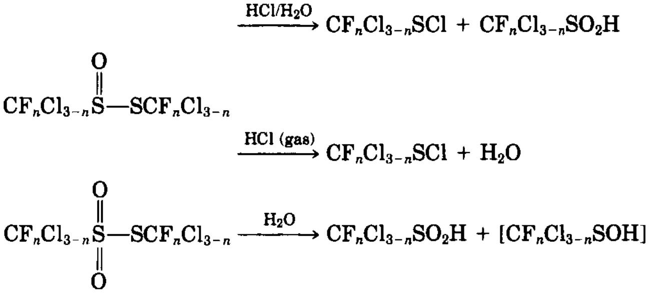
^{19}F- AND ^{13}C-NMR DATA[a]

(a)	(b)	F(a)	F(b)	C(a)	C(b)	$^5J_{(F-F)}$	$^1J(^{13}C-^{19}F)$ (a)	$^1J(^{13}C-^{19}F)$ (b)
$CFCl_2S$	$-S(O)CFCl_2$	−13.6	−54.9	118.4	125.5	—	336.3	344.0
CF_2ClS	$-S(O)CF_2Cl$	−20.1[b]	−56.0[b]	129.4	131.1	—	327.9	345.5
CF_3S	$-S(O)CF_3$	−34.2	−69.5	129.7	125.6	1.5	311.3	336.9 (*43*)
$CFCl_2S$	$-S(O)_2CFCl_2$	−21.4	−58.9	117.3	123.8	17.8	346.1	343.5
CF_2ClS	$-S(O)_2CF_2Cl$	−24.9	−61.0	127.3	126.7	9.8	335.9	339.1
CF_3S	$-S(O)_2CF_3$	−36.3	−76.8 (*55*)	122.9	116.0 (*43*)	5.0 (*55*)	314.9	327.1 (*43*)
$CFCl_2$	$-SO_2H$		−65.3	—	—	—	—	—
CF_2Cl	$-SO_2H$		−66.4	—	—	—	—	—

[a] δ in parts per million, J in Hertz.

[b] ABXY spectrum; coupling constants in the range of 1 Hz.

were synthesized by special methods on a preparative scale and used for the following reactions:

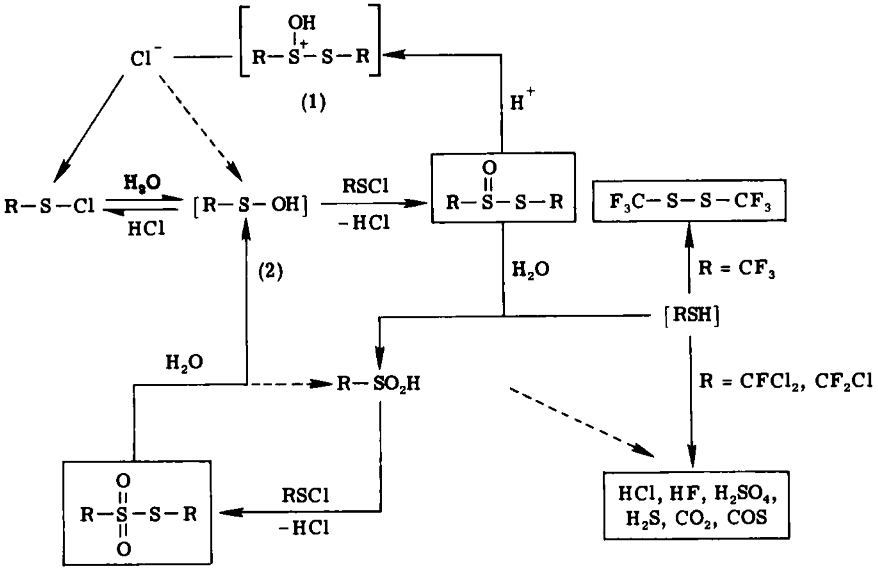


$$CF_nCl_{3-n}\overset{\overset{O}{\|}}{S}-SCF_nCl_{3-n}\ \begin{cases}\xrightarrow{HCl/H_2O} CF_nCl_{3-n}SCl + CF_nCl_{3-n}SO_2H \\ \xrightarrow{HCl\ (gas)} CF_nCl_{3-n}SCl + H_2O\end{cases}$$

$$CF_nCl_{3-n}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-SCF_nCl_{3-n} \xrightarrow{H_2O} CF_nCl_{3-n}SO_2H + [CF_nCl_{3-n}SOH]$$

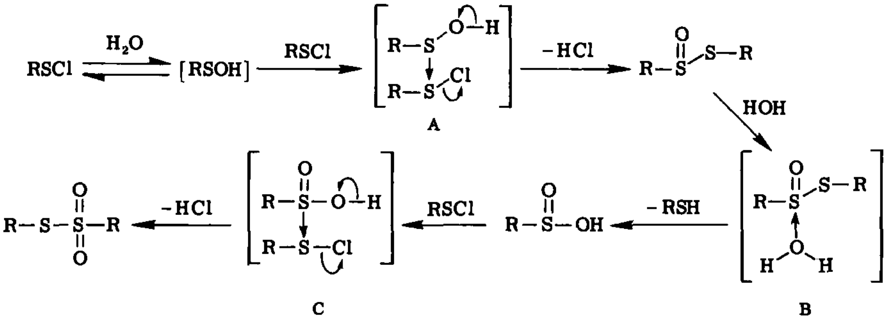
The conditions are the same as those of the hydrolysis reactions. The sulfinic acids were identified in the aqueous layer by ^{19}F-NMR-spectroscopy (see Table V).

