Russian Chemical Reviews **70** (3) 231 – 264 (2001) © 2001 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2001v070n03ABEH000626

Chemistry of xenon derivatives. Synthesis and chemical properties

V K Brel, N Sh Pirkuliev, N S Zefirov

Contents

I.	Introduction	231
II.	Synthesis and properties of xenon difluoride-based reagents	231
III.	Reactions of xenon difluoride and its derivatives with unsaturated compounds	233
IV.	Reactions of xenon derivatives with aromatic and polyfluoroaromatic compounds	236
V.	Reactions of xenon difluoride with organic acids and their derivatives	239
VI.	Organic xenon(II) compounds containing the C – Xe bond	242
VII.	Reactions of xenon difluoride with nitrogen-containing compounds	245
VIII.	Oxidative fluorination of organoelement compounds by xenon difluoride and its derivatives	248
IX.	Miscellaneous reactions	258

Abstract. The published data on the synthesis and chemical transformations of xenon derivatives are generalised and analysed. The bibliography includes 489 references.

I. Introduction

Xenon derivatives were obtained for the first time in 1962 by Bartlett [1] who used elementary xenon and PtF_6 as the oxidant to synthesise a xenon-containing salt.

$$Xe + PtF_6 \longrightarrow XePtF_6$$

Further studies showed that xenon compounds can be synthesised from elementary xenon and other oxidants. For example, the oxidation of elementary xenon by AgF_2 in anhydrous HF in the presence of BF_3 (see Ref. 2) results in XeF_2, whereas in the presence of AsF_5 the cation $Xe_2F_3^+$ is formed (see Refs 2 – 5).

$$2AgF_2 + 2BF_3 + Xe \xrightarrow{HF(liq)} 2AgBF_4 + XeF_2$$

$$4AgF_2 + 5AsF_5 + 2Xe \xrightarrow{HF(liq)} 4AgAsF_6 + Xe_2F_3^+AsF_6^-$$

Mass-spectrometric studies of the reaction of xenon with SiF_4 in the gas phase revealed the presence of the cation F_3SiXe^+ (see Ref. 6), whereas the formation of the cations $C_2H_4Xe^+$ and $C_2H_4XeF^+$ was established in reactions where the cations Xe_2F^+ or XeF_2^+ were generated in the presence of ethene (see Ref. 7). These reactions present substantial theoretical interest, since they illustrate the high synthetic potential of xenon.

At present xenon chemistry rests predominantly on fluorinated derivatives of xenon, such as xenon tetrafluoride and particularly xenon difluoride, the latter being produced by different manufacturers. The methods for the direct synthesis of XeF_2 and XeF_4 from fluorine and xenon at elevated temperatures were published in the early 1960's independently by several groups of investigators.[8,9] Further studies [10] were mostly directed at the elaboration of more convenient and simpler procedures for the preparation of xenon derivatives. A variety of inorganic xenon derivatives, both unstable and sufficiently stable in a broad temperature interval, were synthesised within a relatively short period of time. The first xenon derivatives containing Xe – N (see Ref. 11), Xe – B (see Ref. 12) and Xe – C bonds (see Ref. 13) were also prepared.

The interest in xenon chemistry stimulated the appearance of numerous reviews. Some of those [14 – 35] dealt with the discovery of noble gases, the chemistry of inorganic xenon derivatives and their applications in the fluorination of unsaturated and aromatic compounds. The physical and chemical properties of noble gas derivatives have been documented.[22 – 24] In some publications (see, *e.g.*, Refs 26, 27 and 32), xenon chemistry is considered in only a little detail and mostly in connection with other fields of chemistry, *e.g.*, the synthesis of organofluorine compounds, *etc.* All of these reviews generalised the literature data published before the early 1990's.

The aim of this review is to systematise, analyse and generalise the literature data concerning the synthesis and chemical properties of xenon derivatives with special emphasis on the chemistry of xenon difluoride and its derivatives.

II. Synthesis and properties of xenon difluoride-based reagents

At present, xenon difluoride is the only commercially available xenon derivative. A characteristic feature of this reagent is that it behaves as a radical fluorinating agent in the gas phase or under irradiation and as an electrophilic agent under other conditions. It is of note that the reactivity of XeF_2 increases dramatically in the presence of Lewis acids, apparently due to ionization of the XeF_2 molecule resulting in the formation of $XeF^+MF_n^-$ or $Xe_2F_3^+MF_n^-$ salts which are both strong oxidants.[35,36]

Some properties of xenon difluoride, *e.g.*, melting point, enthalpy of formation, critical parameters, solubility, maximum permissible concentrations, *etc.*, have been documented in earlier publications.[3,20 – 24,29,30,36 – 39]

V K Brel, N Sh Pirkuliev Institute of Physiologically Active Compounds, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax (7-095) 913 21 13. Tel. (7-095) 913 21 13.
E-mail: brel@ipac.ac.ru (V K Brel).
Tel. (7-095) 939 51 55 (N Sh Pirkuliev)
N S Zefirov Department of Chemistry, M V Lomonosov Moscow State University, Leninskie Gory, 119899 Moscow, Russian Federation.
Fax (7-095) 932 88 46. Tel. (7-095) 939 16 20, (7-095) 524 50 62

Received 5 September 2000
Uspekhi Khimii **70** (3) 262 – 298 (2001); translated by R L Birnova

The methods used for the synthesis of inorganic xenon derivatives can arbitrarily be divided into two main groups, *viz*., reactions of elementary xenon with various oxidising systems and synthesis of fluorinated xenon derivatives directly from xenon and fluorine. Xenon difluoride, -tetrafluoride and -hexafluoride were obtained in good yields by varying xenon and fluorine ratios as well as by selecting appropriate reaction conditions (pressure, temperature).[40–43] A photochemical method was developed in addition to the thermal procedure. Thus UV irradiation of a xenon–fluorine mixture results in xenon fluorides in satisfactory yields.[44–48] By virtue of their simplicity, thermal and photochemical methods are especially popular. These methods allow the synthesis of xenon difluoride with 99% purity. Other fluorinating reagents (with the exception of elementary fluorine) can also be used for the fluorination of elementary xenon. Thus the more readily available and safe ClF_3 was successfully used in the synthesis of large amounts of xenon difluoride,[49] whereas O_2F_2 was used in the synthesis of xenon tetrafluoride and -hexafluoride.[50] Other examples of xenon fluoride synthesis by oxidation of elementary xenon [13–23], *e.g*., irradiation of crystalline xenon by a flux of fluorine atoms, thermocatalytic synthesis,[51,52] γ-irradiation of a fluorine–xenon mixture [53] and electrochemical fluorination, have also been described.[54]

Other xenon halides, *e.g*., xenon chlorides [55,56] and -bromides,[57] are also known, but these compounds are difficult to access due to their low stabilities and are therefore virtually noninvestigated.

Some xenon compounds are synthesised by substitution of ligands for fluorine in the corresponding fluorides. For example, the reaction of xenon fluorides with oxygen-containing substrates yields compounds containing covalent Xe–O or Xe=O bonds.[58] The formation of the Xe=O bond usually occurs upon hydrolysis of xenon fluorides. The hydrolysis of xenon difluoride which gives xenon and hydrogen peroxide has been studied in detail. The Appelman hypothesis [59] about the formation of the oxidising species Xe=O in the first step of hydrolysis was corroborated by other authors.[60–64]

Aqueous solutions of XeF_2 oxidise both inorganic [58–60] and organic compounds.[61–64] The reactions of xenon difluoride with alcohols give reactive alkoxyxenonium fluorides ROXeF which manifest pronounced electrophilic properties (see Section III).

Hydrolysis of xenon hexafluoride by two equivalents of water results in xenon oxytetrafluoride $XeOF_4$ (**1**);[65] the highly explosive xenon trioxide XeO_3 is formed in the presence of excess water, apparently, *via* xenon dioxydifluoride (**2**). Compound **2** reacts with AsF_5 to yield the cation $[XeO_2F]^+$ (compound **3**) or the bridged cationoid structure **4**.[66,67]

$$XeF_6 + 2H_2O \longrightarrow \underset{\mathbf{1}}{XeOF_4} + 2HF$$

$$\underset{\mathbf{2}}{XeO_2F_2} + AsF_5 \xrightarrow{HF} \underset{\mathbf{3}}{[XeO_2F]^+AsF_6^-}$$

$$\underset{\mathbf{2}}{2XeO_2F_2} + AsF_5 \xrightarrow{HF} \underset{\mathbf{4}}{[FO_2XeFXeO_2F]^+AsF_6^-}$$

Xenon oxytetrafluoride $XeOF_4$ (**1**) is formed upon reactions of xenon hexafluoride with SeO_2F_2,[68] $NaNO_3$ [69–71] and TcO_3F.[72] However, these methods have some limitations connected with the use of toxic reagents and the possibility of formation of the explosive xenon trioxide as a by-product. These problems can be overcome by carrying out the reaction with phosphorus oxyfluoride. This reaction proceeds with a nearly quantitative yield; XeO_3 is not formed.[73]

$$XeF_6 + POF_3 \longrightarrow \underset{\mathbf{1}}{XeOF_4} + PF_5$$

Xenon oxytetrafluoride (**1**) can form complexes with alkali metal fluorides [74,75] which are attractive as regards their structural parameters and salts of the $[XeOF_5]Y$ type, *e.g*., where $Y = NO^+$ (see Refs 76–80).

$$XeOF_4 + ONF \longrightarrow NO^+XeOF_5^-$$

Perxenonates pertaining to octavalent xenon derivatives can be obtained by the following scheme:[81]

$$XeF_6 \xrightarrow{HOPOF_2} XeO_3 \xrightarrow{NaOH} Na_4XeO_6 + Xe.$$

Perxenonates are the starting compounds in the preparation of perxenates [82,83] and hydroxenates.[84] Perxenates of virtually all alkali metals,[85] alkaline-earth metals and actinide elements have presently been synthesised.[35] All of them are potent oxidants.[86]

Xenon fluorides react with various oxo acids to give compounds rather stable at low temperatures.[87–95] These reactions have been especially well studied for XeF_2 which forms mono- (**5a–j**) or diesters (**6a–j**) depending on the reagent ratio (Scheme 1).

Scheme 1

$$XeF_2 \xrightarrow[-78\ ^\circ C]{CH_2Cl_2} \begin{cases} \xrightarrow{HOR} \underset{\mathbf{5a-j}}{FXeOR} + HF \\ \xrightarrow{2\,HOR} \underset{\mathbf{6a-j}}{Xe(OR)_2} + 2\,HF \end{cases}$$

Compounds **5** and **6**	R	Ref.
a	OSO_2F	87, 88
b	OSO_2CF_3	89
c	OSO_2Me	89
d	$OCOCF_3$	89–91
e	$OPOF_2$	92
f	$OIOF_4$	93, 94
g	$OClO_3$	87–89
h	$OSeF_5$	95, 96
i	$OTeF_5$	90, 97–99
j	ONO_2	88

The Xe–O bond can also be formed through insertion of XeF_2 into the E=O bond. This approach was used in the reaction of XeF_2 with SO_3 [100] and resulted in mono- (**5a**) or difluorosulfate (**6a**) depending on the reagent ratio.

$$XeF_2 \begin{cases} \xrightarrow{SO_3} \underset{\mathbf{5a}}{FXeOSO_2F} \\ \xrightarrow{2\,SO_3} \underset{\mathbf{6a}}{Xe(OSO_2F)_2} \end{cases}$$

XeF_2 or the monoesters **5a**,**f** react with iodine trifluorodioxide analogously.[94]

$$XeF_2 + IO_2F_3 \xrightarrow[BrF_5 \text{ or } CFCl_3]{SO_2ClF} \underset{\mathbf{5f}}{FXeOIOF_4}$$

$$\underset{\mathbf{5a,f}}{FXeR} + IO_2F_3 \xrightarrow[BrF_5 \text{ or } CFCl_3]{SO_2ClF} \underset{\mathbf{6f,k}}{RXeOIOF_4}$$

R = OSO_2F (**5a**, **6k**), $OIOF_4$ (**5f**, **6f**).

