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REVIEW PAPER

AROMATIC COMPOUNDS WITH NEW FLUORINE-CONTAINING SUBSTITUENTS

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SUMMARY

The introduction of strong electron-accepting fluorine-containing substituents into the aromatic moiety gives compounds with unique properties. Determination of the electronic nature of the grouping $(R_f)_2PO$ in arylbis(perfluoroalkyl)-phosphine oxides has shown that this substituent is comparable with R_fSO_2, one of the most electron-accepting groups.

A general principle is proposed for the construction of the new superstrong electron-accepting substituents by the replacement of oxygen atoms for trifluoromethylsulfonylimino groups. For example, when the oxygen atoms in CF_3SO and CF_3SO_2 groups are replaced by $CF_3SO_2N=$, new stable and even more electron-accepting substituents are formed. The grouping $CF_3S(O)=NSO_2CF_3$ corresponds to two nitro groups. A similar increase in electron-accepting ability is observed in groupings derived from other elements by replacement of oxygen atoms by the $CF_3SO_2N=$ group.

INTRODUCTION

The introduction of different substituents into aromatic or heterocyclic systems makes possible a targetted modification of the properties of compounds over rather wide ranges.

Work carried out at our laboratory, at the laboratories of W.Sheppard and elsewhere developed synthetic methods for

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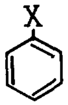
the introduction of more than 50 new fluorine-containing substituents into aromatic rings [1-19].



X = CH_2F, CHF_2, CF_3, CH_2CF_3, $CF(CF_3)_2$, $C(CF_3)_3$,
$CH{=}CH{-}CF_3$, $CF{=}CF{-}CF_3$, $C{\equiv}C{-}CF_3$, OCF_3, SCF_3,
$SeCF_3$, TeC_3F_7, CH_2SCF_3, $CH(SCF_3)_2$, $C(SCF_3)_3$,
$SOCF_3$, SO_2CF_3, $SeOCF_3$, SeO_2CF_3, $N(CF_3)_2$, PF_4,
$P(CF_3)_2$, $P(O)(C_3F_7)_2$, $N(SO_2CF_3)_2$, SiF_3, GeF_3,
SbF_4, SF_3, SF_5, JF_2, $J(OCOCF_3)_2$, JF_4, HgF,
$HgCF_3$, $HgSCF_3$, $HgSO_2CF_3$

Their electronic nature, the orientation influence in aromatic electrophilic substitution reactions and their effect on acid- base properties, spectral characteristics and biological activity of aromatic compounds have been determined.

Because of the strength of the fluorine-carbon bond and the high electronegativity of the fluorine atom, these groups are usually very stable and frequently give the aromatic compounds new properties that are impossible to achieve by the introduction of other substituents. Though in the periodic system there is no place for further halogens such groups as trifluoromethoxy or trifluoromethylthio are very similar to the halogen atoms in the effects they exert as is seen from their σ-constants, **although** with some peculiarities.

	σ_I	σ_R	σ_P
CF_3O	0.55	-0.18	0.37
CI	0.40	-0.18	0.22
CF_3S	0.42	0.06	0.48

Among fluorine-containing substituents, groups with the strongest electron acceptor properties have been found. For a long time the nitro group was considered the queen of electronegativity then its throne was occupied by perfluoroalkylsulfonyl groups. Even such substituents, as the trimethylammonium group, bearing a cation charge, are inferior in their electronseeking effect to the trifluoromethylsulphonyl group [17].

	σ_I	σ_R	σ_P
NO_2	0.56	0.20	0.76
CF_3SO_2	0.73	0.31	1.04
$\overset{+}{N}(CH_3)_3$	0.92	0.00	0.92

Now new "superstrong" substituents, equal in their strength to two nitro groups have been found. The data obtained have expanded considerably theoretical investigations as well as have allowed synthesis of fundamental new compounds. Interest in investigations of aromatic and heterocyclic compounds with fluorine-containing substituents is growing because many of them have found a wide application in industry, agriculture and medicine. Because of the rapid development of synthetic methods in organofluorine chemistry a large number of new compounds with interesting properties has become available. At our laboratory alone more than five thousand such new substances have been prepared.

Thus, during the last 25 years an exciting new field in the chemistry of aromatic and heterocyclic compounds has been developed. The results of investigations in this field carried out at the Institute of Organic Chemistry of the Academy of Sciences of the Ukrainian SSR are presented in this paper.

New synthetic methods for aromatic compounds with fluorine-containing substituents

The CF_3SO_2 group is the most electron-accepting substituent but the methods for the preparation of aryltrifluoromethylsulfones have not been studied sufficiently. They are usually prepared from the corresponding sulfides by oxidation.

We have proposed convenient methods for the preparation of aryltrifluoromethyl sulfides. One of them consists in the interaction of aromatic iodide or bromide with trifluoromethylthiocopper [20]. This method is of a general nature. The problem was that trifluoromethylthiocopper was formerly expensive and not easily available as it was prepared in an autoclave by the use of silver fluoride.

$$CS_2 \xrightarrow[-Ag_2S]{AgF,\ 140^{\circ}} CF_3SAg \xrightarrow[-AgBr]{CuBr} CF_3SCu$$

We have found that it can be prepared quantitatively from the reaction of easily available bis(trifluoromethyl)disulfide with copper powder in polar solvents [21]. The suggested procedure is general, we have applied it to the preparation of trifluoromethylseleno- and pentafluorophenylthio or -selenocopper.

$$CCl_3SCl \xrightarrow{NaF} CF_3SCl + CF_3S\text{-}SCF_3$$

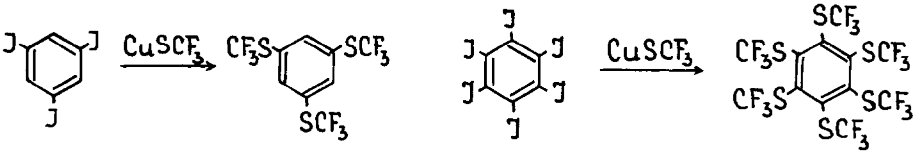
$$CF_3S\text{-}SCF_3 \xrightarrow{Cu} CF_3SCu$$

$$CF_3Se\text{-}SeCF_3 \xrightarrow{Cu} CF_3SeCu$$

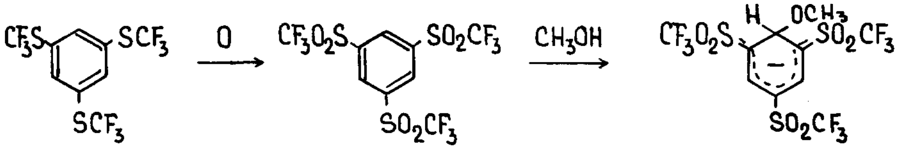
$$C_6F_5S\text{-}SC_6F_5 \xrightarrow{Cu} C_6F_5SCu$$

$$C_6F_5Se\text{-}SeC_6F_5 \xrightarrow{Cu} C_6F_5SeCu$$

These reagents have made possible the replacement from one to six iodine atoms in an aromatic ring by the corresponding perfluororganothio- or -seleno groups. In this way tris(trifluoromethylthio) and hexakis(trifluoromethylthio) or -seleno benzenes were prepared [21].