With this additional information, the picture of the hydrolysis of $CF_nCl_{3-n}SCl$ (n = 1, 2, 3) becomes more complete and a qualitative description of the reaction paths can be provided.

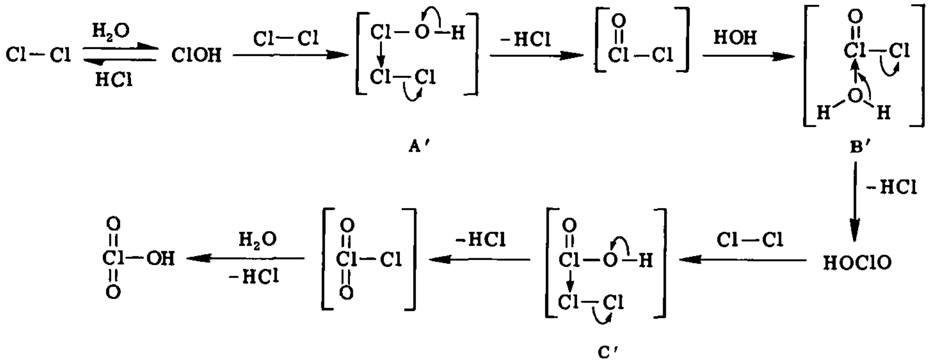


From this scheme it can be deduced that RSSR is not a primary product, as the disulfides are stable to water and HCl under the conditions studied. The precursor needed is RSH, which only with R = CF_3 reacts with CF_3SCl or CF_3SOH to form CF_3SSCF_3. For R′ = CF_2Cl and

$CFCl_2$, decomposition of R'SH is faster than condensation with R'SCl or R'SOH. Therefore no R'SSR' is observed. Two reaction cycles, (1) and (2), maintain the equilibria found. The scheme below provides possible intermediates and their reactions.

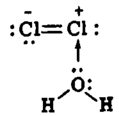


The first step is the formation of RSOH, which is attacked electrophilically by excess RSCl, forming an intermediate A. Stabilization takes place by giving off HCl and producing RS(O)SR. The electrophilic center in the thiosulfinate is S(IV), which on hydrolysis forms RS(O)OH and RSH via intermediate B. Condensation of RS(O)OH with RSCl gives, via C, RSO_2SR. This proposed mechanism is in good agreement with reactions of organic sulfenic acids and organosulfenylhalides (*46, 58*). The system RSCl and H_2O is sensitive toward reactions conditions, e.g., the amount of H_2O (concentration of H^+), temperature, and reaction time (*57*). According to the element displacement principle RS is a first-derivative parachlorine. Therefore the hydrolysis model mentioned can be transferred—with reservation—to the reaction of Cl_2 plus H_2O. An overall picture is gained by looking at the following scheme.

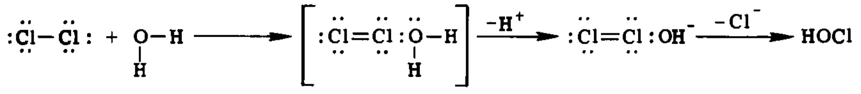


The reaction steps are obtained by replacing RS by Cl. The hydrolysis of chlorine is only complete in basic media. In H_2O the equilibrium $Cl_2 + H_2O \rightleftharpoons HCl + HOCl$ is almost completely on the left side. The first step is the formation of HOCl, which is attacked by the electrophile Cl_2 to form A′. By elimination of HCl an unstable intermediate [Cl(O)Cl] is formed, which reacts with H_2O via B′ to HOClO. This mechanism is repeated and via C′ [$Cl(O_2)Cl$] and its hydrolysate $HOClO_2$ is formed. Unfortunately, little is known about the hydrolysis of chlorine. Only the formation of HOCl has been well investigated and an equilibrium constant of 6×10^{-4} was measured at 20°C (*45*). The disproportionation of HOCl to $HClO_3$ and HCl is not significant at room temperature but its rate increases with higher temperature. For the reaction $3H_2O + 3Cl_2 \rightleftharpoons HClO_3 + 5HCl$, $K = [H^+]^6[Cl^-]^5[ClO_3^-][Cl_2]^{-3} = 4.3 \times 10^{-7}$ at 91°C (*56*).

Transferring the results, obtained from the reactions of RSCl with H_2O, from parachlorine to chlorine we get a suggestive mechanism which remains speculative till further results on this subject are available. One piece of support for this mechanism can already be provided. Kinetic studies on the reaction $Cl_2 + H_2O \rightarrow H^+ + Cl^- + HClO$ show that the most probable first step is the nucleophilic addition of H_2O at the electrophile atom in Cl_2, forming the intermediate



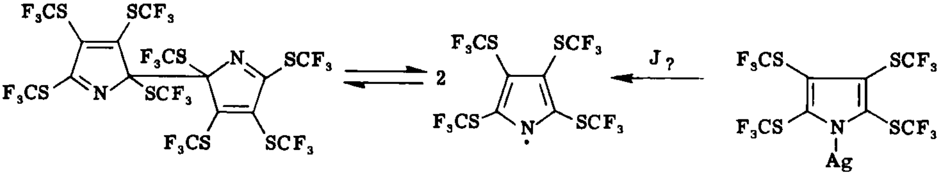
which on losing H^+ forms Cl_2OH^-, which stabilizes to HOCl and Cl^- (*45*) according to



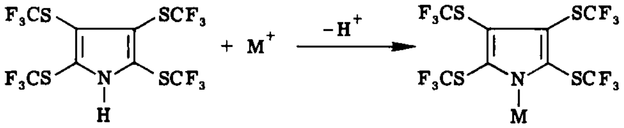
Although this step has not been discussed in the hydrolysis of RSCl, the first intermediates $[:\underset{\cdot\cdot}{\dot{C}l}=\underset{\cdot\cdot}{\dot{C}l}:\underset{\cdot\cdot}{\ddot{O}}:H_2]$ and $[:\underset{\cdot\cdot}{\dot{C}l}=\underset{\cdot\cdot}{\dot{C}l}OH]^-$ are similar to B and B′ and also their decompositions are comparable with the mechanism given above.