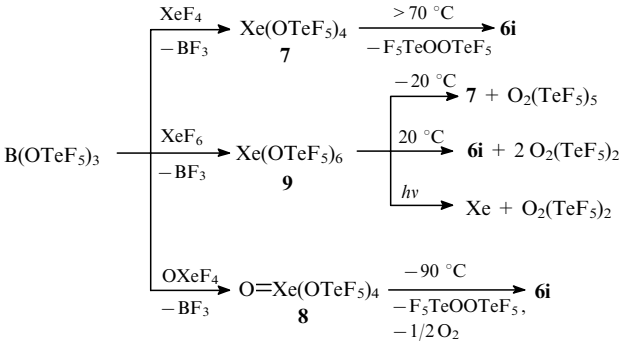
Exchange of ligands (other than fluorine) at the xenon atom is also possible, although this reaction has not been well studied yet.[94]

$$\underset{\mathbf{6i}}{Xe(OTeF_5)_2} + 2\,HOIOF_4 \xrightarrow{CFCl_3} \underset{\mathbf{6f}}{Xe(OIOF_4)_2} + 2\,HOTeF_5$$

In some cases, synthesis of bivalent xenon derivatives is accompanied by the formation of undesirable side products directly from acids and XeF_2. Hydrogen fluoride liberated can be bound by $(Me_3Si)_2NH$ or its formation can be prevented by boric anhydrides of the type $B(OR)_3$ (R = SO_2CF_3, $C(O)CF_3$).[101]

$$XeF_2 \begin{cases} \xrightarrow{B(OSO_2CF_3)_3} \underset{\mathbf{5b}}{FXeOSO_2CF_3} \\ \xrightarrow{2/3B(OC(O)CF_3)_3} \underset{\mathbf{6d}}{Xe(OCOCF_3)_2} + BF_3 \end{cases}$$

The ligands $OTeF_5$ and $OSeF_5$ manifesting pronounced electron-withdrawing properties and maximum stabilising effect in comparison with other known oxygen ligands are the most suitable for the synthesis of tetra- and hexavalent xenon derivatives containing covalent Xe–O bonds.[102,103] The Xe(IV) **7**[104–108] and Xe(VI) **8** and **9**[106–109] derivatives were obtained using $OTeF_5$ as the ligand.



The synthesis of bis(pentafluorotellurium) xenonate (**10**) and tetrakis(pentafluorotellurium) xenonate (**8**) made use of the corresponding boric anhydride.[110]

$$3XeO_2F_2 + 2B(OTeF_5)_3 \longrightarrow \underset{\mathbf{10}}{3(F_5TeO)_2XeO_2} + 2BF_3$$
$$\mathbf{2}$$

$$3XeOF_4 + 4B(OTeF_5)_3 \longrightarrow \underset{\mathbf{8}}{3OXe(OTeF_5)_4} + 4BF_3$$

The reaction of xenon with O_2BF_4 results in the evolution of O_2 and F_2 and the formation of white crystals with the composition $FXeBF_2$ (see Ref. 11). This is the only currently known compound containing a Xe–B bond. At 243 K, it decomposes to yield an equimolar mixture of Xe and BF_3.

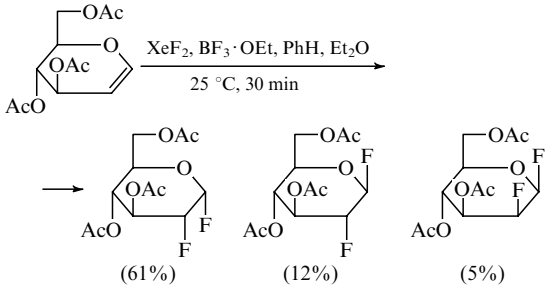
$$Xe + O_2BF_4 \longrightarrow FXeBF_2 + O_2 + F_2$$

III. Reactions of xenon difluoride and its derivatives with unsaturated compounds

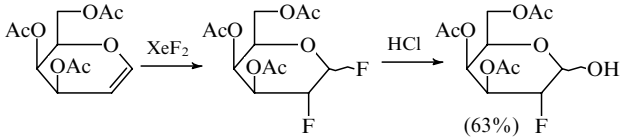
Reactions of XeF_2 with alkenes, alkynes and dienes have been described in detail in reviews.[20,30–33] In the general case, XeF_2 reacts with ethylene and terminal alkenes to afford mixtures of the addition products to the double bond and of the substitution products of fluorine for an alkene hydrogen atom.[111–113] This reaction occurs more selectively in the presence of HF, *viz.*, the addition products to the double bond are formed in up to 95% yields.[114–119] In addition to fluorine derivatives, the reaction of alkenes with XeF_2 in CF_3CO_2H also gives the corresponding trifluoroacetates.[120] 1-Phenyl-substituted cycloalkenes react with XeF_2 in the presence of HF to give a mixture of *cis*- and *trans*-difluorides (in up to 90% yields); the isomer ratio depends on the ring size.[121,122] Fluorohalogenation of the substrate occurs in the presence of a chlorine or a bromine source.[122] The reaction of XeF_2 with acenaphthylene, indene, 1,2- and 1,4-dihydronaphthalenes,[123,124] norbornene[125–130] and norbornadiene[125,130,131] results in the corresponding difluorides. The reaction of aliphatic 1,3-dienes with XeF_2 in the presence of $BF_3 \cdot Et_2O$ gives 1,2-addition products (75%–100%).[132] The reaction of enols with XeF_2 results in α-fluorocarbonyl compounds.[133–140] The reaction of diphenylacetylene with XeF_2 catalysed by trace amounts of HF gives 1,2-diphenyltetrafluoroethane in 50% yield.[141]

The fluorination of acetyl derivatives of D-fucal, D-glucal and D-galactal by XeF_2 has been described.[142–144]

Thus tri-*O*-acetyl-D-glucal reacts with XeF_2 in the presence of $BF_3 \cdot OEt_2$ to give a mixture of 2-fluoroglycosyl fluorides.[142]



The fluorination of tri-*O*-acetyl-D-galactal by XeF_2 in $CFCl_3$ and subsequent hydrolysis of the reaction product with hydrochloric acid affords 2-deoxy-2-fluoro-D-galactose.[144]



A versatile procedure for chemical doping of π-conjugated polymers, *e.g.*, polyacetylene and poly(*p*-phenylene), has been developed which allows introduction of various anions (A^-) into the polymer. The polymer is treated with xenon difluoride used as the oxidant and the corresponding acid, *e.g.*, HA ($XeF_2 : HA = 1 : 2$) in liquid HF or CH_2Cl_2.[145] Such a modification of polymers is not accompanied by incidental formation of degradation or fluorination products.

$$P + 1/2n\,XeF_2 + 1/n\,HA \longrightarrow P^{n+}(A^-)_n + 1/2n\,Xe + 1/n\,H$$

where P is the elementary unit of the polymer (CH or C_6H_4), *n* is the degree of doping, A = BF_4, AsF_6, SbF_6, OSO_2F, OSO_2Me or $OCOCF_3$.

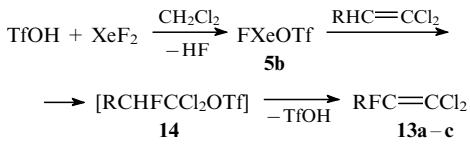
The degree of doping of the polymers under study by the XeF_2–2HA system increases with increase in the reaction time and the reagent : polymer molar ratio. The doping ability of anions decreases in the following order: $SbF_6^- > AsF_6^- \geqslant BF_4^- \geqslant OSO_2F^- > OSO_2Me^- > OCOCF_3^-$, which correlates with the order of the relative withdrawing capacity of the corresponding acids in reactions with XeF_2.[22] The maximum degree of doping of poly(*p*-phenylene) (0.97) is achieved with the anion SbF_6^-. This is probably due to the generation of the active species XeF^+ [its electron affinity is 10.4 eV (see Ref. 3)] as a result of complete ionisation of the XeF_2–2HA complex and the formation of $XeF^+SbF_6^-$ (see Ref. 146). It should be noted that the oxidising system XeF_2–2 HA allows variations of the anion A in a broad range, which makes this system superior to oxidants of the AsF_5 and I_2 type.[145]

Reactions of alkenes of different structures with other xenon derivatives including fluoroxenon triflate (**5b**), fluorosulfate (**5a**) and nitrate (**5j**), have been studied.[147–150] These reagents appeared to be more reactive than XeF_2. Xenon bis(fluorosulfate) (**6a**) reacts explosively with ordinary unsaturated hydrocarbons even at low temperatures. On the other hand, electron-deficient alkenes (**11**) yield covalent bis(fluorosulfonates) **12**.[149]

$$\underset{\mathbf{11}}{Cl(R)C{=}C(R)Cl} + \underset{\mathbf{6a}}{Xe(OSO_2F)_2} \xrightarrow[-Xe]{\text{Freon 113, } -10\ ^\circ C} \longrightarrow \underset{\mathbf{12}}{(FSO_2O)Cl(R)CC(R)Cl(OSO_2F)}$$

R = H, Cl, F.

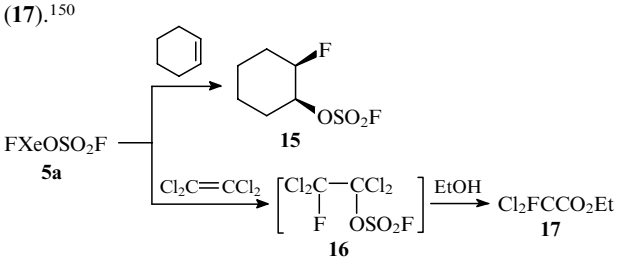
A one-step procedure for the preparation of fluorohalogenoalkenes using the reagent **5b** has recently been proposed.[151] Thus mixing of equimolar amounts of XeF_2 and CF_3CO_2H in anhydrous CH_2Cl_2 and subsequent addition of 1,1-dichloroalkene results in fluorodichloroalkenes **13a–c**, *viz.*, the products of formal substitution of fluorine for the vinylic hydrogen atom.[151] This approach is an alternative to the Swarts fluorination.[152]



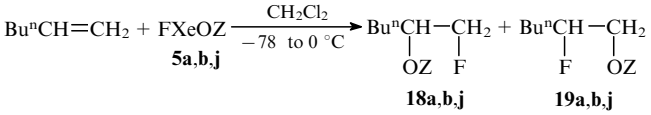
Tf = CF_3SO_2; R = H (**13a**, 65%), Me (**13b**, 66%), Et (**13c**, 63%).

The addition of the reagent **5b** follows the Markownikoff rule and yields the adducts **14**. Spontaneous elimination of trifluoromethanesulfonic acid from the adducts **14** can be attributed to the fact that the easily leaving triflate group and two electronegative chlorine atoms are localised at the same carbon atom.

cis-β-Fluorocyclohexyl fluorosulfate (**15**) was obtained as the main product in 50% yield in the reaction of xenon fluorosulfonate fluoride (**5a**) with cyclohexene; the reaction with tetrachloroethylene gave the adduct **16**, which was unstable at room temperature and could be identified as ethyl dichlorofluoroacetate (**17**).[150]

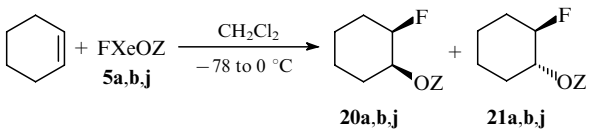


The reactions of compounds **5a**,**b**,**j** with hex-1-ene result in β-fluoroalkyl sulfonates or nitrates **18** and **19** with the predominance of the Markownikoff regioisomers **18a**,**b**,**j**.[148,149]



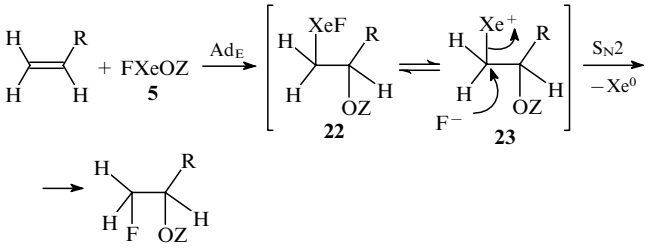
Reagent	Z	Yield (%)	
		18	**19**
5a	SO_2F	34	17
5b	Tf	48	15
5j	NO_2	18	9

Analogous reactions with cyclohexene yield predominantly *cis*-adducts. Thus *cis*-2-fluorocyclohexyl triflate **20b** is exclusively formed in 75% yield when the reagent **5b** is used. The reagent **5a** reacts with cyclohexene to give a mixture of the *cis*- and *trans*-isomers **20a** and **21a** in a 3 : 1 ratio (the total yield is 64%). The reaction of cyclohexene with the reagent **5j** gives a mixture of the isomers **20j** and **21j** in a total yield of 25%.[148,150]



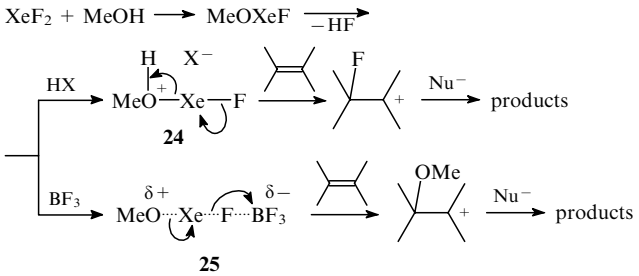
Z = OSO_2F (**a**), OTf (**h**), ONO_2 (**j**).

Earlier, it was assumed[20,30–34] that the addition of the reagents **5a**,**b**,**j** to alkenes occurs by a carbocationic mechanism involving the 'electrophilic' fluorine. However, the selective formation of *cis*-adducts in the reaction with cyclohexene cannot be rationalised within the framework of this mechanism. Based on the fact that the addition of triflates and perchlorates of trivalent iodine to alkenes also results in *cis*-adducts[153–162] and taking into account the isoelectronic nature of I(III) and Xe(II) derivatives, a reaction mechanism was proposed[148] which includes electrophilic addition of the reagents **5** to the double bond and the formation of the intermediate **22**.