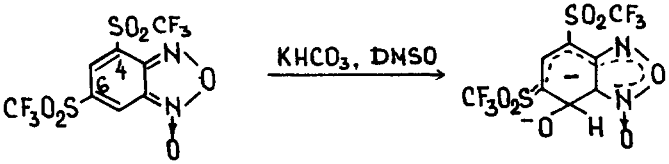


By the oxidation of tris(trifluoromethylthio) substituted benzene an analog of 1,2,3-trinitrobenzene - 1,2,3-tris(trifluoromethylsulfonyl)benzene - was prepared. This is a fundamentally new compound for the investigation of anionic σ-complexes of the Meisenheimer type [22,23].

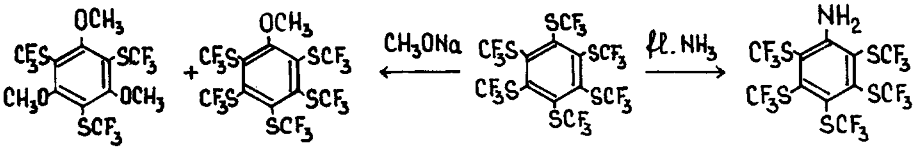


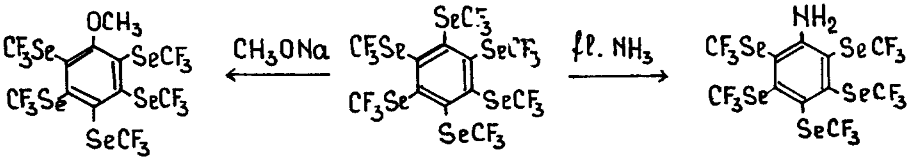
It was supposed earlier that such stable complexes could be derived only from polynitro substituted aromatics. We have now shown that tris(trifluoromethylsulfonyl)benzene, unlike trinitrobenzene, forms σ-complexes not only with sodium methylate but also with methanol itself. This is the first known example where methanol attacks the unsubstituted carbon atom of an aromatic ring. The resultant σ-complex is significantly more stable than the corresponding adduct of 1,3,5-trinitrobenzene with the equilibrium constant for the formation of the σ-complex with sodium methylate having a value 10^6 higher than that for 1,3,5-trinitrobenzene [24].

Recently we have found an even more nucleophilic system - bis(trifluoromethylsulfonyl)furoxane. This compound reacts with sodium hydrogencarbonate in DMSO to give a hydroxy complex that is completely ionized in solution. The analogous dinitrocompound having one tenth of the acidity gives under similar conditions only the usual nonionized derivative [25].



Hexakis(trifluoromethylthio)- and -selenobenzenes are more electrophilic system than hexafluorobenzene. Their half-wave reduction potentials (-0.95 V and -1.07 V respectively) are near to that of tris(trifluoromethylsulfonyl)benzene (-0.88 V) and they react with such nucleophiles as liquid ammonia or sodium methylate under much milder conditions than hexafluorobenzene to give the corresponding derivatives of aniline and anisole. In the case of hexakis(trifluoromethylthio)benzene, reaction proceeds so rapidly that even with one mole of sodium methylate a mixture of mono and trimethoxy substituted derivatives was obtained [26].





A further interesting method developed in our laboratory is the ion-radical perfluoroalkylation reaction. This allows preparation of not only different trifluoromethylthio derivatives but also previously inaccessible aryl perfluoroalkyl sulfides through the use of perfluoroalkyl iodides of any chain length with a normal or iso structure [27,28]. Aryl perfluoroalkyl selenides and the previously unknown tellurides can also be prepared **by this method** [29,30].

$$C_6H_5SH \xrightarrow[h\nu]{C_3F_7J} C_6H_5SC_3F_7$$

$$C_6H_5SeH \xrightarrow[h\nu]{CF_3J} C_6H_5SeCF_3$$

$$C_6H_5TeH \xrightarrow[h\nu]{C_3F_7J} C_6H_5TeC_3F_7$$

Perfluoroalkyl iodides unlike alkyl iodides do not show alkylating properties. This is explained by the polarization of perfluoroalkyl iodides which is opposite to that of alkyl halides, because the electronegativity of the CF_3 group (3.3) is higher than that of iodine (2.5).

$$\overset{\delta+}{CH_3}-\overset{\delta-}{J} \qquad\qquad \overset{\delta-}{CF_3}-\overset{\delta+}{J}$$

However we have shown that under conditions where an ion-radical $S_{RN}1$ mechanism is involved (UV irradiation in liquid ammonia or polar solvents in the presence of sodium hydroxide or methylate) perfluoroalkyliodides smoothly perfluoroalkylate thio-, seleno- and tellurophenols in a Pyrex flask within 5 minutes [27-30].

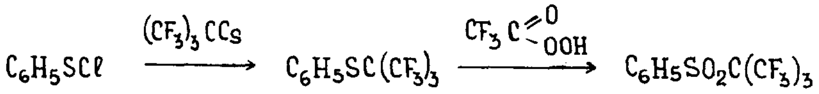
This reaction has also been carried out in aqueous organic solvents under conditions of phase-transfer catalysis [28]. Sulfinic acids also undergo an ion-radical perfluoroalkylation with a single-stage formation of aryl trifluoromethyl sulfones. However the yields in this case are low [31].

$$C_6H_5SO_2H \xrightarrow[h\nu]{CF_3J} C_6H_5SO_2CF_3$$

$$RC_6H_4SH \xrightarrow[h\nu]{CF_3Br} RC_6H_4SCF_3$$

We have found that the cheaper perfluoroalkyl bromides can be used instead of iodides in these reactions [32]. Recently analogous results were reported by Wakselmann [33].