D. Equivalence between Tetrakis(trifluoromethylthio)pyrrolyl— and Chlorine

Pseudohalogens according to Grimm (*1*) (OH, NH_2, CH_3), to Birkenbach and Kellermann (*2*) (CN, SCN, NCS, OCN, NCO, N_3 . . .), and to Lagowski (*3*) (CF_3, CF_3S) can be considered with the aid of the element displacement principle as a unique, causative, and continuous class of molecule radicals that originate in the periodic system. The tetrakis(trifluoromethylthio)pyrrolle radical reacts in spite of its size, complexity, and derivation as a parahalogen. It dimerizes according to Eq. (1) at 20°C reversibly to 2,2′,3,3′,4,4′,5,5′-octakis(trifluoromethylthio)-2,2′-bi-2*H*-pyrrolle (*81*). The hydrogen derivative 2,3,4,5-tetrakis(trifluoromethylthio)pyrrole is an acid ($pK_D = 9.2$ in water/dioxane) and its proton can be replaced by various cations according to Eq. (2) (*82*). The radical is made by reacting the silver salt with iodine in pentane [Eq. (1)] or by oxidizing the tetrasubstituted pyrrolle by PbO_2 or nickel peroxide in C_6H_6 or C_6F_6 (*81*). Among the many salts synthesized so far the silver and potassium salts are very good starting materials for N-substitutions. They react with S_xCl_2 or RSCl, forming the corresponding derivatives according to Eq. (3). Among these, pentakis(trifluoromethylthio)pyrrole was used to study its sulfenylating properties and to compare them with CF_3SCl. Compounds containing an acidic hydrogen such as primary, secondary, and

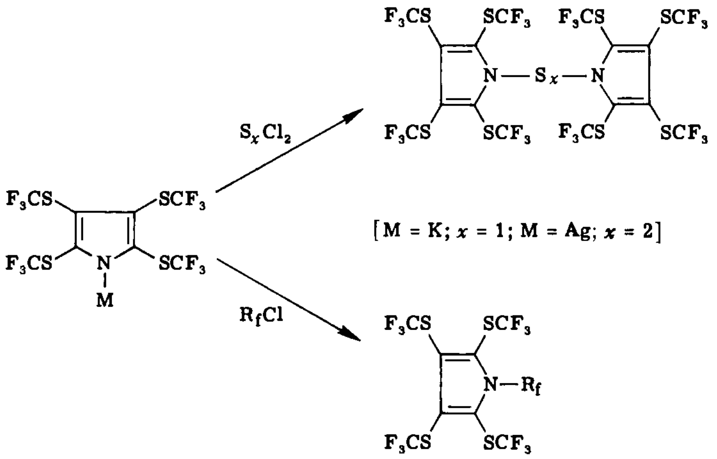


(1)



(2)

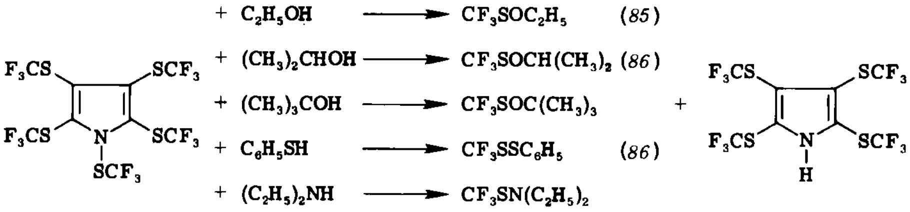
[M = Ag (*83*), K, Na, NH_4, C_6H_5NH, $(CH_3)_3NH$ (*82*), Zn, CuI, $(C_6H_5)_3PC_2H_5$, $(C_6H_5)_4As$, $(C_6H_5)_4Sb$, $(CH_3)_3S$, $(C_2H_5)_3Se$, and $(C_6H_5)_2J$ (*84*)]



(3)

[M = Ag, R_f = CF_3S, CF_2ClS, ClC(O)S, CF_3Se;
M = Ag or K, R_f = $CFCl_2S$, CCl_3S; M = K,
R_f = $(CF_3S)_2CClS$]

tertiary alcohols, thiols, and secondary amines react with $(CF_3SC)_4NSCF_3$, substituting H for CF_3S according to Eq. (4). It is interesting to note that CF_3SCl does not react with $(CH_3)_3COH$ to give $(CH_3)_3COSCF_3$. The sulfur–nitrogen bonds in these materials are sensitive to hydrolysis. On irradiation with UV light (λ = 250 nm), $(CF_3SC)_4NSCF_3$ dissolved in C_6F_6 gives the radical $(CF_3SC)_4N\cdot$ and CF_3SSCF_3 (*82*). When the radical dimerizes, surprisingly not the N—N but the C—C linked dimer is obtained. This could be proved by an X-ray structure analysis of both isomers. On heating the C—C dimer to 120–130°C, rearrangement to the N—N dimer takes place according to Eq. (5). The structure of both compounds is shown in Figs. 1 and 2. Surprisingly, the N—N dimer is rather stable and melts at 122–123°C without dissociation (*81*). Methylation of $(CF_3SC)_4NH$ succeeds with