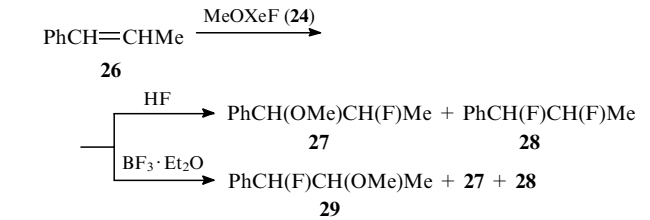


This reaction occurs in a *trans*-selective manner as in the case of trivalent iodine compounds.[153–162] Its second step includes stereospecific nucleophilic substitution of fluorine for xenon by the S_N2 mechanism, which is accompanied by an inversion of configuration and the formation of the *cis*-product.[163] Additional evidence in favour of the intermediate formation of the organoxenon compounds **22** and **23** containing the C–Xe bond in these reactions will be given in Section VI.

The reaction of XeF_2 with alkenes in the presence of aliphatic alcohols has been studied.[164–169] It was shown that methanolysis of XeF_2 yields an unstable electrophilic intermediate with hypothetical composition MeOXeF, which generates a potential electrophilic fluorine donor **24** in the presence of HX. MeOXeF reacts with boron trifluoride to give the positive oxygen electrophile **25**. The reaction of the intermediates **24** or **25** with alkenes results in carbocations containing F or OR in the α-position.[164]



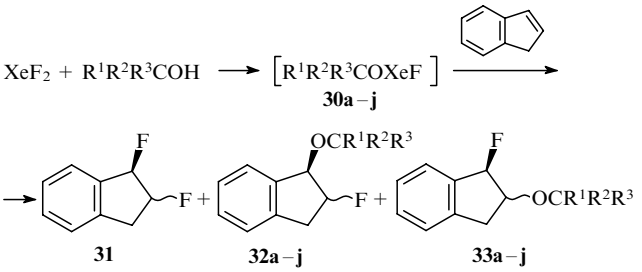
It was found[164] that the reaction of XeF_2 with alkenes in methanol involves MeOXeF rather than MeOF[170] the formation of which requires a stronger oxidant than XeF_2 (*e.g.*, F_2). In the absence of alkenes, MeOXeF disproportionates quantitatively with the formation of HF, Xe and CH_2O. The presence of an acid catalyst strongly affects the regioselectivity of the reaction. In the presence of hydrogen fluoride, MeOXeF reacts with *cis*- and *trans*-1-phenylpropenes **26** to give the final Markownikoff products **27** and **28**, whereas in the presence of BF_3 (in Et_2O or MeOH) the anti-Markownikoff products **29** predominate in the reaction mixture.[164,165]



Catalyst	Yield of **27** (%)		Yield of **28** (%)		Yield of **29** (%)	
	erythro	*threo*	*erythro*	*threo*	*erythro*	*threo*
cis-**26** as the substrate						
HF	0	25	2	73	0	0
$BF_3 \cdot Et_2O$	0	1	3	26	27	43
trans-**26** as the substrate						
HF	0	2	2	96	0	0
$BF_3 \cdot Et_2O$	1	0	3	29	20	47

^1H and ^{13}C NMR spectroscopy and mass spectrometry were used to study the regio- and stereochemistry of reactions of indene

with the unstable intermediates **30a–j** formed upon the reaction of XeF_2 with the corresponding alcohols.[164–166, 169]



31 **32a–j** **33a–j**

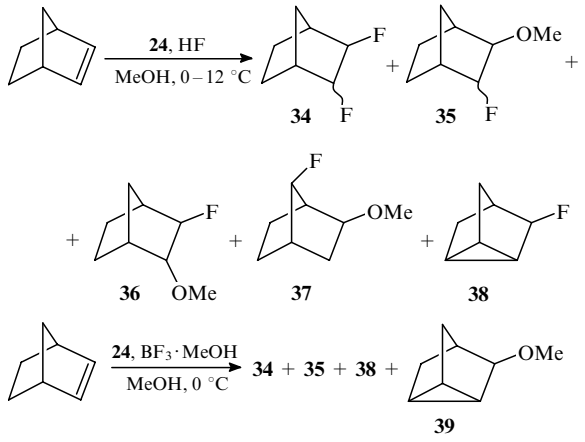
$R^1 = R^2 = R^3 = H$ (**a**); $R^1 = R^2 = Me$, $R^3 = H$ (**b**); $R^1 = R^2 = R^3 = Me$ (**c**); $R^1 = ClCH_2$, $R^2 = R^3 = H$ (**d**); $R^1 = FCH_2$, $R^2 = R^3 = H$ (**e**); $R^1 = CF_3$, $R^2 = R^3 = H$ (**f**); $R^1 = R^2 = R^3 = CF_3$ (**g**); $R^1 = CF(NO_2)_2$, $R^2 = R^3 = H$ (**h**); $R^1 = C(NO_2)_3$, $R^2 = R^3 = H$ (**i**); $R^1 = MeC(NO_2)_2$, $R^2 = R^3 = H$ (**j**).

The reaction with xenon methoxyfluoride (**30a**) in the presence of HF (MeOH, 0–12 °C) gives predominantly a mixture of *cis*- and *trans*-isomers of the methoxy fluoride **32a** (52% and 46%, respectively); the yield of yet another reaction product, *viz*., the difluoride *cis*-**31**, is 2%.

The anti-Markownikoff adducts **33** (26% of the *cis*-isomer and 52% of the *trans*-isomer) are the main products of the reaction carried out in the presence of $BF_3 \cdot Et_2O$ (MeOH, 0 °C).[164, 165]

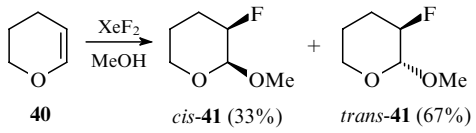
Alkoxyfluorides **32b**,**c** (*cis*- and *trans* isomers) are the main reaction products formed in the presence of protic catalysts (HF generated *in situ*) in Pr^iOH or Bu^tOH. Alkoxy fluorides **33b**,**c** (*cis*- and *trans*-isomers) are formed first in the presence of $BF_3 \cdot OEt_2$. In both cases, *cis*- and *trans*-difluoroindanes **31** are formed as admixtures. Compounds **33b**,**c** rearrange under the reaction conditions into the thermodynamically more stable adducts **32b**,**c**. In the absence of $BF_3 \cdot Et_2O$, the rearrangement occurs more slowly, *viz*., within several days. Reactions with alcohols containing electron-withdrawing substituents occur faster due to their higher acidities. The product yields in CF_3CO_2H decrease owing to the polymerisation of indene.[166, 169]

The nortricyclane derivatives **38** and **39** were also identified in reactions with norbornene along with the isomeric difluorides **34** and the methoxy fluorides **35**, **36** and **37**.[164, 165]



The reaction of 1,3-dimethylbuta-1,3-diene with XeF_2 in methanol in the presence of a catalyst (HF or $BF_3 \cdot MeOH$) affords a mixture of various 1,2- and 1,4-adducts, *viz*., difluorides and methoxy fluorides. The addition occurs both according to the Markownikoff rule and against it.[165]

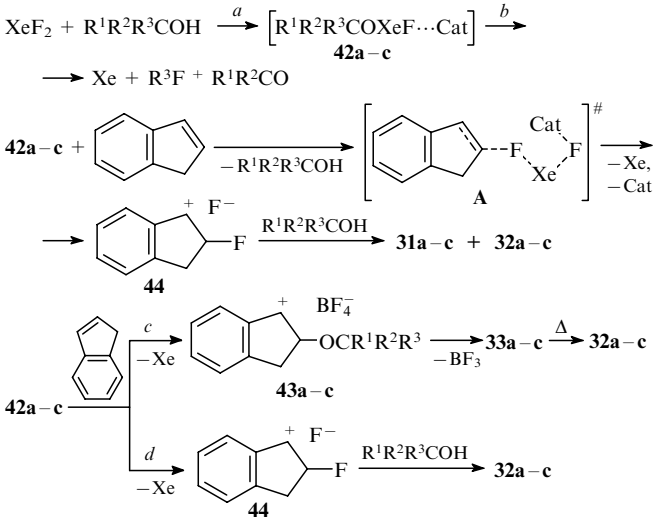
In the absence of a catalyst, dihydropyrane (**40**) reacts with XeF_2 and MeOH to give *cis*- and *trans*-isomers of the adduct **41**.[165]



40 *cis*-**41** (33%) *trans*-**41** (67%)

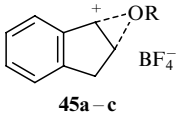
It is of note that hex-1-ene, buta-1,3-diene and methyl crotonate do not react with MeOXeF; in this case, the latter rapidly disproportionates to afford formaldehyde quantitatively.[165]

Shellhamer *et al*.[166] studied the mechanism of the reaction of alkenes with XeF_2 in the presence of alcohols using indene as an example.



(*a*) Cat, slow step; (*b*) fast step; (*c*) BF_3, fast step; (*d*) HF, fast step.

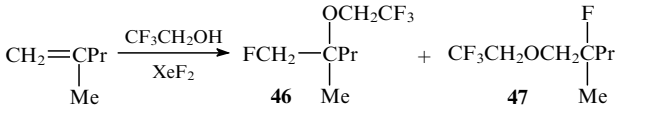
In the absence of alkenes or in the case of their low reactivities, alcohols undergo oxidation into aldehydes or ketones with the concomitant formation of alkyl fluorides and evolution of elementary xenon (routes *a* and *b*). It is believed that the complexes **42a–c** of xenon alkoxy fluorides **30a–c** with the catalyst are the intermediate products of this reaction. The intermediates **42a–c** are trapped by highly reactive alkenes (*e.g*., indene) to give complexes **A**; further conversions depend on the nature of the alcohol and the catalyst. In the presence of BF_3, xenon alkoxy fluorides **30a–c** react with indene as positive oxygen electrophiles to give, after elimination of xenon, 2-alkoxyindan-1-ylium tetrafluoroborates (**43a–c**). Their stabilisation is accompanied by the liberation of BF_3 and the formation of compounds **33a–c** (route *c*). The latter rearrange into more stable isomers **32a–c**. The intermediates **42a–c** act as electrophilic fluorine donors in the reaction with protic catalysts (HF); after the intermediate 2-fluoroindan-1-ylium fluoride **44** has been formed, they give compounds **32a–c** (route *d*).[166] The dependence of the direction of the reaction on the nature of the alcohols used (*e.g*., their acidity) is explained in the following way. In the presence of alkoxy substituents containing electron-withdrawing groups (CF_3CH_2, CF_3) in the intermediates **42**, they react as open ions (route *d*), whereas in the presence of electron-donor groups in alkoxy substituents they react with indene to afford the soft bridged intermediates **45a–c**. The reaction of these intermediates with the tetrafluoroborate anion results in the predominant formation of the *trans*-adducts **33a–c** which are transformed into compounds **32a–c** under the reaction conditions.[166]



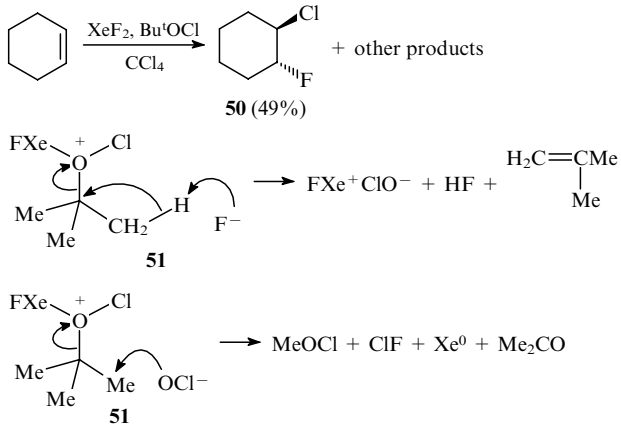
45a–c

R = Me (**a**), Pr^i (**b**), Bu^t (**c**).

The reaction of 2-methylpent-1-ene with XeF_2 in CF_3CH_2OH at 0–25 °C yields the alkoxy fluorides **46** (route *c*) and **47** (route *d*) in a total yield of 76% and in a *ca.* 1 : 1 ratio (these compounds were isolated by preparative GLC). Only the difluorides **48** and **49** could be prepared from hex-1-ene under analogous conditions, which corresponds to direct fluorination (route *d*).