As has already been noted, perfluoroalkyliodides with an iso carbon skeleton can also be used in perfluoroalkylation but the yields of aryl perfluoroisopropyl sulfides are 10-15% lower and accompanied by the formation of disulfides. When perfluoro-tert-butyl iodide is used, the thiophenols are quantitatively converted to diaryl disulfides apparently as a result of a competitive decomposition of this iodide to a stable perfluoro-tert-butyl radical and an iodide radical, with the latter oxidizing the thiophenolate anion to a disulfide. Thus ion-radical perfluoroalkylation cannot be used for the introduction of a perfluoro-tert-butyl group on to S and Se atoms in thiophenols and selenophenols. We have found a convenient method for the synthesis of aryl perfluoro-tert-butyl sulfides and selenides by the reaction of arylsulfenyl- and arylselenyl chlorides with perfluoro-tert-butylcesium in acetonitrile. The corresponding sulfones have been synthesized by oxidation of the sulfides [34].

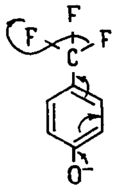


$$C_6H_5SCl \xrightarrow{(CF_3)_3CCs} C_6H_5SC(CF_3)_3 \xrightarrow{CF_3C(=O)OOH} C_6H_5SO_2C(CF_3)_3$$

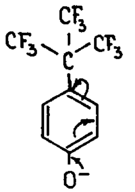
The perfluoro-tert-butylsulfonyl group was found to be even more electron-accepting than the trifluoromethylsulfonyl group. This is due to the fact that the perfluoro-tert-butyl group is more electron-accepting by the value of its σ_p-constant than the trifluoromethyl group, mainly because of an increase in the inductive effect. It is of interest that its σ_R value is equal **to zero** [7].

	σ_I	σ_R	σ_P
CF_3	0.41	0.10	0.51
$C(CF_3)_3$	0.55	0.00	0.55
SO_2CF_3	0.73	0.31	1.04
$SO_2C(CF_3)_3$	0.79	0.34	1.13
μ $C_6H_5SO_2CF_3$	4.32 D		
μ $C_6H_5SO_2C(CF_3)_3$	5.12 D		

Recently we have synthesized p-perfluoro-tert-butyl phenol which, in contrast to p-hydroxybenzotrifluoride, does not split off fluoride ions even when heated **with** sodium hydroxide solutions. This and the lower acidity of p-perfluoro-tert-butylphenol confirm once again the hypothesis of the presence of a hyperconjugative effect of the fluorine atom which manifests itself only under the strong electron-donating influence of phenolate ion.



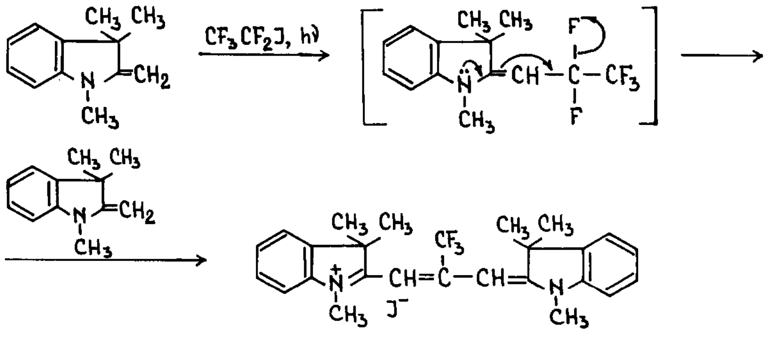
pKa 9.49



9.75 in 50% C_2H_5OH

When we carried out this investigation and obtained for the perfluoro-tert-butylsulfonyl group the value of σ_p as 1.13 we considered it to be the most electron-accepting among the stable uncharged substituents. But we have now found ways for the construction of even more electron- accepting substituents.

It is of interest that C-nucleophiles also undergo an ion-radical perfluoroalkylation. We have shown this for β-diketones [35] and especially of the reaction of methylene bases of nitrogen-containing heterocycles [36]. The UV-irradiation of the mixture of Fischer base with pentafluoroethyl iodide leads to mesotrifluoromethyl substituted indocarbocyanines in excellent yield.

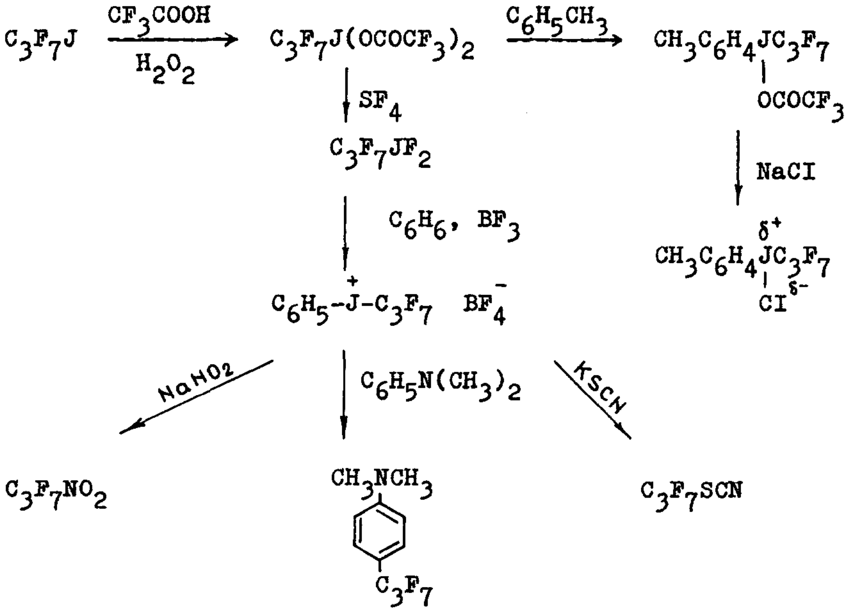


λ_{max}=572 nm

This reaction proved to be general. Thus it was shown that unlike the non-fluorinated cyanine dyes, which are usually protected from light during synthesis, perfluoroalkyl substituted cyanine dyes, because of their greater lightfastness, can be prepared under UV-irradiation [37].