(4)

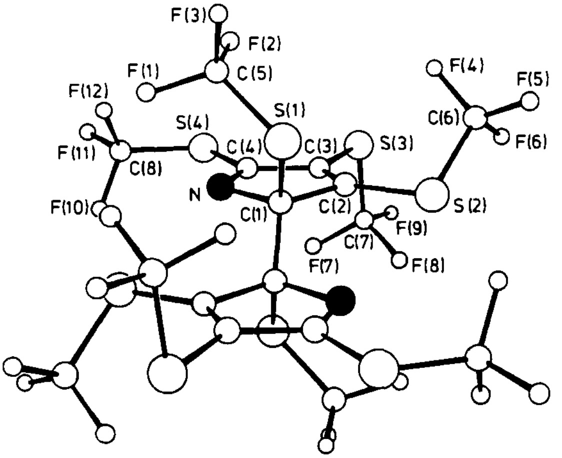
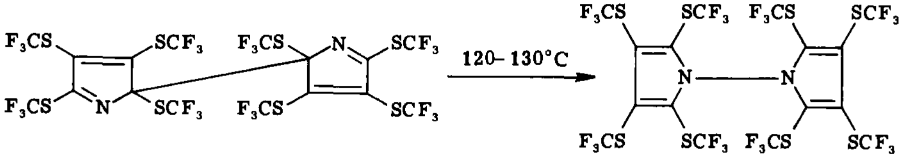


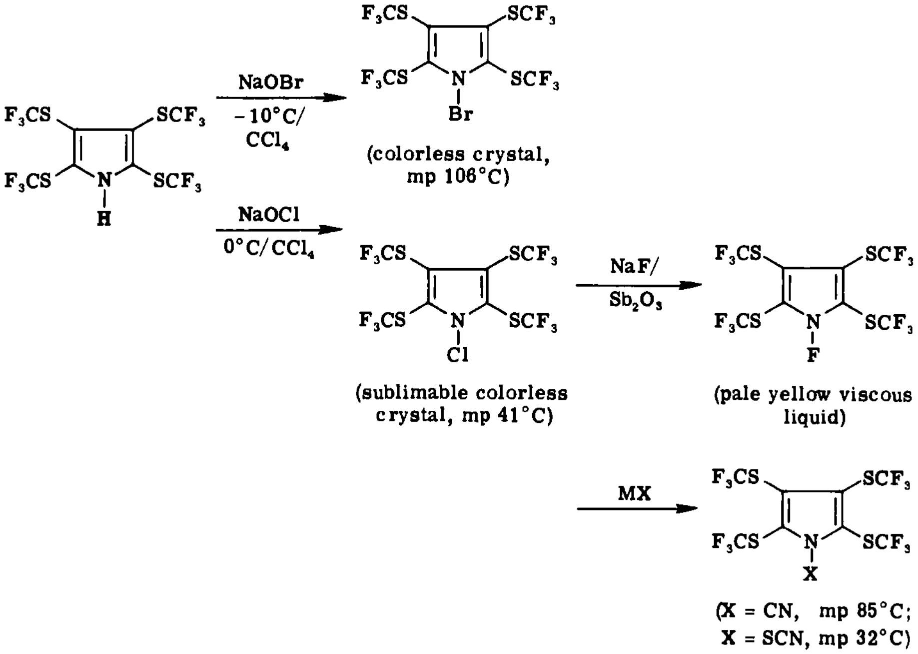
FIG. 1. A C—C linked dimer.



(5)

CH_3I in a two-phase reaction catalyzed by strong bases, e.g., KOH (*87*). After many unsuccessful attempts to chlorinate tetrakis(trifluoromethylthio)pyrrolle or its salts with Cl_2 or other chlorinating reagents, it was finally possible to synthesize the wanted material. When $(CF_3S—C)_4NH$ is treated with NaOCl or NaOBr the corresponding N—Cl or N—Br substituted compounds are obtained in good yield. By metathetical reaction $(CF_3SC)_4NCl$ is converted by NaF in the presence of Sb_2O_3 to $(CF_3SC)_4NF$. Similarly, by using KCN or NaSCN the desired N-substitution takes place. The reactions can be illustrated by Eq. (6).

Unexpectedly, $(CF_3SC)_4NCl$, in the few cases studied so far, does not act as a chlorinating agent. Under the influence of UV light (24 hr) with toluene, $(CF_3SC)_4N \cdot CH_2 \cdot C_6H_5$ and HCl are formed. In boiling CCl_4 it reacts with C_6H_5COOH analogously to form $(CF_3SC)_4$-$NC(O)C_6H_5$, which can also be made from the potassium salt and $C_6H_5C(O)Cl$. These reactions show that the N—Cl bond is unexpectedly polarized to $\overset{\delta-}{N}—\overset{\delta+}{Cl}$ and therefore it acts as a pyrrolating agent.