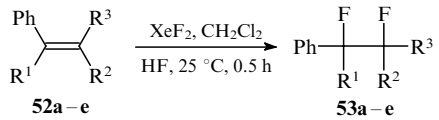
tert-Butyl hypochlorite and XeF_2 react with cyclohexene in CCl_4 to give a complex mixture of compounds with *trans*-1-chloro-2-fluorocyclohexane (**50**) as the main product.[171]



In this case, the lack of selectivity is attributed[171] to the formation of an intermediate complex of xenon fluoride with Bu^{t}OCl (**51**), which generates various reactive species upon decomposition. It should be noted that *tert*-butyl hypochlorite and XeF_2 do not react with cyclohexene when used separately.[171]

This reaction was extended to other hypohalites (MeOX, Bu^{t}OX, where X = Cl, Br).[171,172] It is assumed that the reaction of hypohalites with XeF_2 gives the corresponding interhalides HalX (Hal = Br, Cl), which are weaker electrophilic reagents than Cl_2 or BrCl. Therefore, they react more selectively with electron-enriched unsaturated and aromatic compounds to give the corresponding difluorides in high yields. Cyclohexene, methylenecyclohexane, hex-1-ene, hept-1-ene, hex-3-yne, 3,4-dihydro-2*H*-pyran, anisole, *etc*., were used as substrates.[171,172]

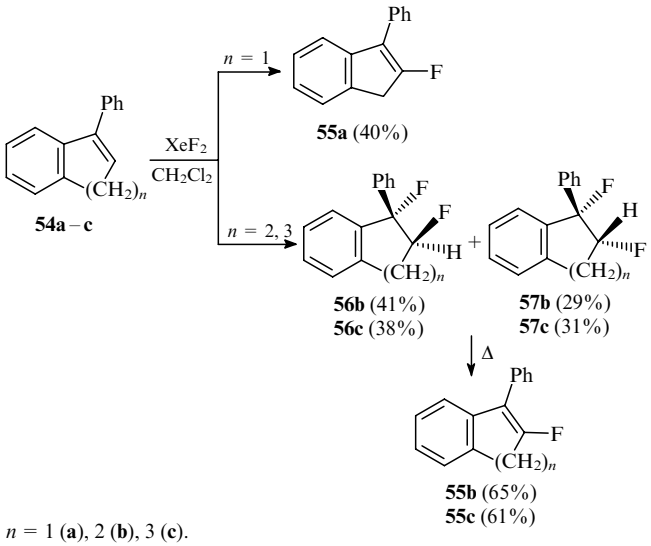
The fluorination of the phenyl-substituted alkenes **52a–e** with XeF_2 in the presence of 0.1–0.2 equiv. of anhydrous HF results in the difluorides **53a–e**.[173]



52a–e **53a–e**

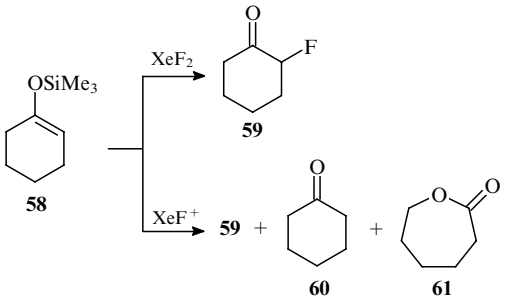
$R^1 = R^2 = R^3 = H$ (**a**); R^1 = Me, $R^2 = R^3 = H$ (**b**); R^2 = Me, $R^1 = R^3 = H$ (**c**); R^1 = Ph, $R^2 = R^3 = H$ (**d**); R^1 = Ph, R^2 = Me, $R^3 = H$ (**e**).

The reaction of XeF_2 with 3-phenyl-1*H*-indene (**54a**) affords 3-phenyl-2-fluoro-1*H*-indene (**55a**) as a result of addition–elimination. The fluorination of 4-phenyl-1,2-dihydronaphthalene (**54b**) and 9-phenyl-6,7-dihydro-5*H*-benzocycloheptene (**54c**) by XeF_2 yields diastereomeric pairs of the vicinal difluorides **56a**,**b** and **57a**,**b**. They are unstable on heating and eliminate HF at 200 °C, being converted into 3-fluoro-4-phenyl-1,2-dihydronaphthalene (**55b**) and 8-fluoro-9-phenyl-6,7-dihydro-5*H*-benzocycloheptene (**55c**).[173]



n = 1 (**a**), 2 (**b**), 3 (**c**).

The reaction of enol trimethylsilyl ethers with XeF_2 has recently been studied.[174] Thus 1-trimethylsilyloxycyclohexene (**58**) reacts with XeF_2 to give α-fluorocyclohexanone (**59**) in a quantitative yield. In the case of XeF^+, this reaction gives a mixture of three products (**59**–**61**); their formation is interpreted in terms of a single-electron transfer mechanism.[174]



IV. Reactions of xenon derivatives with aromatic and polyfluoroaromatic compounds

Xenon difluoride is a convenient fluorinating agent for the preparation of fluorine-containing mono- and polycyclic aromatic compounds. The reaction of aromatic and polyfluoroaromatic hydrocarbons with XeF_2 has been described in detail in reviews,[20,30–33] therefore, in Table 1 we shall cite only the most common reactions. Special attention will be given only to those papers which have not been surveyed in the literature.

Several papers are devoted to the reactions of functional derivatives of aromatic hydrocarbons with XeF_2. Thus the reaction of XeF_2 with anisole and 1,2-dimethoxybenzene gives 4-fluoroanisole and 4-fluoro-1,2-dimethoxybenzene (yields 72% and 37%, respectively).[198] The reaction of phenol with XeF_2 in CH_2Cl_2 yields a mixture or isomeric fluorophenols (47%);[198] in water, phenol is oxidised into *p*-benzoquinone.[63,199,200] Hydroquinone and 4-*tert*-butylcatechol are oxidised by XeF_2 into benzoquinone derivatives,[201] whereas catechol affords 4-fluorocatechol in 38% yield.[198] The initially proposed structure of the reaction product of pentafluorophenol with XeF_2 ($C_6F_5OOC_6F_5$)[202] was later refuted;[203] it was shown that this reaction yielded perfluoro-4-phenoxycyclohexa-2,5-dienone and perfluorocyclohexa-2,5-dienone. The reaction of (perfluoroaryl)-trimethylsilanes (Ar_F = C_6F_5, 4-$CF_3C_6H_4$, 4-C_5F_4N) with XeF_2 results in desilylation and formation of perfluorobiaryls.[204,205]

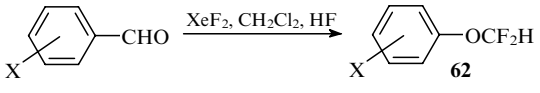
The fluorination of the aromatic nucleus of L-3-methoxy-4-hydroxyphenylalanine[206,207] used in the synthesis of L-6-fluorodihydroxyphenylalanine-[^{18}F] occurs smoothly.[207]

Table 1. The reaction products of aromatic compounds with xenon difluoride.

Starting compound	T/°C	Solvent	Catalyst	Reaction products	Yield (%)	Ref.
PhH	165			mixture of mono-, di and trifluorobenzenes		175
	145			the same		175
	25	CCl_4	HF	C_6H_5F	68	176–178
PhMe	25	CCl_4	HF	C_6H_4FMe (mixture of *o*-, *m*- and *p*-isomers)	32	177, 179, 180
PhCl	25	CCl_4	HF	C_6H_4FCl (mixture of *o*-, *m*- and *p*-isomers)	65	177, 179, 180
PhF	25	CCl_4	HF	$C_6H_4F_2$ (mixture of *o*-, *m*- and *p*-isomers)	47	177, 179, 180
$PhCF_3$	25	CCl_4	HF	$C_6H_4FCF_3$ (mixture of *o*-, *m*- and *p*-isomers)	75	177, 179, 180
PhOMe	20	CCl_4	HF	$C_6H_4(OMe)F$ (mixture of *o*-, *m*- and *p*-isomers)	65	177, 179, 180
$PhNO_2$	120			mixture of *o*-, *m*- and *p*-nitrofluorobenzenes		175
	167			the same	81	177, 179, 180
1,4-$F_2C_6H_4$	100			1,2,4-$C_6H_3F_3$: 1,2,4,5-$C_6H_2F_4$ = 8 : 1		175
1,2-$F_2C_6H_4$	100			1,2,4-$C_6H_3F_3$: 1,2,4,5-$C_6H_2F_4$ = 42 : 1		175
1,2,3-$C_6H_3Me_3$	25	CH_2Cl_2	HF	1,4-F_2-3,4,5-C_6HMe_3 : 1-F-2,3,4-$C_6H_2Me_3$ = 1 : 2	38	181
C_6Me_6	25	CH_2Cl_2	HF	$C_6Me_5CH_2F$	72	182
	25	CH_2Cl_2	CF_3CO_2H	$C_6Me_5CH_2OCOCF_3$	68	182
Indan	25	CH_2Cl_2	HF	5-fluoroindan	60	183
5-Fluoroindan	25	CH_2Cl_2	HF	5,6-difluorindan	62	183
Tetralin	25	CH_2Cl_2	HF	5-fluorotetralin,	30	183
				6-fluorotetralin	70	
9,10-Dihydro-anthracene	25	CH_2Cl_2	HF	1-fluoro-9,10-dihydroanthracene,	9	184
				3-fluoro-9,10-dihydroanthracene	21	
Acenaphthene	25	CH_2Cl_2	HF	3-fluoroacenaphthene,	50	184
				5-fluoroacenaphthene	20	
Trypticene	25	CH_2Cl_2	HF	1-fluorotrypticene,	12	184
				2-fluorotrypticene	23	
Naphthalene	−78 – 20 [a]	CH_2Cl_2		1-fluoronaphthalene,	50	185
				2-fluoronaphthalene	11	
		CH_2Cl_2		mixture of 1-fluoro, 2-fluoro- and 1,4-difluoronaphthalenes	75	186
Anthracene	−12 – 12 [a]	CH_2Cl_2		9-fluoroanthracene,	26	185
				1-fluoroanthracene,	45	
				2-fluoroanthracene	9	
Phenanthrene	−78 – 20 [b]	CH_2Cl_2		9-fluorophenanthrene	33–40	185, 187
	25	CH_2Cl_2	HF	mixture of mono-, di-, tri- and tetrafluoro-phenanthrenes	79	188
Pyrene	−125 to −78 [b]	CH_2Cl_2		mixture of monofluoropyrenes	52	189
Benzo[*a*]pyrene	−78 to −45	CH_2Cl_2		6-fluorobenzo[*a*]pyrene	26	190
Perylene	25	C_6F_{12}		difluoroperylene,	10	191
				3-fluoroperylene	30	
1-XC_6F_5 (X = F, H, Cl, Br, C_6F_5)	20	CH_2Cl_2	BF_3	1-X-heptafluorocyclohexa-1,4-dienes	> 80	192
C_6F_5Cl	25	CH_2Cl_2	BF_3	1-chloroheptafluorocyclohexa-1,4-diene	83	193
C_6F_5Br	25	CH_2Cl_2	BF_3	1-bromoheptafluorocyclohexa-1,4-diene	81	193
Decafluorobiphenyl	25	CH_2Cl_2	BF_3	1-(pentafluorophenyl)heptafluorocyclohexa-1,4-diene	73	193
C_6F_5H	25	CH_2Cl_2	BF_3	1,2,3,3,4,6,6-heptafluorocyclohexa-1,4-diene	75	193
C_6F_6	25	CH_2Cl_2	BF_3	octafluorocyclohexa-1,4-diene	74	193
	20	CH_2Cl_2	HF	the same	40	194
Octafluoro-naphthalene	20	CH_2Cl_2	HF	perfluoro-1,4-dihydronaphthalene,	42	194–196
				perfluoro-1,2-dihydronaphthalene	4	
2-Methoxyhepta-fluoronaphthalene	25	CH_2Cl_2	BF_3	2-methoxynonafluoro-1,4-dihydronaphthalene	35	197
2-Ethoxyheptafluoro-naphthalene	25	CH_2Cl_2	BF_3	2-ethoxynonafluoro-1,4-dihydronaphthalene	40	197

[a] At 10^{-6} mm Hg; [b] at 10^{-5} mm Hg.

Aromatic aldehydes react with XeF_2 in CH_2Cl_2 in the presence of HF to give the ethers **62** in 67%–86% yields, the maximum yields being achieved with 4–5 equiv. of HF.[208, 209]

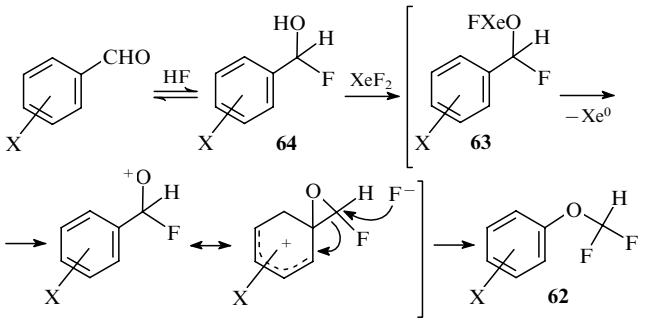


62

X = H, 4-Me, 4-Cl, 4-OMe, 4-OC_5H_{11}, 4-CO_2H, 4-CO_2Me, 2-NO_2, 3-NO_2, 4-NO_2, Ts.