We have also proposed a new method for the introduction of perfluoroalkyl groups into organic compounds by an electrophilic mechanism [38,39]. Perfluoroalkyl groups are usually introduced into the organic moiety only as a carbanion or a radical. To make these groups react by an electrophilic mechanism as cationic species one should construct a molecule in which the perfluoroalkyl radical would be bound to a heteroatom carrying a positive charge. That would ensure the maximum withdrawal of electrons from the perfluoroalkyl group and realization of cationic perfluoroalkylation. For this purpose we have prepared aryl perfluoroalkyliodonium salts by the reaction of bis(trifluoroacetoxy)iodoperfluoroalkanes with benzene or toluene in trifluoroacetic acid followed by replacement of the trifluoroacetoxy group by other anions [40].

However in a number of cases the nucleophilic chloride anion of the iodonium salt is capable of competing with the attacking nucleophile leading to the formation of perfluoroalkyl chlorides as by-products. Therefore aryl perfluoroalkyl iodonium salts with the non-nucleophilic BF_4^- anion have been synthesized by the reaction of difluoroiodoperfluoroalkanes with benzene in the presence of boron trifluoride in an organic solvent at low temperatures [41]. In the resultant phenyl perfluoroalkyliodonium tetrafluoroborates a complete separation of charges is achieved and these compounds are therefore more effective perfluoroalkylating agents than chlorides. Because of the strong electron-accepting effect of the iodonium cation these salts are capable of easily transferring perfluoroalkyl groups in the form of cations to nucleophilic agents [38,39,41].

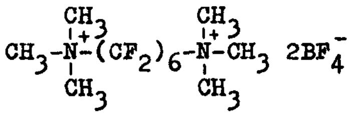


In this way thio- and selenophenols are converted to arylperfluoroalkyl sulfides and selenides. Secondary and tertiary alkylanilines are perfluoroalkylated in the para position.

Inorganic salts, such as sodium nitrite, potassium cyanide, thio- and selenocyanides also participate in cationic perfluoroalkylation reactions. In these processes nitro, cyano-, cyanothio- and cyanoselenoperfluoroalkanes are formed.

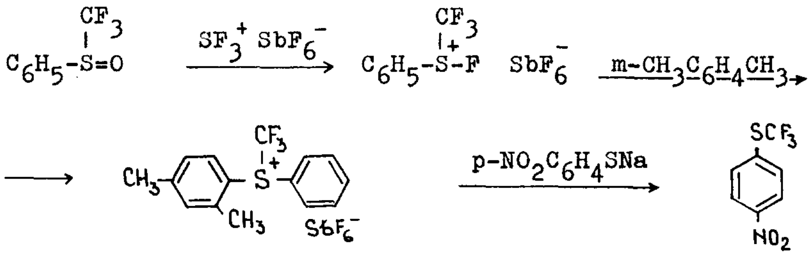
Analogously to the arylmonoperfluoroalkyliodonium trifluoroacetates and tetrafluoroborates, α,ω-bis(aryliodonium)perfluoroalkanes have been synthesized from the corresponding α,ω-bis(ditrifluoroacetoxyiodo)- and α,ω-bis(difluoroiodo)-perfluoroalkanes. Different α,ω-disubstituted perfluoroalkanes can be obtained from these salts [42].

$$C_6H_5\overset{+}{J}(CF_2)_6\overset{+}{J}C_6H_5\ 2BF_4^-$$
$$\downarrow 2\ p\text{-}ClC_6H_4SNa$$
$$p\text{-}ClC_6H_4S(CF_2)_6SC_6H_4Cl\text{-}p$$

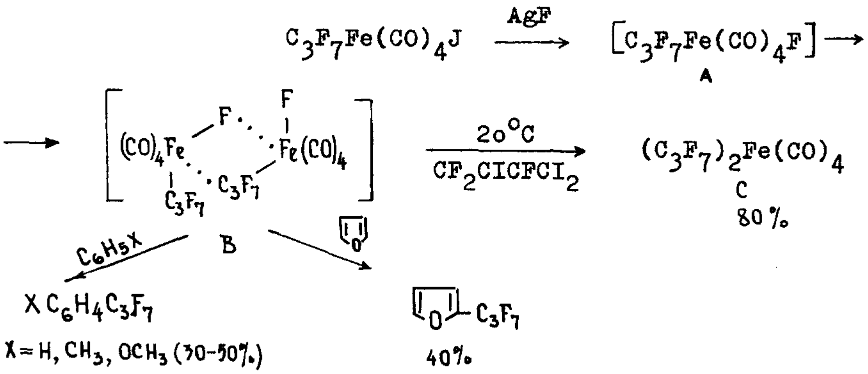

$$CH_3\text{-}\overset{CH_3}{\underset{CH_3}{\overset{|+}{\underset{|}{N}}}}\text{-}(CF_2)_6\text{-}\overset{CH_3}{\underset{CH_3}{\overset{|+}{\underset{|}{N}}}}\text{-}CH_3\ 2BF_4^-$$

It is of interest that α,ω-bis(aryliodonium)perfluoroalkanes possess the same physiological activity as the analogous ammonium salts which were earlier synthesized at our laboratory and show a rather strong anticholinesterase action [43]. We have synthesized aryliodonium salts with different perfluoroalkyl radicals bonded to the iodine atom although we have not been able to link the trifluoromethyl group.

We have also found a method of synthesis of diarylperfluoroalkylsulfonium salts. These show a perfluoroalkylating action analogous but somewhat weaker to that of the iodonium salts. Thus, for example, they convert p-nitrothiophenolates to p-nitrophenyltrifluoromethyl sulfide [44].



We have found the symmetrization of iron complexes to the corresponding bis(perfluoroalkyl)derivatives (C) with silver fluoride. The reaction, evidently, proceeds through unstable carbonyl fluorides (A) and dinuclear complexes (B). If the reaction is carried out in the presence of aromatic compounds, such as benzene, toluene, anisole or furan at ambient temperature, the products of perfluoroalkylation of the aromatics rather than complex (C) are formed [45].



The isomeric ratio of the perfluoroderivatives of toluene and anisole indicates the cationic nature of the reaction. Earlier Umemoto obtained an analogous mixture of isomers for the perfluoroalkylation of anisole by perfluoroalkyl aryliodonium trifluoromethyl sulfonate [46].