(6)

The N—Br derivative is less stable and decomposes slowly at 20°C in Br_2 and the C—C dimer (*88*). In order to understand this unexpected bond polarization it was necessary to determine the group electronegativity of the radical. This can be done by applying the Kagarise (*112*) equation $\nu(C{=}O)cm^{-1} = 1536.5 + 48.85\ (\kappa_x + \kappa_y)$ for molecules of the type XC(O)Y 89, provided a compound like $(CF_3SC)_4NC(O)F$ can be prepared. It was made by reacting the potassium salt with FC(O)Cl dissolved in ether at 20°C (3 hr) in good yields, according to Eq. (7), and showed $\nu(C{=}O)$ in the IR spectrum at 1872 cm^{-1}. The group electronegativity for the tetrakis(trifluoromethylthio)pyrrolyl radical was estimated to 2.90, which lies between chlorine (3.0) and the CF_3S group (2.7). This value accounts very well for the observed polarization and reactivity of $(CF_3SC)_4NCl$. The close relation between the radical and chlorine can also be demonstrated in an additional case. In an aqueous two-phase system $(CF_3SC)_4NH$ reacts with CH_2I_2 in the presence of concentrated NaOH to 1,1′-bis[tetrakis(trifluoromethylthio)pyrrolyl]-methylene according to Eq. (7). It shows in the ^1H-NMR-spectrum

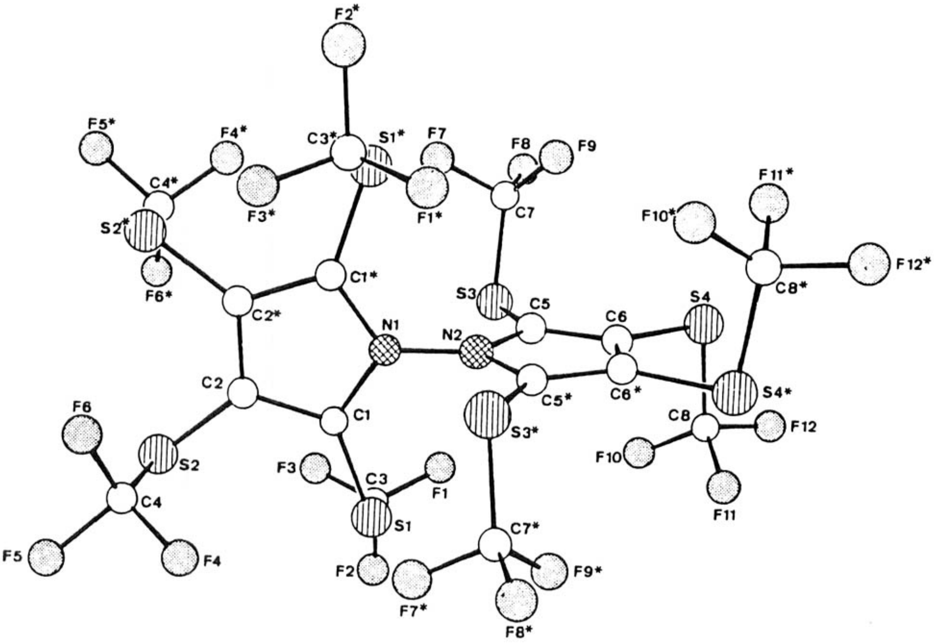
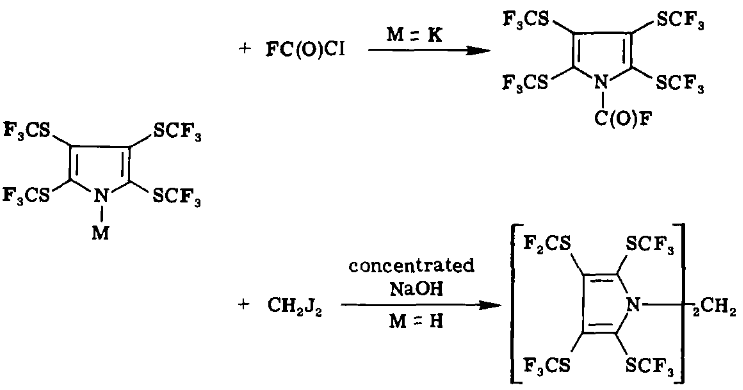


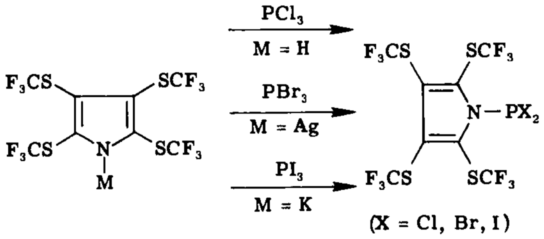
FIG. 2. An N—N linked dimer.

$\delta(CH_2)$ = 6.9 ppm (*84*). Such unusually high chemical shifts for methylene protons are also observed in dihalogenomethanes, e.g., $\delta(CH_2)$ in CH_2Cl_2 = 5.3 ppm.