The difluoromethoxylation of aromatic aldehydes carrying electron-donor substituents, such as acetamido- and methoxy groups, is accompanied by fluorination of the aromatic ring.[208]

The difluoromethyl ethers **62** are formed as a result of rearrangement which probably occurs *via* the intermediates **63** in the reaction of the fluorohydrins **64** with XeF_2.[208]



The aryl ketones **65** and **66a–c** react with XeF_2 in a similar way to give the fluorinated phenol ethers **67** and **68a–c** in low yields with considerable recovery of the starting compounds.[141,210,211]

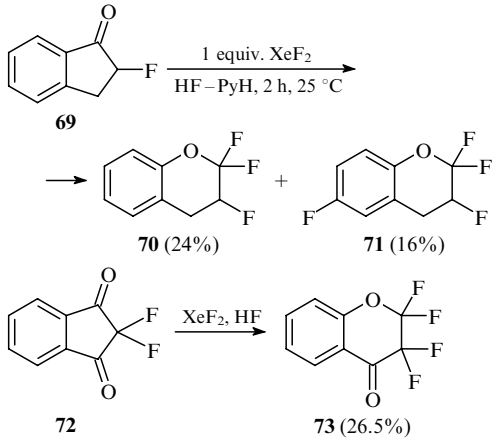
$$\underset{\mathbf{65}}{ArCOCH_2X} \xrightarrow[24\ h,\ 25\ ^\circ C]{1\ equiv.\ XeF_2,\ HF,\ CH_2Cl_2} \underset{\mathbf{67}}{ArOCF_2CH_2X}$$

Ar = Ph, C_6F_5, 2-$NO_2C_6H_4$; X = H, F.

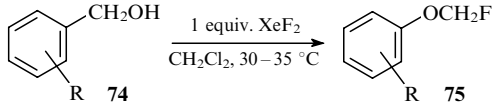
$$\underset{\mathbf{66a-c}}{Ar^1COAr^2} \xrightarrow[24\ h,\ 25\ ^\circ C]{1\ equiv.\ XeF_2,\ HF,\ CH_2Cl_2} \underset{\mathbf{68a-c}}{Ar^1OCF_2Ar^2}$$

$Ar^1 = Ar^2$ = Ph (**a**); Ar^1 = Ph, Ar^2 = 4-$NO_2C_6H_4$ (**b**);
$Ar^1 = Ar^2 = C_6F_5$ (**c**).

2-Fluoroindan-1-one (**69**) reacts with 1 equiv. of XeF_2 in HF–Py to give 2,2,3-trifluoro-3,4-dihydro-2*H*-benzo[*b*]pyran (**70**) and 2,2,3,6-tetrafluoro-3,4-dihydro-2*H*-benzo[*b*]pyran (**71**) as the main products.[210] 2,2-Difluoroindanedione **72** yields tetrafluorobenzopyrone **73** with XeF_2 in the presence of HF.

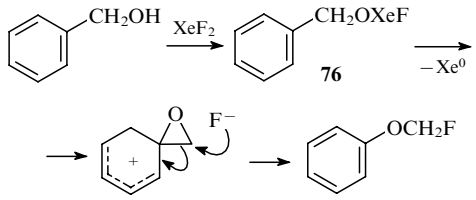


The reactions of the benzyl alcohols **74** with XeF_2 afforded the aryl fluoromethyl ethers **75** in high yields.[212] The yield of the main product increases in the presence of electron-withdrawing substituents, *e.g.*, for R = 3-NO_2, it reaches 85%. Fluorinated ethers are not formed if benzyl alcohols contain hydroxy-, alkoxy- or alkylamino groups.[212]

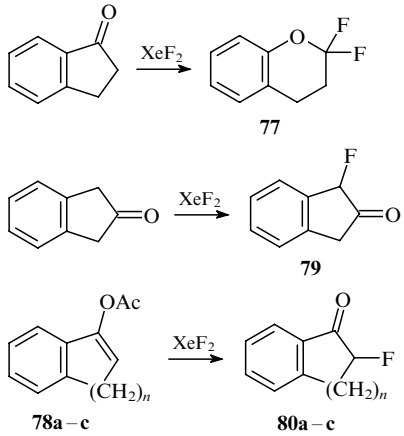


R = H, 2-NO_2, 3-NO_2, 4-NO_2, 4-Me, 3-F.

Presumably, this reaction occurs *via* the intermediate **76** and according to the same mechanism as does the synthesis of the difluoromethyl ethers **62** from aldehydes. The reaction is probably catalysed by HF; therefore, on the whole, it represents an autocatalytic process.[212]

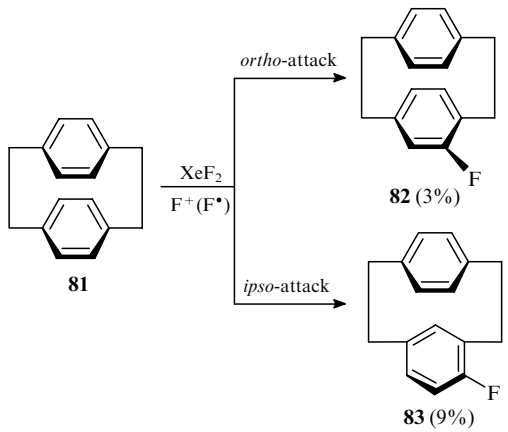


The reaction of indan-1-one with XeF_2 is accompanied by ring expansion resulting in the difluoro-substituted dihydrobenzopyran **77**. The α-fluoroketones **79** and **80a–c** are formed in the reaction of indan-2-one and the enol acetates **78a–c** with XeF_2. The fluorination products of the aromatic ring have not been found in either case.[211]



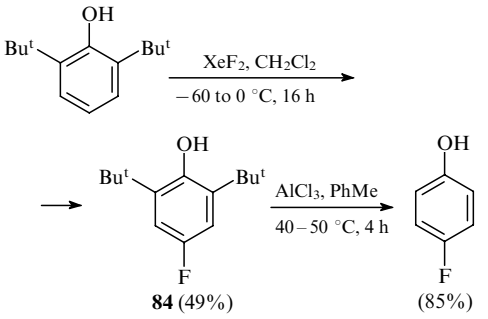
n = 1 (**a**), 2 (**b**), 3 (**c**).

The [2.2]metaparacyclophane system contains two types of aromatic rings, *viz.*, *para*- and *meta*-substituted ones. Reutov *et al.*[213] proposed a method for selective introduction of functional groups into this compound based on the use of XeF_2. It was shown that two cyclophane derivatives (**82** and **83**) containing a fluorine atom in the *para*- and *meta*-substituted benzene rings are formed from non-substituted [2.2]paracyclophane (**81**) after addition of an equimolar amount of XeF_2. Mixing of the reaction components in a Teflon vessel with CH_2Cl_2 did not result in any reaction between them, at least within one hour. The reaction could be initiated only after addition of an equimolar amount of CF_3CO_2H.



As mentioned above, the reaction of phenol with XeF_2 is nonselective.[198] 4-Fluorophenol was obtained from 2,6-di-*tert*-butylphenol in high yield using a two-step synthesis, *viz.*, fluorination by XeF_2 at low temperatures and subsequent treatment of the monofluoride **84** with $AlCl_3$ resulting in the elimination of

isobutylene and the formation of *p*-fluorophenol.[214] It is of note that fluorination of phenols can also be achieved through the use of *N*-fluoropyridinium triflate.[215, 216]



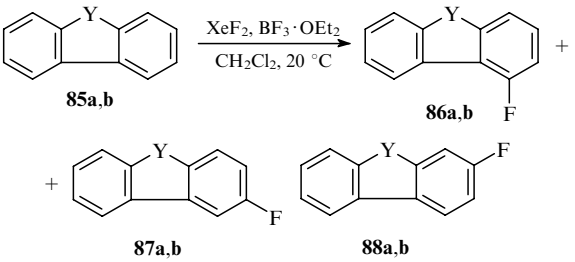
84 (49%) (85%)

It is known [217] that XeO_3 and XeF_2 decompose in the presence of water to form a vast array of products, *e.g.*, HO$^{\bullet}$ radicals, hydrogen peroxide, molecular oxygen, XeO and the superoxide ion. It can be assumed that these products will effectively hydroxylate arenes. Indeed, heating or irradiation of a XeO_3 solution with a high-pressure mercury lamp at 20 °C in aqueous acetonitrile in the presence of benzene results in hydroxylation of the latter. The induction period of this reaction can be significantly reduced by addition of a catalytic amount of CrO_3.[218, 219] Xenon difluoride in aqueous acetonitrile is a more efficient hydroxylating reagent. In this case, the induction period is small, the initial rate of the reaction and the yield of phenol being strongly dependent on the concentration of water in the solution. HOXeF is a likely intermediate.[219]

Ethylbenzene is slowly oxidised by XeO_3 to acetophenone in the presence of the tetraphenylporphyrin manganese complex (TPP)MnOAc (TPP is tetraphenylporphyrin) in aqueous acetone. In this case, XeO_3 acts as an oxygen donor and is transferred by the metal-porphyrin catalyst to the substrate containing C–H bonds.[218]

A method for iodination of aromatic compounds by a mixture of XeF_2 with iodine or *N*-iodosuccinimide has recently been described.[172, 220] It is noteworthy that the same mixture was used for iodofluorination of alkenes. The IF generated from xenon difluoride is less reactive than that synthesised from I_2 and F_2. Presumably, in this case we deal with the reaction of an IF–XeF_2 complex with alkenes and aromatic compounds.[206]

The reaction of fluorene (**85a**) or dibenzofuran (**85b**) with XeF_2 in the presence of $BF_3 \cdot OEt_2$ gives a mixture of the monofluorides **86a**,**b**–**88a**,**b**.[221]



Y = CH_2 (**a**), O (**b**).

The reaction of XeF_2 with 1-R-2,3,4,5-tetrafluorobenzene (R = H, F, Br, NO_2) or 1-R-2,3,4,6-tetrafluorobenzene (R = H, CF_3) in HF or CH_2Cl_2–$BF_3 \cdot OEt_2$ results in the substitution of F for the hydrogen atom in the aromatic ring.[222] Only the addition reaction occurs in 1-R-2,3,5,6- (R = H, Br, CF_3) or 1-bromo-2,3,4,6-tetrafluorobenzenes under these conditions. The role of radical cations as intermediate compounds has been discussed.[222]

V. Reactions of xenon difluoride with organic acids and their derivatives

Earlier, it was shown (see Section II) that the reaction of XeF_2 with protic oxygen-containing acids gives unstable compounds of the FXeOR and $Xe(OR)_2$ types, which manifest strong electrophilic properties with respect to unsaturated and aromatic compounds. The reaction of benzoic acid with XeF_2 in an excess of benzene which gives phenyl benzoate in up to 70% yield is an example.[223, 224]

$$PhCO_2H + PhH + XeF_2 \longrightarrow PhCO_2Ph + 2\,HF + Xe$$

Biphenyl (1%–5%) is formed along with phenyl benzoate. Kinetic studies have shown that this reaction occurs *via* the formation of $PhCO_2XeF$ or $(PhCO_2)_2Xe$ with their subsequent reactions with benzene.[224]

For different benzoic acid derivatives, the yields of phenyl esters depend essentially on the structure of the original acid.[225] In the case of *p*-fluorobenzoic acid, the yield of the corresponding phenyl ester reached 68%, whereas for *o*-toluic acid it was as small as 3%, which can be due to steric hindrances preventing the formation of the intermediate compound.

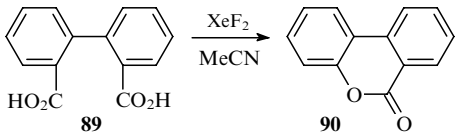
$$RC_6H_4CO_2H + XeF_2 \longrightarrow RC_6H_4CO_2XeF + HF$$

$$RC_6H_4CO_2XeF + PhH \longrightarrow RC_6H_4CO_2Ph + HF + Xe$$

R = H, 2-NO_2, 3-NO_2, 4-NO_2, 2-Me, 3-Me, 4-Me, 4-Br, 4-F, 4-Cl.

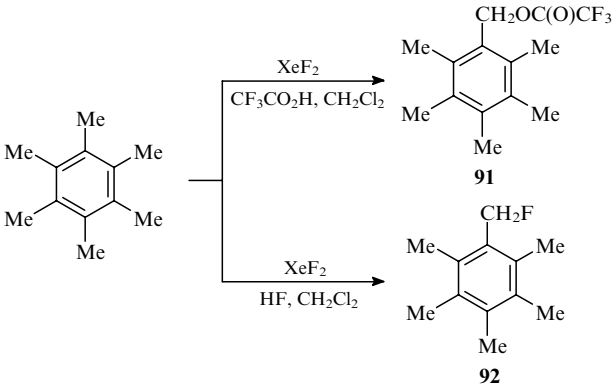
The possibility of incorporation of benzoyloxy groups into toluene, fluoro-, chloro-, bromo- and nitrobenzene using the XeF_2–$PhCO_2H$ system has been studied.[226] The kinetic data and the isomeric composition of the reaction products suggest that the benzoyloxy group is introduced into *o*- and *p*-positions of toluene, chloro- and bromobenzene. The nitro group deactivates the nucleus so that no esters are formed. The relative rates of acyloxylation of benzene derivatives in the presence of XeF_2 decrease in the following order: $MeC_6H_5 > ClC_6H_5 > BrC_6H_5 > NO_2C_6H_5$. The experimental data suggest the electrophilic type of this reaction. The electrophilic reagent PhCOOXeF is deficient of electrons on the xenon atom and therefore attacks the positions with increased electron density in substituted benzenes.[226] Kinetic studies of the reaction of benzene with Ph[^{14}C]OOH revealed that benzoic acid is involved in the formation of phenyl benzoate and is not decarboxylated with the liberation of radiolabelled carbon dioxide.[227]

Aromatic dicarboxylic acids can be dehydrated by XeF_2 or undergo more profound conversions. The reaction of phthalic acid with XeF_2 (1 : 2) results in phthalic anhydride in 26% yield. Under the same conditions, 2,2′-diphenic acid (**89**) generates 3,4-benzocoumarin (**90**) in 30% yield along with a small amount of the anhydride.[228] The formation of compound **90** is due to partial decarboxylation of the intermediate with subsequent intramolecular acyloxylation.