The new synthetic methods discussed have made it possible to prepare aryl perfluoroalkyl sulfides, selenides and tellurides with normal or iso-perfluoroalkyl carbon skeletons of any chain length.

Electronic effects of fluorine-containing substituents

From a comparison of electronic effects of perfluoroalkylthio and perfluoroalkylsulfonyl groups it is seen that the greatest differences are observed for the substituents with divalent sulfur. Perfluoroalkyl substituents with divalent sulfur, selenium and tellurium are very similar in their electronic nature. A gradual lengthening of the perfluoroalkyl radical bonded to the sulfur and selenium atoms and, particularly its branching, slightly increases the inductive effect and more than doubles the conjugative effect. In the series of perfluoroalkylsulfonyl groups the electron-accepting inductive and conjugative effects are slightly increased upon transition from trifluoromethylsulfonyl to perfluoro-tert-butylsulfonyl group. The latter, as has already been mentioned, was up to recently considered to be the most electron-accepting substituent [47,48].

It is interesting to note that in the case of p-aminophenyltrifluoromethyl and p-aminophenyl-tert-butyl sulfones a significant difference (approximately 1.4D) between the experimental and calculated values of dipole moments were found. For p-nitroaniline, for comparison, this difference is only 1 D. These data as well as the high value of σ_R (0.31) show that contrary to earlier suppositions perfluoroalkylsulfonyl groups in corresponding sulfones show not only an inductive but also a conjugative effect.

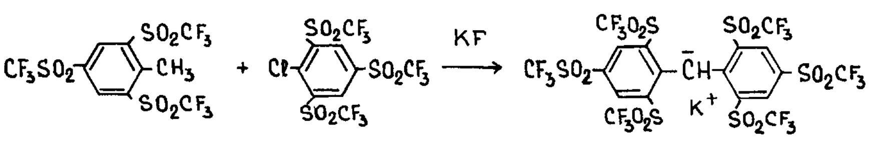
	σ_I	σ_R	σ_P
CF_3S	0.42	0.06	0.48
C_2F_5S	0.42	0.07	0.49
C_3F_7S	0.42	0.07	0.49
$(CF_3)_2CFS$	0.42	0.09	0.51
$(CF_3)_3CS$	0.43	0.13	0.56
CF_3Se	0.42	0.04	0.46
$(CF_3)_3CSe$	0.43	0.10	0.53
C_3F_7Te	0.45	0.05	0.50

	σ_I	σ_R	σ_P
CF_3SO_2	0.73	0.31	1.04
$C_2F_5SO_2$	0.76	0.31	1.07
$C_3F_7SO_2$	0.76	0.31	1.07
$(CF_3)_2CFSO_2$	0.77	0.31	1.08
$(CF_3)_3CSO_2$	0.77	0.34	1.11

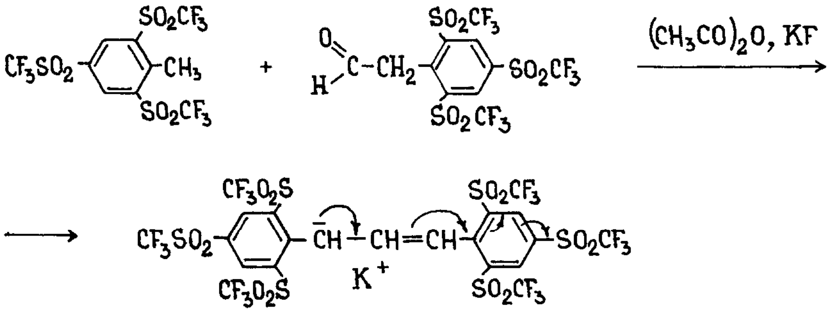
Apparently, the electron-accepting perfluoroalkyl groups make the d-orbitals of the sulfur atom more diffuse and make their participation in the conjugation easier, especially in the presence of a strong electron-donating amino group.

The ability of the trifluoromethylsulfonyl group to delocalize electrons in a benzene ring leads to the already mentioned formation of stable anionic σ-complexes and also in an recent synthesis of a new type of anionic dyes hexakis-(trifluoromethylsulfonyl)diphenylmethane, 1,3-diphenylpropene and diphenylamines.

Diphenyl and triphenylmethane dyes are a well known class of cationic dyes. We supposed that the presence of trifluoromethylsulfonyl groups on the aromatic nuclei of diphenylmethane or its vinylene homologs would make possible the preparation of a new type of anionic dyes where the easily formed anion would be stabilized through the distribution of the negative charge on to CF_3SO_2 groups. The synthesis of these compounds was performed according to the following scheme [49].



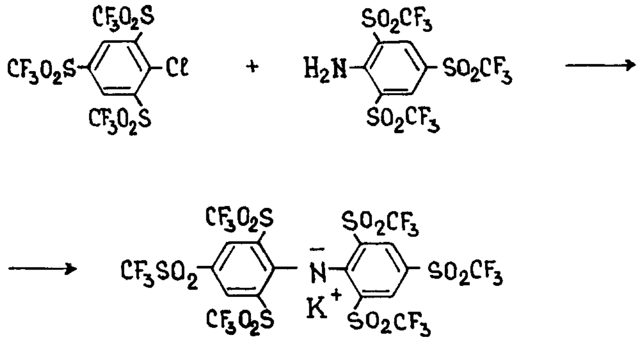
λmax 590nm



λ_{max} 640 nm

Potassium fluoride is the most convenient catalyst for this condensation. The resultant diphenylmethane and propene, colourless in the solid state, give deep blue solutions in acetone, ethanol and even ether especially on heating or in the presence of the traces of water. These polar solvents are strong enough to withdraw a proton from the methylene group. Potassium salts of these dyes are stable on storage.

The analogous derivatives of diphenylamine, synthesized in our laboratory, precipitate yellow salts with alkalis. We have identified an analytical reagent not only for potassium, but also, in the form of the lithium salt, for sodium cations [50].



λ_{max} 370 nm

All these examples show that the trifluoromethylsulfonyl group is well conjugated with a negative charge which makes possible its delocalization and its ability to be a good auxochrome. At present the chemistry of this group is so well studied that it has already become trivial and it is a high time for it to occupy a deserved place in organic chemistry textbooks. I think that all chemists working in the field of fluorine chemistry must contribute to its popularization.