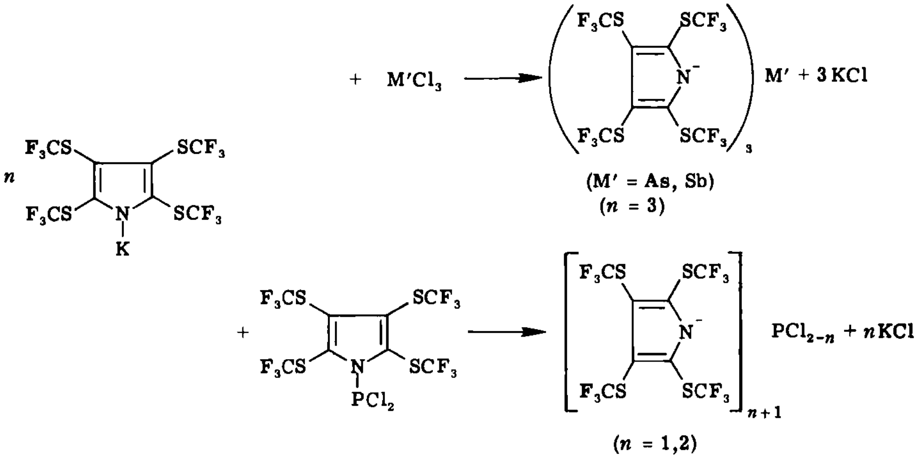


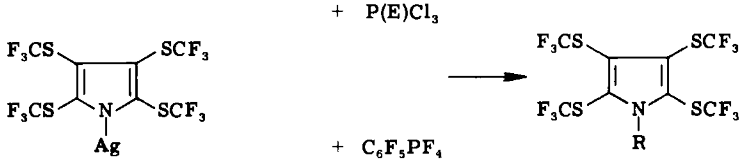
(7)

The tetrakis(trifluoromethylthio)pyrrolyl radical replaces halogen in PX_3 (X = Cl, Br, I). Monosubstitution is observed when stoichiometric amounts of the pyrrolle or its salts are reacted with PX_3.



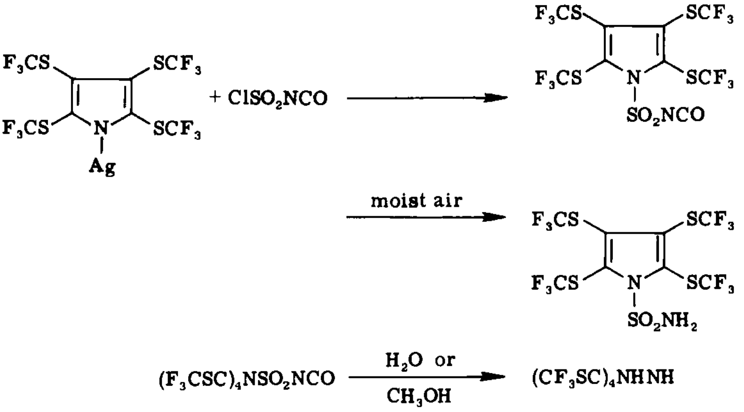
When the dichlorophosphane is treated with the potassium salt in a 1 : 1 molar reaction disubstitution and with an excess a complete substitution is observed. It was, however, not possible to convert PCl_3 either by the silver or by the potassium salt to the trisubstituted phosphane at once. But the reaction between the potassium salt and $AsCl_3$ or $SbCl_3$ goes straight through to a complete replacement. Formation of intermediates is not observed. Complete substitution cannot be achieved with phosphorus(V) halides. If $P(E)Cl_3$ or $C_6H_5PF_4$ is treated with the silver salt only one halogen is replaced. These reactions are shown below



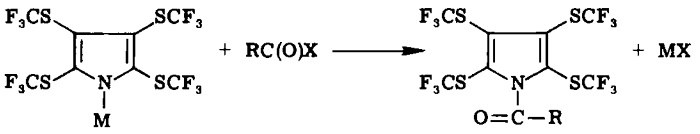


[R = $P(O)Cl_2$, $P(S)Cl_2$, $P(C_6H_5)F_3$]

All these substances are very sensitive to hydrolysis (*89*). Functionalization at the nitrogen also takes place in the reaction of the silver salt with $ClSO_2NCO$. The sulfonyl isocyanate obtained does not show typical isocyanate reactions. It solvolyzes with H_2O or CH_3OH without forming intermediates to $(CF_3SC)_4NH$. However, with moist air partial hydrolysis leads to the corresponding sulfonamide according to Eq. (8). A number of acyl derivatives were synthesized via Eq. (9). The oxalyl

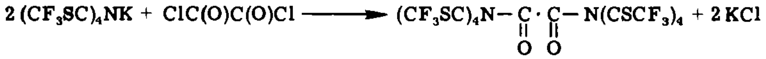


(8)



(9)

M = Ag, X = Cl, R = C_6H_5
M = K, X = Cl, R = CH_3, CCl_3,
M = K, X = $OC(O)CF_3$, R = CF_3



$$2\,(CF_3SC)_4NK + ClC(O)C(O)Cl \longrightarrow (CF_3SC)_4N-\underset{\underset{O}{\|}}{C}\cdot\underset{\underset{O}{\|}}{C}-N(CSCF_3)_4 + 2\,KCl$$

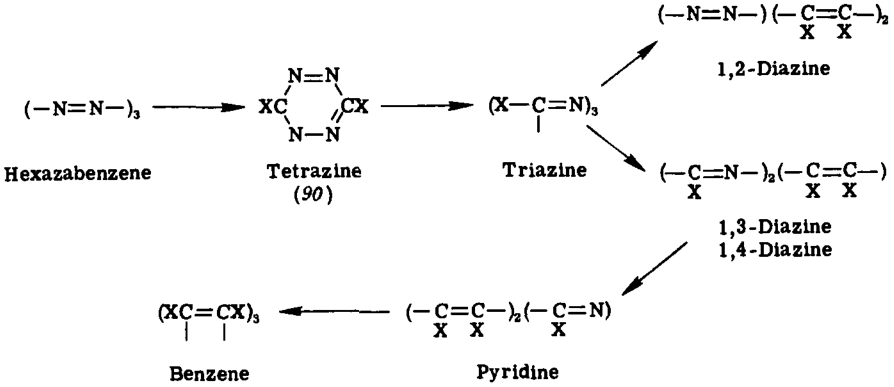
derivative $(CF_3SC)_4NC(O)C(O)N(CSCF_3)_4$ is very stable toward UV light (λ = 254 nm). It remains unaffected even after several days of irradiation (*91*). The manifold reactivities of this halogen-like parachlorine and its influence as a radical on other functional groups are so far not fully elucidated. Additional interesting results can be expected in this field of chemistry.