89 **90**

The reaction of fluoroxenon trifluoroacetate (**5d**) with aromatic derivatives has also been studied. It was shown in particular that hexamethylbenzene reacts with the *in situ* generated compound **5d** to give pentamethylbenzyl trifluoroacetate (**91**) in good yield, while the reaction with XeF_2 in the presence of HF in CH_2Cl_2 gives pentamethylbenzyl fluoride (**92**) in 72% yield.[182]



91 **92**

Acids react with one equivalent of XeF_2 in dichloromethane or chloroform to give alkyl fluorides in 20% to 95% yields.[229, 230] This reaction, like other reactions occurring in the presence of XeF_2, is catalysed by HF and thus represents an autocatalytic process. This conversion is a method for carbon chain shortening by one atom as a result of the halodecarboxylation reaction.

$$RCO_2H + XeF_2 \xrightarrow{25\ ^\circ C,\ 8-16\ h} RF + Xe + HF + CO_2$$

R = $PhCH_2$ (76%), $Ph(CH_2)_2$ (76%), $Ph(CH_2)_3$ (60%), $Me(CH_2)_8$ (54%), Ph_2CHCH_2 (63%), $Me(CH_2)_{14}$ (62%), $MeC(O)CH_2CH_2$ (82%), 2-norbornyl (74%), 1-adamantyl (82%), $PhOCH_2$ (64%), 2,4-$Cl_2C_6H_3OCH_2$ (84%), Ph_3C (65%), $PhC(OMe)CF_3$ (95%), $PhCH_2$ (76%), $PhCH(CH_2CO_2H)CH_2$ (60%), $PhCH_2CHCO_2H$ (68%), Ph (20%), $Br(CH_2)_3$ (91%).

Alkanoic and arylalkanoic acids containing primary radicals, aryloxyacetic and dicarboxylic acids are highly susceptible to fluorodecarboxylation. Carboxylic acids containing secondary radicals form fluoro derivatives in low yields, whereas carboxylic acids with tertiary radicals react as smoothly as the acids with primary radicals. Those acids which contain other protic functional groups, *e.g.*, amino acids, cholic acid, *etc.*, as well as cinnamic acid do not enter into this reaction. Benzoic acid yields benzoyl fluoride in a low yield.

The proposed mechanism [230] of fluorodecarboxylation entails the intermediate formation of xenon carboxylates.[91, 116, 182, 226]

$$RCO_2H \xrightarrow[-HF]{XeF_2} [RCO_2XeF] \xrightarrow[F^-]{a} RF + Xe + HF + CO_2$$

$$[RCO_2XeF] \xrightarrow{b} RCO_2^{\bullet} + Xe + F^{\bullet}$$

$$RCO_2^{\bullet} \xrightarrow[-CO_2]{} R^{\bullet} \xrightarrow[-Xe,\ -F^-]{XeF^{\bullet}} R^+ \xrightarrow{F^-} RF$$

According to Patrick *et al.*,[230] the reaction follows both ionic (route *a*) and radical mechanisms (route *b*). Acids containing primary and secondary radicals react by route *a*, whereas acids containing tertiary radicals and arylalkanoic acids react by route *b*. Route *a* is realised when the reaction is carried out in the presence of $[Bu_4^nN]^+[^{18}F]^-$. This made it possible to obtain 2-phenyl-1-[^{18}F]fluoroethane and 3-bromo-1-[^{18}F] fluoropropane in high radiochemical yields [230, 231] and opened a possibility of replacing the carboxy group by substituents other than the fluorine atom.[230]

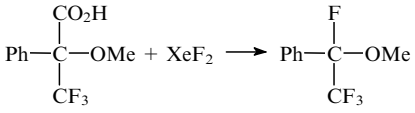
$$PhCH_2CH_2CO_2H + XeF_2 + [^{18}F]^- \longrightarrow PhCH_2CH_2[^{18}F]\ (40\%)$$

$$Br(CH_2)_3CO_2H + XeF_2 + [^{18}F]^- \longrightarrow Br(CH_2)_3[^{18}F]\ (78\%)$$

The reaction with 3-phenylpropionic acid affords no elimination side products or those involving the aromatic ring. 4-Phenylbutyric acid also reacts smoothly with XeF_2 and undergoes no intramolecular rearrangements characteristic of radical processes,[230] which makes it different from the reaction with $Pb(OAc)_4$, which results in cyclisation.[232]

It could be expected that 1,2-diphenylethane would be the main reaction product of XeF_2 with 3,3-diphenylpropionic acid, since such rearrangement is well known for phenylethyl radicals.[233] However, 2,2-diphenyl-1-fluoroethane is formed instead. Presumably, this reaction is in some respect analogous to the Borodin – Hunsdiecker reaction [234, 235] where the rearrangement products are not detected either, which makes it different from the Kochi reaction.[236, 237]

Racemic 1-methoxy-1-phenyl-1,2,2,2-trifluoroethane (**94**) was obtained in 95% yield by fluorodecarboxylation of the optically active (+)-α-methoxy-α-trifluoromethylphenylacetic acid (**93**). In the presence of $[Bu_4^nN]^+[^{18}F]^-$, this reaction gave compound **94**-[^{18}F] in 65% radiochemical yield.[230]



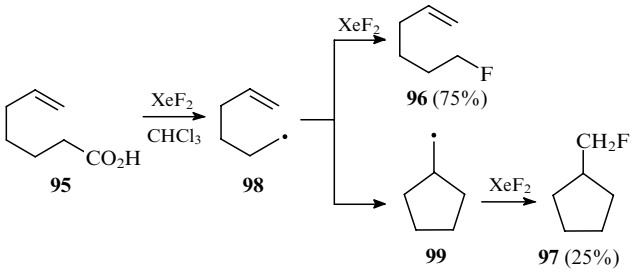
93 **94**

Pyridylacetic acid reacts with XeF_2 in the presence of HF in dichloromethane to give products the compositions of which are typical of a radical reaction.[238]

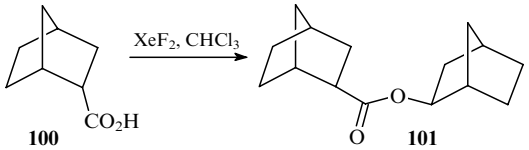
$$PyCH_2COOH \xrightarrow[CH_2Cl_2]{XeF_2,\ HF} PyCH_2CH_2Py + PyMe + PyCH_2F + PyCHCl_2 + PyCH_2Cl$$

(58%) (10%) (<1%) (17%) (11%)

The reaction of hept-6-enoic acid (**95**) with XeF_2 gives 6-fluorohex-1-ene (**96**) and fluoromethylcyclopentane (**97**).[238, 239] Fluorocyclohexane was not detected. In this case, the feasibility of a radical mechanism was unambiguously confirmed by direct EPR identification of the alkyl radicals **98** and **99** (trapped by α-phenyl-*N*-*tert*-butylnitrone). Additional experiments demonstrated the impossibility of interconversion of the fluorides **96** and **97**. The rate constant for the second-order reaction ($k = 1.1 \times 10^6$ litre mol^{-1} s^{-1}) was determined at 25 °C.[239]

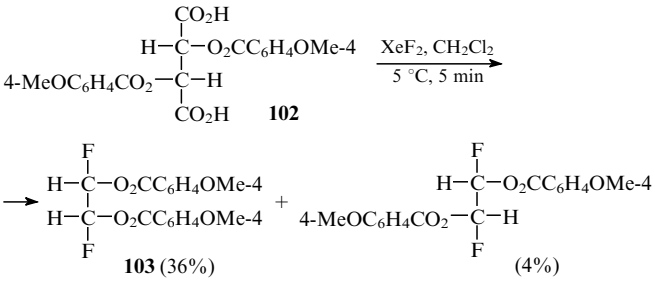


endo-Norbornane 2-carboxylic acid (**100**) does not afford fluoro derivatives in the reaction with XeF_2, but rather gives 2-*exo*-norbornyl *endo*-norbornane-2-carboxylate (**101**) in 72% yield. The *exo*-position of the alcoholic function is explained by the generation of the 2-norbornyl cation, which reacts with nucleophiles to give exclusively products with an *exo*-configuration of the substituents.[238]

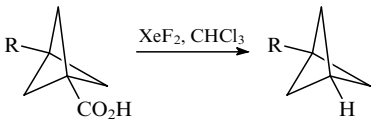


100 **101**

The reaction of the L-tartaric acid derivatives **102** with XeF_2 is non-stereospecific. The *meso*-difluoro derivative **103** (yield 36%) was isolated as the main product.[238]

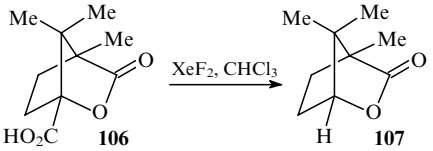


Patrick *et al.*[230] suggested that the reaction of 3-phenylbicyclo[1.1.1]pentane-1-carboxylic acid (**104a**) with XeF_2 generates a dimer; however, later it was shown [238] that this reaction yields the hydrocarbon **105a**. 3-Methoxycarbonylbicyclo[1.1.1]pentane-1-carboxylic acid (**104b**) and (−)-camphanic acid **106** are also decarboxylated by XeF_2 to give compounds **105b** and **107** in 80% and 85% yields, respectively.[239]

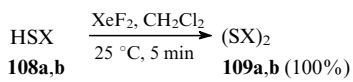


104a,**b** **105a**,**b**

R = Ph (**a**), CO_2Me (**b**).

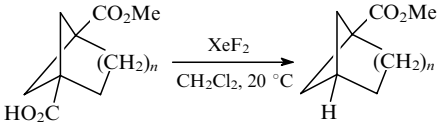


The reaction of XeF_2 with the carboxylic acids **108a**,**b** containing a thiol group gives the disulfides **109a**,**b** in a quantitative yield,[238] which is consistent with the data described in Section VIII.2.

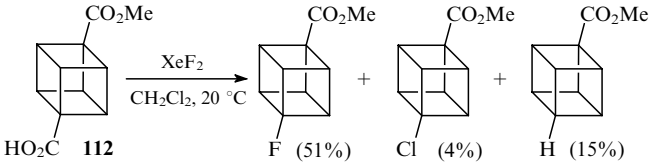


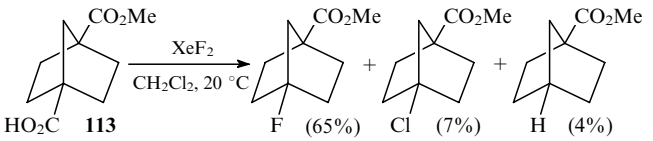
X = CH_2CO_2H (**a**), $CH_2CH_2CO_2H$ (**b**).

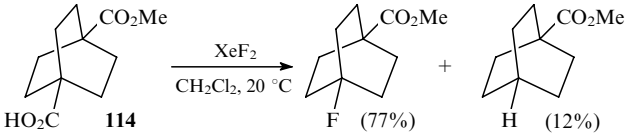
Fluorodecarboxylation with 1.5 equiv. of XeF_2 in dichloromethane was successfully employed for the synthesis of bridged cage fluorides.[238, 240]



n = 0 (**104b**, **105b**); 1 (**110**, **111**).





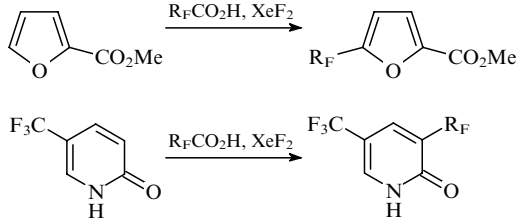


The yields and the compositions of the reaction products depend on the cage compound used. For example, 3-methoxycarbonylbicyclo[1.1.1]pentane-1-carboxylic (**104b**) and 3-methoxycarbonylbicyclo[2.1.1]hexane-1-carboxylic (**110**) acids yield exclusively the reduced decarboxylation products **105b** and **111**, whereas the monoester of a dicarboxylic acid of the cubane series (**112**) and 4-methoxycarbonylbicyclo[2.2.1]heptane-1-carboxylic acid (**113**) afford a mixture of fluorides, chlorides and reduction products. 4-Methoxycarbonylbicyclo[2.2.2]octane-1-carboxylic acid **114** forms no chlorination products under these conditions.[240]

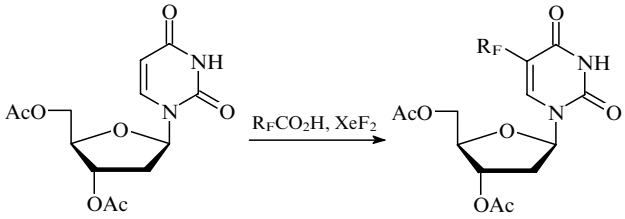
Decarboxylation of some carboxylic acids by XeF_2 is accompanied by the formation of free radicals and can be used for their generation. Halogenocarboxylic acids, particularly trifluoroacetic acid, are especially prone to such reactions. The reaction of trifluoroacetic acid with the corresponding substrate in the presence of XeF_2 was used by Tanabe *et al.*[241] for the incorporation of the trifluoromethyl radical into aromatic and heterocyclic compounds. The reaction with benzene gives trifluoromethylbenzene in 33%–38% yield. An analogous reaction takes place in the case of other perfluorocarboxylic acids.[241]



Ar = Ph, 1,4-$Cl_2C_6H_4$, 4-$ClC_6H_4CO_2Me$, 4-ClC_6H_4NHAc, 3,5-$Cl_2C_6H_3NHAc$, 2,5-$F_2C_6H_3NHAc$.