Constantly looking for the new more and more electron-accepting substituents which would ensure the creation of novel compounds with extreme properties we decided to undertake the synthesis of aryl bis(perfluoroalkyl)phosphinoxides and to determine the electronic nature of the $(R_f)_2PO$ group.

As has already been shown perfluoroalkyl radicals differ only slightly in their electronic nature. Therefore as an example the $(C_3F_7)_2PO$ group was taken as it was the easiest for us to introduce into the aromatic ring. The synthesis of aryl bis(heptafluoropropyl)phosphinoxides was performed according to the following scheme [51].

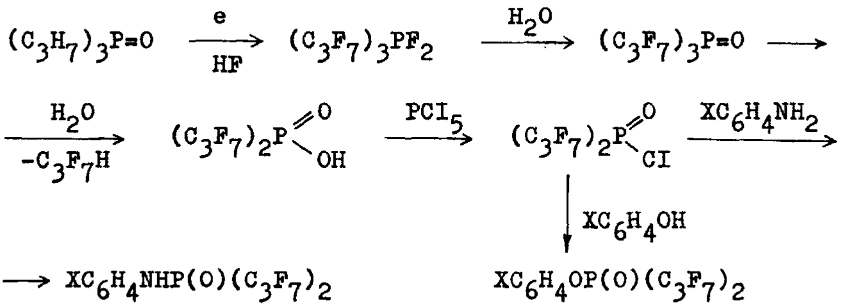
$$XC_6H_4MgBr + (C_3F_7)_2PCI \longrightarrow XC_6H_4P(C_3F_7)_2 \xrightarrow{CI_2}$$

$$\longrightarrow XC_6H_4PCI_2(C_3F_7)_2 \xrightarrow{HCOOH} XC_6H_4P(O)(C_3F_7)_2$$

X = H, m-F, p-F

The resultant phosphinoxides are fairly stable compounds that are not hydrolyzed by water and can be stored without decomposition for a long period of time.

To clarify the mechanism of the transfer of electron effects through the atoms of oxygen and nitrogen, aryl esters and anilides of bis(heptafluoro)phosphinic acid were synthesized. The latter has become accessible through electrochemical fluorination of alkylphosphine oxides, as found at our laboratory [52]. The electrochemical fluorination process previously applied only to sulfur, oxygen or nitrogen-containing compounds. There was even a supposition that phosphorus would poison the electrodes. We decided to check up this supposition and an electrochemical process for the synthesis of tris(perfluoroalkyl)phosphine oxides with perfluoroalkyl radicals of a different chain length was devised. The resultant compounds are not stable to hydrolysis and in the presence of water form bis(perfluoroalkyl)phosphinic acids. From the chloroanhydride of bis(heptafluoropropyl)phosphinic acid its aryl ester and anilide were prepared [51].



X = H, m-F, p-F

The Hammet-Taft σ-constants of the $(C_3F_7)_2PO$ group were determined from ^{19}F NMR spectra. They completely tally with the corresponding constants of the CF_3SO_2 group. Thus, it appears that the $(C_3F_7)_2PO$ group is very similar in its electronic nature to the CF_3SO_2 group - one of the strongest electron-accepting substituents [51].

As can be seen from the table

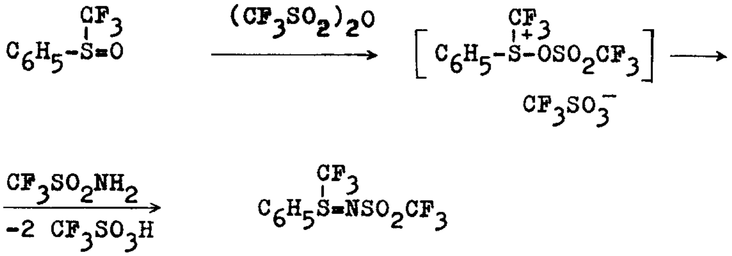
	σ_i	σ_R	σ_p
CF_3SO_2	0.73	0.31	1.04
$O{=}P(C_3F_7)_2$	0.74	0.31	1.05
$NHSO_2CF_3$	0.42	-0.15	0.27
$NHP(O)(C_3F_7)_2$	0.39	-0.21	0.18
OSO_2CF_3	0.75	-0.15	0.60
$OP(O)(C_3F_7)_2$	0.77	-0.21	0.56

oxyphosphonic and amidophosphonic groups are very similar in their electronic nature to the corresponding oxy and amido trifluoromethylsulfonyl substituents. They do not differ in their inductive effects but are slightly better donors in conjugative effects.

The substitution of two alkyl radicals in the R_2PO group for two perfluoroalkyl transforms this weak electron-acceptor into the one of the strongest electron-accepting substituents. But, as can be seen, this group is not stronger than perfluoroalkylsulfonyl groups.

The new superstrong electron-accepting fluorine-containing substituents

For the construction of significantly stronger electron-accepting substituents a new approach was found. We have thus recently proposed the replacement of the oxygen atoms in the different substituents for a $CF_3SO_2N=$ radical. We checked our supposition firstly on the CF_3SO group. For the synthesis of S-trifluoromethyl-S-aryl-N-trifluoromethylsulfonylsulfimides the reaction of aryl trifluoromethyl sulfoxides with trifluoromethylsulfonic anhydride was investigated. In the presence of trifluoroacetic anhydride aryl trifluoromethyl sulfoxide does not react even with arylsulfonyl amides. But trifluoromethylsulfonic anhydride forms complexes with aryl trifluoromethyl sulfoxides and the reaction with sulfonylamides is significantly facilitated [53].



$$C_6H_5\text{-}\overset{\overset{\displaystyle CF_3}{|}}{S}{=}O \xrightarrow{(CF_3SO_2)_2O} \left[C_6H_5\text{-}\overset{\overset{\displaystyle CF_3}{|+}}{S}\text{-}OSO_2CF_3\right] \underset{CF_3SO_3^-}{} \longrightarrow$$

$$\xrightarrow[-2\ CF_3SO_3H]{CF_3SO_2NH_2} C_6H_5\overset{\overset{\displaystyle CF_3}{|}}{S}{=}NSO_2CF_3$$

In this way S-trifluoromethyl substituted sulfimides, colourless crystalline solids were prepared. Unlike their non-fluorinated analogs which are easily hydrolyzed by sulfuric or hydrochloric acids, these compounds are not affected even when heated with concentrated sulfuric acid at 70° C. They are stable toward such strong oxidizing agents as chromium trioxide or trifluoroperacetic acid. p-Nitrophenyl substituted derivative can be reduced to the corresponding amine.