V. Interchangeability of Elements and Paraelements in Known Structures

The structures of known compounds made up entirely of elements remain unaltered if the elements are substituted partially or totally by pseudo- or paraelements.

A. TRANSITION FROM HEXAZABENZENE $(—N{=}N—)_3$ TO BORAZOLE $(—\overset{\delta+}{N}H—\overset{\delta-}{B}H—)_3$

The planar aromatic benzene molecule may be thought of as a resonance-stabilized trimeric pseudonitrogen molecule $(HC—CH)_3$. Hexazabenzene $(—N{=}N—)_3$, which is the associated analogous parent compound containing a single element, is stable only under extreme conditions (*110*). If, however, alternate N atoms or all the N atoms in $(—N{=}N—)_3$ are replaced by a paranitrogen such as, for example, FC, ClC, BrC, IC, CF_3C, etc. (= X), the following series is obtained.



By partial substitution of C—X by BH_2 (pseudonitrogen) in triazine $(\cdot\underset{\cdot\cdot}{N}{=}BH_2)_3$ is first produced and this is stabilized by resonance through rearrangement to borazol $(\cdot\overset{\delta+}{N}H—\overset{\delta-}{B}H)_3$, which has polarized B—N bonds.

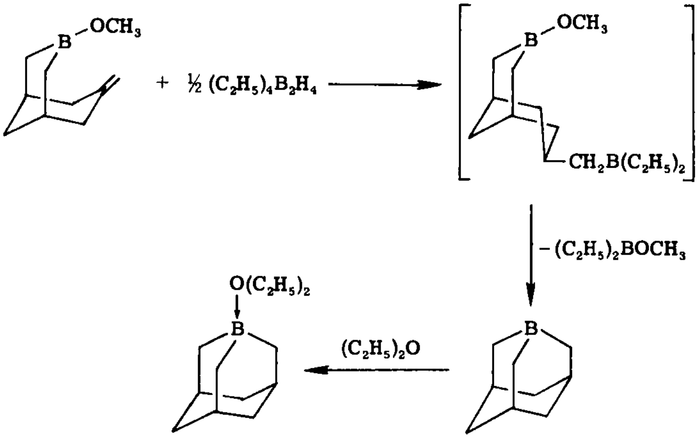
B. EXCHANGEABILITY WITHIN ADAMANTANE STRUCTURES

Phosphorus, arsenic, and antimony form oxides with the formula E_4O_6 (E = P, As, Sb) which have the adamantane structure. No nitrogen compound N_4O_6 with a corresponding structure is known other than N_2O_3 and this is stable only at low temperatures. If, though, the oxygen is replaced by a pseudooxygen unit such as, e.g., CH_2, hexamethylenetetramine $N_4(CH_2)_6$ is obtained.

It has been established quite generally that compounds with the adamantane structure are formally made up of elements of Group V and VI in the ratio 4 : 6. These may be replaced either completely or in part by the corresponding pseudo- or paraelements. Accordingly, adamantane, $(CH)_4(CH_2)_6$, consists of four pseudonitrogen and six pseudooxygen atoms. All substances with an adamantane structure so far synthesized correspond to this composition (*92, 93*). Adamantanes containing paraelements are, for example, $(BrC)_4(CH_2)_6$, $(CH_3C)_4S_6$, $(ClSi)_4(CH_2)_6$, $P_4(NCH_3)_6$, and $(RSi)_4O_6$ (*93*).

Very recently it was possible to synthesize two basic adamantanes of the formula $(HSi)_4S_6$ and $(HSi)_4Se_6$. They were made by reacting $HSiCl_3$ with $(H_3Si)_2E$ (E = S, Se). An X-ray structure determination proved the expected adamantane structure for $(HSi)_4S_6$ and spectroscopic investigations left no doubt that $(HSi)_4Se_6$ has the same structure (*94*).

Among the elements able to form adamantane structures boron and its higher analogs should also be considered. Like the elements of Group V they have as sp^2 hybrids three unpaired electrons at their disposal. Compounds of the formula MX_3 (M = B, Al, Ga ...) are planar and are not equivalent to $M'X_3$ (M′ = N, P, As ...). A formal equivalence between the elements of Groups III and V can be arrived at through adduct formation with Lewis bases, e.g., $R_3N{:}BX_3$. Here boron is tetrahedrally coordinated and is electronically isovalent with, e.g., nitrogen. This element–paraelement relationship should make possible the substitution of, e.g., N, CH ... for $R_3N{:}B{\equiv}$, and in fact it does. B. M. Mikkailov (*95*) has provided methods of preparation for 1-boradamantane. The following synthesis is chosen for illustration:



The relatively stable etherate of 1-boradamantane dissociates partially in its components even at 20°C. It can be used for synthesizing complexes with other ligands just by mixing the etherate with stronger Lewis bases. 1-Boradamantane forms colorless, well-formed prisms which on heating to 190–200°C lead to a liquid mass. The boron atom is sp^3 hybridized and the CBC angle is almost tetrahedral. Complex formation with Lewis bases take place through the vacant sp^3-type orbital (*95*). The preparation of $(HC)_4(BCH_3)_6$ (*96*) is an example of an adamantane with CH_3B as a chalkogen type of ligand. The crystal structure determined proves the adamantane shape and gives angles at boron at 117.2° and those at carbon in the range of 103.1 to 106.4° (*97*). Oxidation of P_4O_6 to P_4O_{10} depends on coordination bonding of the electrophilic oxygen atom to the free electron pair of a phosphorus atom without change in the adamantane structure. Since the pseudonitrogen atom CH possesses no free electron pair, oxidation products of the composition $(OCH)_4(CH_2)_6$, for example, are unknown. The electrophile O in P_4O_{10} may be replaced by others, whereby compounds of the general formula $Y_nP_4O_6$ are obtained. A number of derivatives have been prepared (see Table VI).