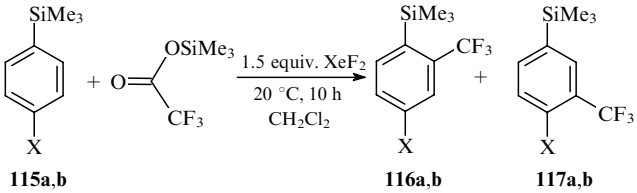
R_F = CF_3, C_2F_5, C_3F_7.



R_F = CF_3, C_2F_5.

If a heterocyclic compound contains a thiol group, perfluoroalkylation occurs exclusively at the sulfur atom.[242] In this case, disulfides are formed as side products in the same manner as in the case of acids containing a thiol group.[238]

The trifluoromethylation [243] was extended to trimethylsilyl derivatives of arenes.[241] Thus the reaction of compounds **115a**,**b** with trimethylsilyl trifluoroacetate yields a mixture of the regioisomers **116a**,**b** and **117a**,**b**. The products of *ipso*-substitution of the trimethylsilyl group were not detected.[241]



Compound	X	Yield (%)	
		116	**117**
115a	Cl	9	34
115b	NHAc	8	29

Perfluorodicarboxylic acids can generate biradicals in the reaction with XeF_2. Thus the reaction of perfluoroglutaric acid (**118**) with XeF_2 in benzene results in 1,3-diphenylhexafluoropropane (**119a**) (yield 47%). 1,3-Bis(*p*-tolyl)- (**119b**) and 1,3-bis-(4-fluorophenyl)hexafluoropropane (**119c**) are formed in toluene or fluorobenzene in 62% and 65% yields, respectively.[244] The reaction of the dicarboxylic acid **118** with XeF_2 in the presence of elementary chlorine or bromine was used to prepare 1,3-dichloro- or 1,3-dibromohexafluoropropanes.

$$HO_2C(CF_2)_3CO_2H + XeF_2 \longrightarrow$$

118

ArH, 15–20 °C → $Ar(CF_2)_3Ar + HF + CO_2 + Xe$ (**119a–c**); Ar = Ph (**a**), MeC_6H_4 (**b**), FC_6H_4 (**c**)

Cl_2 or Br_2, 0–5 °C → $X(CF_2)_3X + HF + CO_2 + Xe$; X = Cl (54%), Br (71%)

The reaction of XeF_2 with the corresponding aromatic substrate in the presence of carboxylic acids containing different functional groups allows the introduction of polyfunctional substituents into the molecule of an aromatic compound. The high value of this reaction was demonstrated using chlorofluoro- or difluoronitroacetic acid as examples.[245]

$$O_2NCF(R^1)CO_2H + 1/2\ XeF_2 + PhR^2 \longrightarrow$$

120

R^1 = Cl → $O_2NCFClC_6H_4R^2$ (**121a–c**)

R^1 = F → $O_2NCF_2C_6H_4R^2$ (**121d–f**) + $O_2NCF_2CO_2C_6H_4R^2$ (**122d–f**)

R^1 = Cl: R^2 = H (**a**), Me (**b**), F (**c**); R^1 = F: R^2 = Me (**d**), F (**e**), H (**f**).

It was found that the structures of the reaction products depend on the substituent R^1 in the original acid **120**. Thus for R^1 = Cl, the reaction gives the alkylation products **121a–c**, whereas for R^1 = F, aryl difluoronitroacetates **122d–f** are formed in addition to compounds **121d–f**, which is probably due to the higher stability of the intermediate difluoronitroacyl radical.[245]

In contrast with non-substituted carboxylic acid, the reactions of the halogeno nitro carboxylic acids **123a,b** with XeF_2 yield halogenodinitromethanes.[246]

$$O_2NCFXCO_2H \xrightarrow{XeF_2}$$

123a,b

X = F → $CF_2(NO_2)_2 + CF_4 + CO_2 + Xe + HF$

X = Cl → $CFCl(NO_2)_2 + CFCl_2NO_2 + CF_4 + CO_2 + Xe + HF$

X = F (**a**), Cl (**b**).

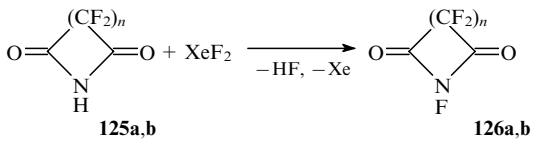
If this reaction is carried out in the presence of chlorine, bromine or nitrogen oxides, the carboxy group in fluorochloro- (**123a**) or difluoronitroacetic acids (**123b**) can be replaced by the corresponding functional groups; compounds **124** are formed in satisfactory yields.[247] If the reaction is carried out in aromatic solvents, they undergo alkylation.[245, 248]

$$O_2NCF(X)CO_2H + XeF_2 \xrightarrow{Y_2} O_2NCFXY + CO_2 + Xe + HF$$

123a,b → **124a–f**

$Y_2 = Cl_2, Br_2, N_2O_4$; X = F, Y = Br (**a**); X = Cl, Y = Br (**b**); X = F, Y = NO_2 (**c**); X = Cl, Y = NO_2 (**d**); X = F, Y = Cl (**e**); X = Y = Cl (**f**).

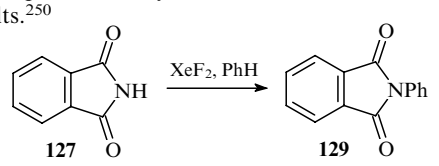
Xenon difluoride reacts with carboxylic acid imides. Thus the reaction of perfluorosuccinimide (**125a**) and -glutarimide (**125b**) with XeF_2 gives *N*-fluoroimides (**126a,b**).[249]



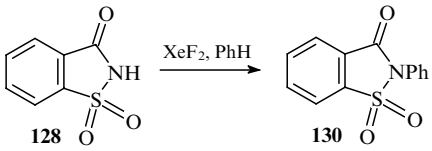
125a,b → **126a,b**

n = 2 (**a**), 3 (**b**).

The reactions of phthalimide (**127**) and saccharin (**128**) or their potassium salts with XeF_2 in dry benzene result in the *N*-phenyl derivatives of the corresponding imides **129** and **130** in 14% – 22% yields. In addition to *N*-phenyl derivatives, biphenyl is formed as a side product; its yield is lower in the reactions of potassium salts.[250]



127 → **129**



128 → **130**

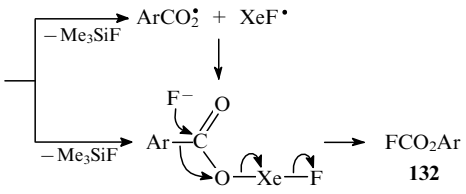
The reaction of trimethylsilyl arenecarboxylates **131** with XeF_2 in dichloromethane or hexaflurobenzene results in the aryloxycarbonyl fluorides **132**. Arenes or aryl fluorides generated from the corresponding aryl radicals are the main reaction products in acetonitrile.[251]

$$ArCO_2SiMe_3\ (\mathbf{131}) \xrightarrow{XeF_2} \begin{cases} \xrightarrow{C_6F_6 \text{ or } CH_2Cl_2} FCO_2Ar + Xe + Me_3SiF\ (\mathbf{132}) \\ \xrightarrow{MeCN} ArF + Xe + Me_3SiF + CO_2 \end{cases}$$

Ar = 4-Bu^tC_6H_4, 4-MeC_6H_4, 3-ClC_6H_4, 4-$MeOC_6H_4$, 4-$CF_3C_6H_4$.

The transformation of compounds **131** into compounds **132** is the first example of the $R^1CO_2R^2 \rightarrow R^2CO_2R^1$ rearrangement. A mechanism for this reaction has been proposed, which includes one-electron oxidation and the formation of a radical cation and a radical anion.[251]

$$(ArCO_2SiMe_3)^{+\bullet} + (XeF_2)^{-\bullet} \longrightarrow$$



Using this approach, the electron-enriched centre, *i.e.*, the oxygen atom of the carbonyl group, can be converted into an electron-deficient centre using a temporary group. This is an example of so-called Umpolung.[251]

VI. Organic xenon(II) compounds containing the C–Xe bond

The chemistry of organoxenon compounds has been developing intensively in the past two decades. This trend was initiated by the appearance of a report [13] on the synthesis of $Xe(CF_3)_2$ (**133**). This compound is sublimed in *vacuo*, is stable at low temperatures and can be stored for two weeks at liquid nitrogen temperature. Upon decomposition, it gives XeF_2 and a mixture of fluorocarbons.

$$C_2F_6 \xrightarrow{\Delta} 2\dot{C}F_3 \xrightarrow[-F_2]{XeF_2} Xe(CF_3)_2\ (\mathbf{133})$$

This experiment and the results of ion cyclotron resonance studies of the reaction mixture containing H_2, Xe and MeF [253,254] which were aimed at the determination [252] of the strength of the Xe–C bond (43±8 kcal mol^{-1}) gave impetus to further investigations into the synthesis of new compounds containing Xe–C bonds. Thus the formation of the methylxenon(II) cation was established in an equilibrium reaction which included a transfer of methyl cation from Me_2F^+ to Xe. The physicochemical characteristics of the equilibrium ($K = 0.16\pm0.05$, $\Delta G^\circ = 1.1\pm0.2$ kcal mol^{-1}, $\Delta S^\circ = 9.6\pm1.0$ kcal mol^{-1} K^{-1}, $S^\circ(MeXe^+) = 60.5$ cal mol^{-1} K^{-1}, $\Delta H^\circ = 4.0\pm0.5$ kcal mol^{-1}) confirmed [255] the earlier obtained [252] data on the strength of the Xe–C bond in $MeXe^+$ (55.2±2.5 kcal mol^{-1}).

Compound **133** had long been the only genuine organic xenon derivative. Further developments in the chemistry of organoxenon compounds confronted the task of creating stable xenon derivatives by a correct choice of ligands linked to xenon atoms. For xenon compounds, as for any other hypervalent compounds,[153,154,256] fluorine-containing ligands are the most suitable ones. However, despite the presence of fluorine-containing ligands in compound **133**, its stability was insufficient even for conducting routine spectral analyses.[257–259] It was suggested [260–262] that perfluorinated compounds containing a Xe–C bond have been formed as intermediates. These conclusions were inferred from the structures of the reaction products assuming that they might be formed exclusively as a result of incorporation of xenon into the C–E bond (E is an element). These investigations provided a basis for the development of a methodology of synthesis of stable organic xenon derivatives.

This approach was realised almost simultaneously by Naumann and Tyrra,[263] and Frohn and Jacobs and coworkers.[257,264,265] A procedure for the preparation of stable organic compounds with a covalent Xe–C bond, *e.g.,* of the $[Xe(C_6F_5)]^+X^-$ type, was proposed based on the cleavage of the C–B bond. Thus the low-temperature reaction of tris(pentafluorophenyl)boron with XeF_2 in CH_2Cl_2 gives the pentafluorophenylxenon salt **134a** (yields 40% [257] and 92% [266]) which separates from the reaction mixture as a colourless precipitate and could be recrystallised from acetonitrile. This compound is stable in the crystalline state for a long time at −60 °C; its solutions in acetonitrile are unstable at room temperature. A similar reaction in acetonitrile gives the pentafluorophenylxenon salt **134b**.[263]

$$B(C_6F_5)_3 + XeF_2 \xrightarrow[-30\ ^\circ C]{CH_2Cl_2} \underset{\mathbf{134a}}{[C_6F_5Xe]^+[C_6F_5BF_3]^-}$$

$$B(C_6F_5)_3 + XeF_2 \xrightarrow[0\ ^\circ C]{MeCN} \underset{\mathbf{134b}}{[C_6F_5Xe]^+[(C_6F_5)_3BF]^-}$$

Presumably, the boron compounds $B(C_6F_5)_3$, $[B(C_6F_5)_3F]^-$, $BF_3\cdot MeCN$ and BF_4^- identified by ^{11}B NMR spectroscopy could be formed by dismutation of a putative intermediate **135**.[263]

$$\underset{\mathbf{135}}{B(C_6F_5)_{3-x}} + XeF_2 \longrightarrow (3-x)\,B(C_6F_5)_3 + x\,BF_3$$

$x = 1, 2.$

It should be noted that the dismutation results also in the formation of a weak BF_3–XeF_2 complex [267] which readily reacts with pentafluorobenzene derivatives to give 1-R-heptafluorocyclohexa-1,4-dienes (R = H, F, Cl, Br, C_6F_5).[193] Heptafluorocyclohexa-1,4-diene and octafluorocyclohexa-1,4-diene were identified as the side products [263] using ^{19}F NMR.