The determination of the σ-constants of the $CF_3SO_2N{=}SCF_3$ group, differing from the trifluoromethylsulfoxy group only by the replacement of the oxygen by the $CF_3SO_2N{=}$ radical led to the astonishing result. The transformation of the substituent without changing the oxidation state of the sulfur atom has resulted in a significant growth of both σ_I and σ_R constants.

	σ_I	σ_R	σ_p
CF_3SO	0.66	0.11	0.77
$CF_3S{=}NSO_2CF_3$	1.07	0.21	1.28
CF_3SO_2	0.73	0.31	1.04

This growth of electronegativity is comparable (see the values of σ_p constants) with the change of the electron-accepting properties of the substituent by the oxidation of the CF_3S group to CF_3SO_2. It is of interest that the inductive influence is most increased; the σ_I constant of the $S(CF_3){=}NSO_2CF_3$ group is 1.5 times more than that of the CF_3SO_2 group. In its electronegativity this new substituent corresponds approximately to the influence of two nitro groups at ortho and para positions to the reaction centre.

A substituent with a tetravalent sulfur atom has become more electron-accepting than the CF_3SO_2 group with hexavalent sulfur atom. Thus our supposition about the possibility of significantly strengthening the electron-accepting properties of substituents through the replacement of oxygen atoms by a $CF_3SO_2N=$ radical was confirmed. The $S(CF_3)=NSO_2CF_3$ group is stable toward acids and oxidizers and possesses unique 'superstrong' electron-accepting abilities.

Then it was of interest to apply this principle to the other substituents. We decided to continue our study on an analog of the CF_3SO_2 group where one of the oxygen atoms was substituted for the $CF_3SO_2N=$ radical. The direct oxidation of S-trifluoromethyl-S-arylsulfimides to the corresponding sulfoximides did not occur. Therefore we tried to iminate aryl trifluoromethyl sulfoxides with sodium azide in concentrated sulfuric acid, but the reaction has not gone apparently because of the strong withdrawal of electrons from the oxygen atoms at the first stage of protonation of the weakly basic oxygen.

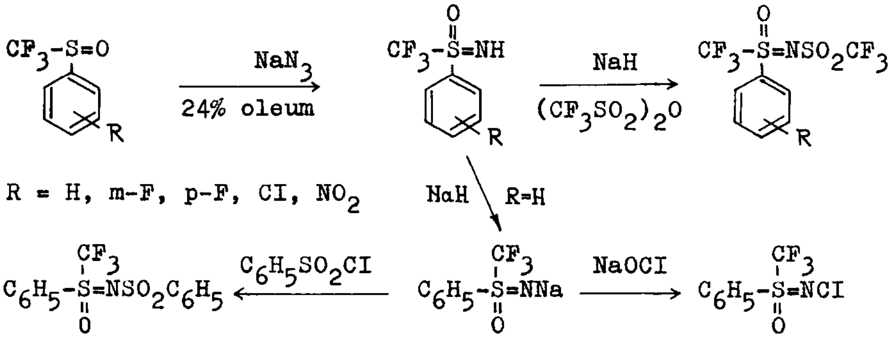
We faced an analogous situation when we tried to apply the Schmidt reaction to the perfluorocarboxylic acids which again did not occur. It was considered that because of the lack of protonation of the carboxy group it would not be possible to apply this process to carboxylic acids containing a perfluoroalkyl group. We have succeeded in fulfilling this reaction using 20% oleum as solvent. Because of the instability of organofluorine compounds containing both fluorine and an amino group bonded to the same carbon atom, the amides of perfluorinated carboxylic acids, resulting from loss of a difluoromethylene group were obtained instead of amines [54].

$$CF_3CF_2CF_2CF_2COOH \xrightarrow[\text{20\% oleum}]{NaN_3} \left[CF_3CF_2CF_2CF_2NH_2\right] \xrightarrow{H_2O}$$

$$\longrightarrow CF_3CF_2CF_2CONH_2$$

Thus, using oleum instead of sulfuric acid we have shown that imination of p-chlorophenyltrifluoromethyl sulfoxide proceeds in 10%, 18% and 24% oleum in 50%, 85% and 96% yield, respectively. In this way S-trifluoromethyl-S-arylsulfoximides, the first analogs of aryl trifluoromethyl sulfones with the $CF_3SO_2N=$ group instead of the oxygen atom, were prepared [55].

These compounds are colourless crystalline solids, insoluble in water, readily soluble in organic solvents. They give sodium salts with 5% water-methanol sodium hydroxide or even sodium hydrogencarbonate solution. The free sulfoximides can be recovered from these salts only by the action of strong mineral acids.

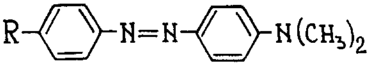


Sodium or lithium salts of these sulfoximides were converted into the corresponding N-trifluoromethylsulfonyl derivatives by the action of trifluoromethylsulfonyl chloride or anhydride. With benzenesulfonyl chloride and sodium hypochlorite, the corresponding N-benzenesulfonyl and N-chloro derivatives were obtained. S-Aryl-S-trifluoromethyl sulfoximides are quite stable compounds, so, for example, the p-nitrophenyl derivative can be reduced to the corresponding aniline. The latter was diazotised in nitrosylsulfuric acid and gave the corresponding dimethylaminoazo dye after condensation with dimethylaniline.

The action of acids on all presently known 4^1-substituted 4-dimethyl aminoazo dyes usually strongly deepens the colour (positive halochromism). The introduction of strongly electron-accepting fluorine-containing substituents has made it possible to obtain azo dyes that do not change colour or indeed even lighten their colour in acid media (negative halochromism).

Previously these phenomena were observed only in the case of azo dyes containing two electron-accepting substituents, usually nitro and trifluoromethylsulfonyl groups.

It is seen from the table where the absorption maxima of dimethylamino azo dyes with electron-accepting substituents at 4^1 position are given, that the introduction of a $CF_3S(O)=NSO_2CF_3$ group into the molecule of an azo dye leads to a lightening of the colour in the acid medium by comparison with the neutral one.