C. INTERCHANGEABILITY WITHIN THE P_4S_3 STRUCTURE

It is very difficult at first sight to understand why substances like P_7R_3, $P_4[Si(CH_3)_2]_3$ and also Sb_7^{3-} should have the same structure as P_4S_3. With the aid of the element displacement principle this question can be answered without difficulty. In the cases mentioned the molecules contain a P_4 and an Sb_4 unit and the other parts can be written as

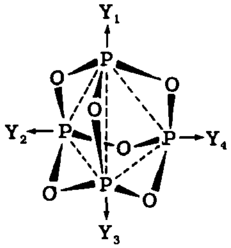


TABLE VI

	x	Y_1	Y_2	Y_3	Y_4
$S_xP_4O_6$	1	S	—	—	—
(*98*)	2	S	S	—	—
	3	S	S	S	—
	4	S	S	S	S
$Se_xP_4O_6$	1	Se	—	—	—
(*98*)	2	Se	Se	—	—
	3	Se	Se	Se	—
$(H_3B)_xP_4O_6$	1	BH_3	—	—	—
(*99*)	2	BH_3	BH_3	—	—
	3	BH_3	BH_3	BH_3	—
$[(OC)_3Ni]_xP_4O_6$	1	$Ni(CO)_3$	—	—	—
(*100*)	2	$Ni(CO)_3$	$Ni(CO)_3$	—	—
	3	$Ni(CO)_3$	$Ni(CO)_3$	$Ni(CO)_3$	—
	4	$Ni(CO)_3$	$Ni(CO)_3$	$Ni(CO)_3$	$Ni(CO)_3$
$[(OC)_4Fe]_xP_4O_6$	1	$Fe(CO)_4$			
(*101*)					

PR, $Si(CH_3)_2$, or Sb^-. The first two radicals are first-order derivative paraelements equivalent to sulfur. The formula P_7R_3 can be written as $P_4(PR)_3$ with R = H, Li (*102*), $(CH_3)_3Si$ (*103*), or CH_3 (*104*), thus accounting for the observed similarity to P_4S_3 (*105*). Analogously, it is found that $Sb_7^{3-} = Sb_4(Sb^-)_3$ has a P_4S_3 structure (*106, 107*). In $P_4[Si(CH_3)_2]_3$ the parasulfur $Si(CH_3)_2$ replaces PR without changing the P_4S_3 cage (*108, 109*).

VI. Electronegativities

Paraelements, derived from element displacement, exhibit chemical properties which are largely determined by the coordinated central element and which resemble those of neighbors on the right. Thus, e.g.,

CF_3 resembles fluorine and CF_3S resembles chlorine. Such an assignment is very difficult for higher order derivative paraelements, e.g., $(CF_3S)_2N$ and $(CF_3SC)_4N$·[tetrakis(trifluoromethylthio)pyrrolyl]. Group electronegativities help to solve such problems. According to the values estimated, $(CF_3S)_2N$ is like fluorine and $(CF_3SC)_4N$· is like chlorine. The chemical properties of these paraelements confirm these assignments. The presumption that Grimm's pseudoelements are, as far as chemical properties are concerned, superior to paraelements, cannot be maintained. The members of the series OH, NH_2, and CH_3 have chemically much less in common with fluorine than OF, NF_2, and CF_3, although the former are isoelectronic and isoprotonic with fluorine and the others only electronically isovalent. The group electronegativities of the two series show this quite convincingly.

OH	2.78–3.51	OF	4.70
NH_2	2.47–2.61	NF_2	3.60–3.64
CH_3	2.27–2.34	CF_3	3.46–3.55

J. E. Huheey (*111*) has calculated group electronegatives for a substantial number of radicals. The values obtained are, despite the general irregularities, in good agreement with those calculated from carbonyl frequency data (*112*) and from phosphoryl frequency data (*113*). They might be a good guide in assigning paraelements.

Group electronegativities of fluorinated paraelements which have been determined experimentally may be placed between those of fluorine and bromine, giving the following sequence: F (4.0); OF (3.8) (*114*); OOF (3.8) (*114*); $(CF_3S)_2N$ (3.7) (*47*); CF_3OO (3.7) (*114*); CF_3 (3.3) (*3*); CF_3SNH- (3.2) (*47*); Cl (3.0); $(CF_3SC)_4N$· (2.9); CF_3S (2.7) (*3*); Br (2.8). This shows that incorporation of paraelements in the periodic system smoothes out sudden changes in the properties of elements in going over from one period to the next.

The concept put forward in this article is the outcome of collecting relevant results from the literature, completing them with the aid of new ideas, and arranging them according to the periodic system of functional groups.

In other words, it can be said that available mosaic stones were complemented by new ones and arranged to form a mosaic picture. The overall picture is now understood but the boundaries are diffuse and should be made clearer by additional work.

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