R	λ_{max} nm		$\Delta\lambda$
	ethanol	ethanol+HCI	
H	407	518	111
NO_2	475	508	33
CF_3SO_2	476	500	24
$CF_3S=NSO_2CF_3$	482	502	20
$CF_3\overset{O}{S}=NSO_2CF_3$	506	500	-6

This is the first example of a monosubstituted dimethylamino azo dye where negative halochromism is observed.

From the ^{19}F NMR spectra the σ-constants of the substituents $CF_3S(O)NH$ and $CF_3S(O)=NSO_2CF_3$ were obtained. The replacement of an oxygen atom for a less electronegative imino group led to the expected reduction in the value of the σ_p constant. However the replacement of oxygen in the CF_3SO_2 group by a $CF_3SO_2N=$ radical has significantly increased the electronegativity of the substituents. It has a σ_p value of 1.39 in heptane. To evaluate this result it is necessary to consider that before our investigations the most electronegative substituents among the stable uncharged groups within the Hammet-Taft scale had σ_p values of 0.8-0.9.

	σ_i	σ_R	σ_p
NO_2	0.57	0.20	0.77
CF_3S	0.42	0.06	0.48
			$\Delta = 0.29$
$CF_3-S=O$	0.66	0.11	0.77
			$\Delta = 0.27$
$CF_3-\overset{O}{\overset{\|}{S}}=O$	0.73	0.31	1.04
$CF_3-\overset{O}{\overset{\|}{S}}=NH$	0.60	0.24	0.84
$(CF_3)_3C-\overset{O}{\overset{\|}{S}}=O$	0.77	0.34	1.11

	σ_i	σ_R	σ_p
$CF_3-S=O$	0.66	0.11	0.77
			$\Delta = 0.51$
$CF_3-S=NSO_2CF_3$	1.07	0.21	1.28
$CF_3-\overset{O}{\overset{\|}{S}}=O$	0.73	0.31	1.04
			$\Delta = 0.35$
$CF_3-\overset{O}{\overset{\|}{S}}=NSO_2CF_3$	1.05	0.34	1.39

The difference between the σ_p values of CF_3SO_2 and $CF_3S(O)=NSO_2CF_3$ groups is 0.35. It is even greater than between the di- and tetravalent sulfur atom in CF_3S and CF_3SO groups or between the tetra- and hexavalent sulfur in CF_3SO and CF_3SO_2 groups (the difference is 0.29 and 0.27, respectively). The impression is created that in this "superstrong" substituent the sulfur atom has obtained even greater valency than six. The growth of the electron-accepting influence of the $CF_3S=NSO_2CF_3$ and $CF_3S(O)=NSO_2CF_3$ groups is mostly caused by the inductive effect. Thus the replacement of the oxygen atom in the CF_3SO group by a $CF_3SO_2N=$ radical has led to an increase in the σ_p constant to 0.51, that is even more than a half of the whole Hammet scale; in the case of CF_3SO_2 group of 0.35, one third of the scale [56].

Of course it was very interesting to find out if this principle is general or if it holds only in the case of sulfur-containing substituents.

To test our supposition the analogous phosphorus compounds were synthesized. They were prepared by the oxidative imination of aryl bis(heptafluoropropyl)phosphine by N,N-dichlorotrifluoromethylsulfonyl amide.

$$ArP(C_3F_7)_2 + CI_2NSO_2CF_3 \longrightarrow ArP(C_3F_7)_2=NSO_2CF_3$$

	σ_i	σ_R	σ_p
$(C_3F_7)_2P{=}O$	0.74	0.31	1.05
$(C_3F_7)_2P{=}NSO_2CF_3$	1.11	0.26	1.37

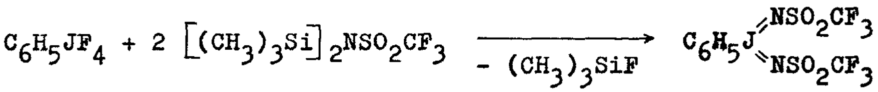
$\Delta = 0.32$

The same increase in the value of σ_p, mostly due to the growth of inductive effect, was observed after the replacement of the oxygen atom for a $CF_3SO_2N{=}$ radical [57].

The analogous growth of the σ_p constant was observed in the aryl iodoso compounds after the replacement of oxygen by a $CF_3SO_2N{=}$ group according to the following scheme.

$$XC_6H_4JF_2 + [(CH_3)_3Si]_2NSO_2CF_3 \xrightarrow[-(CH_3)_3SiF]{} XC_6H_4J{=}NSO_2CF_3$$

X = H, m-F, p-F

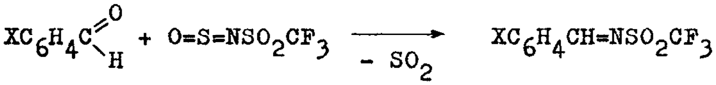


$$C_6H_5JF_4 + 2\,[(CH_3)_3Si]_2NSO_2CF_3 \xrightarrow[-\,(CH_3)_3SiF]{} C_6H_5J(=NSO_2CF_3)_2$$

	σ_i	σ_R	σ_p
J=O	0.56	0.06	0.62
$J{=}NSO_2CF_3$	1.24	0.11	1.35

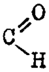
$\Delta = 0.73$

We have obtained yields of not only trivalent but also of pentavalent iodine; the σ-constants of the $(CF_3SO_2N{=})_2J$ group are now being determined. It is of interest that a significant increase in σ_p-constants is also observed after the replacement of oxygen bonded to the carbon atom in aldehydes.



$$XC_6H_4CHO + O{=}S{=}NSO_2CF_3 \xrightarrow[-\,SO_2]{} XC_6H_4CH{=}NSO_2CF_3$$

X = H, m-F, p-F

	σ_i	σ_R	σ_p	
 $\mathrm{C(=O)H}$	0.30	0.29	0.59	$\Delta = 0.41$
$CH{=}NSO_2CF_3$	0.53	0.47	1.00	

The value of σ_p increased in this case by 40%.

Thus to summarize it can be said that the principle of a significant increase of the electron-accepting properties of the substituents by the replacement of an oxygen atom by the $CF_3SO_2N{=}$ radical that we are proposing is general [57].

The new superstrong electron-accepting substituents constructed in this way open before the chemists new ways for the targetted modification of the properties of chemical compounds that can play an important role in the synthesis of new practically useful substances.

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