The structures of compounds **134a**,**b** were established from NMR [268–270] and X-ray diffraction data.[263,271]

Some chemical properties of compounds **134** have been studied. Thus the reaction of the salts **134a**,**b** with water or D_2O is accompanied by the formation of C_6F_5H or C_6F_5D.[257,263] The salt **134a** reacts with halide ions in acetonitrile with the liberation of xenon and the formation of halopentafluorobenzene;[257,263] the salts **134a**,**b** form the corresponding adducts **136**–**139** with halopentafluorobenzenes,[257,263] tellurium-[263] or phosphorus-containing compounds.[257]

$$\underset{\mathbf{134b}}{[C_6F_5Xe]^+[(C_6F_5)_3BF]^-} \xrightarrow{KF} C_6F_6 + Xe + K[(C_6F_5)_3BF]$$

$$\xrightarrow{Te(C_6F_5)_2} \underset{\mathbf{136}}{[(C_6F_5)_3Te]^+[(C_6F_5)_3BF]^-} + Xe$$

$$\xrightarrow{C_6F_5I} \underset{\mathbf{137}}{[(C_6F_5)_2I]^+[(C_6F_5)_3BF]^-} + Xe$$

$$\underset{\mathbf{134a}}{[C_6F_5Xe]^+[C_6F_5BF_3]^-} \longrightarrow$$

$$\xrightarrow[Hal = I, Br]{[R_4N]^+Hal^-} C_6F_5Hal + Xe + R_4N^+[C_6F_5BF_3]^-$$

$$\xrightarrow{(4\text{-}CF_3C_6H_4)_3P} \underset{\mathbf{138}}{[C_6F_5(p\text{-}CF_3C_6H_4)_3P]^+[C_6F_5BF_3]^-} + Xe$$

$$\xrightarrow{C_6F_5Hal} \underset{\mathbf{139}}{[(C_6F_5)_2Hal]^+[C_6F_5BF_3]^-} + Xe$$

The pentafluorophenylxenon cation in compound **134a** reacts with benzylcyanide and triphenylmethane containing activated C–H bonds to give the nitriles **140** and **141** in the former case and tetraarylmethane **142** and the biphenyl derivative **143** in the latter case.[264,265]

$$\mathbf{134a} \xrightarrow[-Xe,\ -HF]{PhCH_2CN} \underset{\mathbf{140}}{Ph(C_6F_5)CHCN} + \underset{\mathbf{141}}{Ph(C_6F_5)_2CCN} + (C_6F_5)_2BF$$

$$\mathbf{134a} \xrightarrow[-Xe,\ -HF]{Ph_3CH} \underset{\mathbf{142}}{Ph_3CC_6F_5} + \underset{\mathbf{143}}{C_6F_5C_6H_4(Ph_2)CC_6F_5} + (C_6F_5)_2BF$$

The reaction of compound **134a** with bis(pentafluorophenyl)-cadmium results in perfluorobiphenyl (**144**) and pentafluorobenzene (**145**). The same products are formed in the reaction of XeF_2 with one equivalent of $Cd(C_6F_5)_2$.[266] Both reactions seem to occur *via* the intermediate **146**, which eliminates xenon to generate the radical $^\bullet C_6F_5$.

$$\underset{\mathbf{134a}}{[C_6F_5Xe]^+[(C_6F_5)_2BF_2]^-} + Cd(C_6F_5)_2 \longrightarrow \underset{\mathbf{146}}{[C_6F_5XeC_6F_5]} \xrightarrow{-Xe} \cdots$$

$$XeF_2 + Cd(C_6F_5)_2 \xrightarrow{-CdA_2}$$

$$\cdots \longrightarrow {}^\bullet C_6F_5 \longrightarrow \underset{\mathbf{144}}{C_6F_5C_6F_5}$$

$$\xrightarrow[-Solv^\bullet]{SolvH} \underset{\mathbf{145}}{C_6F_5H}$$

A = F or $[(C_6F_5)_2BF_2]^-$; SolvH is solvent.

The anion in compound **134b** can be replaced by using AsF_5.[258,272]

$$\underset{\mathbf{134b}}{C_6F_5Xe^+[(C_6F_5)_3BF]^-} + AsF_5 \xrightarrow[-20\ ^\circ C]{MeCN} \underset{\mathbf{134c}}{C_6F_5Xe^+AsF_6^-} + B(C_6F_5)_3$$

The salt **134c** formed is stable at temperatures up to 125 °C. Its chemical properties have been investigated.[272,273] The reaction with halide anions in acetonitrile yields different products depending on the nature of the anion. Thus the reaction with the fluoride anion which is a hard nucleophile yields a C_6F_5H–$C_6F_5C_6F_5$ mixture, whereas the reactions with I^-, Br^- and Cl^- anions give C_6F_5X (X = I, Br, Cl). The reactions with compounds containing the HF_2^- anion gives a mixture of C_6F_6, C_6F_5X and $C_6F_5C_6F_5$.[273] The salt **134c** was further used for the synthesis of the organoxenon compound **147** by anionic exchange with an aqueous solution of cesium pentafluorobenzoate. Compound **147** is thermally stable up to 85±3 °C ($T_{1/2} \approx 3$ h at 35 °C).[272,274,275]

$$C_6F_5Xe^+AsF_6^- + C_6F_5CO_2Cs \xrightarrow{D_2O} C_6F_5XeOCOC_6F_5$$
134c **147**

The structure of compound **147** was established by X-ray diffraction analysis.[275] The length of the C–Xe bond (2.122 Å) is larger than that in the cation $[MeCN\cdots XeC_6F_5]^+$ (2.092 Å), whereas the Xe–O bond (2.367 Å) is much longer than those in other known xenon derivatives (2.12–2.21 Å).[87,89,276–279] It should be noted that the Xe–O bond in compound **147** cannot be regarded as a purely ionic bond because of the essential differences in the lengths of the C–O bonds (1.171 and 1.220 Å) in the C_6F_5COO group,[275] which is inconsistent with an ionic carboxylate (1.26 Å).[280]

The reaction of XeF_2 with arylboranes gave the arylxenonium salts **134d**,**e**.[257,263,271,281–284]

$$(3\text{-}CF_3C_6H_4)_2BF + XeF_2 \longrightarrow [3\text{-}CF_3C_6H_4Xe]^+[3\text{-}CF_3C_6H_4BF_3]^-$$
134d

$$(4\text{-}FC_6H_4)_3B + XeF_2 \longrightarrow [4\text{-}FC_6H_4Xe]^+[(4\text{-}FC_6H_4)_2BF_2]^-$$
134e

The synthesis of organoxenon compounds from arylboranes can be carried out in the presence of boron trifluoride.[257,266,271,281,285,286] The resulting salts **134f**,**g** are obtained in good yields.

$$BAr_3 + 3\,XeF_2 + 2\,BF_3 \longrightarrow 3\,ArXe^+BF_4^-$$
134f,**g**

Ar = C_6F_5 (**f**), 2,4,6-$F_3C_6H_2$ (**g**).

The structure of compound **134g** was established by ^{129}Xe, ^{19}F, ^{13}C and ^1H NMR spectroscopy. The absolute value of $^1J(^{129}Xe-{}^{13}C)$, equal to 103.6 Hz (see Ref. 271), is much smaller than that in the cation $C_6F_5Xe^+$ [$^1J(^{129}Xe-{}^{13}C)$ = 119 Hz],[257,263] which suggests the existence of short and, as a consequence, strong bonds and the relative stability of compound **134g**. Some reactions of compounds **134f**,**g** have been studied.[271]

134f,**g** → ($Te(C_6F_5)_2$, 20 °C) $[Te(C_6F_5)_2Ar]^+BF_4^- + Xe$

134f,**g** → (KCl) $ArCl + Xe + KBF_4$

134f,**g** → (IC_6F_5, 60 °C) $Xe + [C_6F_5IAr]^+BF_4^-$

Compounds **134f**,**g** are inert with respect to atmospheric oxygen and water and can be stored in dry air for 21 days without any visible alterations, while their hydrolysis in aqueous acetonitrile is completed within 7 days.

Cyclic voltammograms of compounds of the X^+Y^- type, where X = C_6F_5Xe, $C_6F_5N_2$, C_6F_5Br, C_6F_5I and $(C_6F_5)_4P$, were obtained in 0.1 M solution of Bu_4NBF_4 in MeCN.[287] The minimum and maximum values of electroreduction potentials were obtained for $C_6F_5Xe^+$ and $(C_6F_5)_4P^+$ cations, respectively. The attachment of the first electron to the cations $C_6F_5Xe^+$ and $C_6F_5N_2^+$ is accompanied by the evolution of Xe or N_2 and the generation of the $^{\bullet}C_6F_5$ radical, which either undergoes dimerisation or abstracts hydrogen from MeCN. The first step in the electroreduction of other cations is followed by the liberation of pentafluorophenyl derivatives, *e.g.*, C_6F_5Br, C_6F_5I or $(C_6F_5)_3P$, which undergo further reduction.[287]

XeF_2 was used in the synthesis of new organoxenon compounds.[288,289] The reaction of stoichiometric amounts of XeF_2 and trifluoroacetic acid in CCl_3F at −20 °C gives xenon bis(trifluoroacetate) **6d**,[89–91] which further reacts with trifluoromethanesulfonic acid at −40 °C. This can be accompanied by the formation of the intermediate **148**; indirect evidence can be derived from the appearance of a singlet in the ^{129}Xe NMR spectrum at δ = 400 and the generation of signals at δ = −69.1 ($OCOCF_3$) and −75.6 (OSO_2CF_3) in the ^{19}F NMR spectrum. Compound **148** reacts with fluorine-containing arenes to give the arylxenon triflates **134h**–**k**.[288]

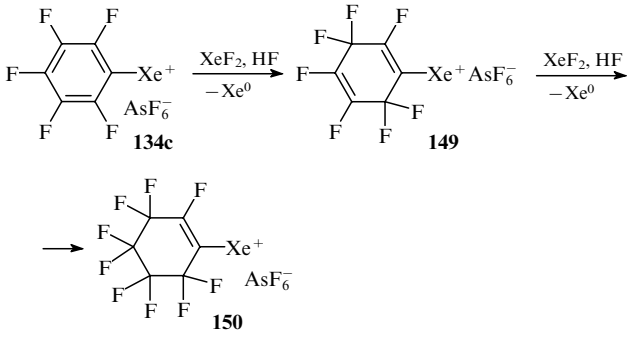
$$XeF_2 + 2\,CF_3CO_2H \xrightarrow[-40\ ^\circ C]{CCl_3F} Xe(OCOCF_3)_2 \xrightarrow{TfOH}$$
6d

$$\longrightarrow [Xe(OCOCF_3)OTf] \xrightarrow{ArH} ArXeOTf$$
148 **134h**–**k**

Ar = 2,4,6-$F_3C_6H_2$ (**h**), 3,5-$(CF_3)_2C_6H_3$ (**i**), 1-F-3-$(CF_3)C_6H_3$ (**j**), 2-F-5-$NO_2C_6H_3$ (**k**).

It is noteworthy that this reaction does not occur if FXeOTf (**5b**) is used as a starting material, while the reaction of 1,3-$F_2C_6H_4$ with the intermediate **148** gives a mixture of Xe(2,4-$F_2C_6H_3$)(OTf) and Xe(3,5-$F_2C_6H_3$)(OTf) (10 : 1) (^{129}Xe NMR data) and several side products. The reaction of 1-F-3-$(CF_3)C_6H_4$ with the intermediate **148** gives compound **134j** and some non-identified products, whereas 1,3,5-$(CF_3)_3C_6H_3$ does not react at all. The addition of arenes devoid of a fluorine, chlorine or trifluoromethyl substituent to the reaction mixture results in immediate decomposition.[288]

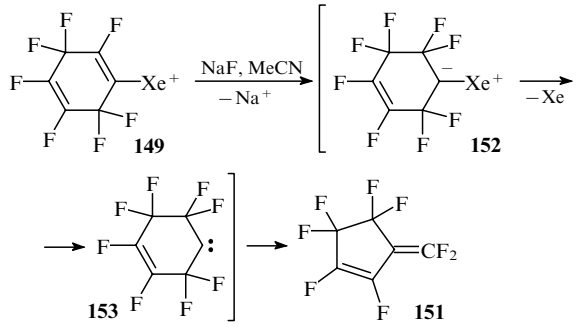
A method for the synthesis of cycloalkenylxenon(II) salts by the reaction of (pentafluorophenyl)xenon(II) hexafluoroarsenate **134c** with XeF_2 in HF has been developed.[273,274,290–295] Thus the reaction of the salt **134c** with XeF_2 results in the addition of two or four fluorine atoms to the aromatic ring to afford the salts **149** or **150**.[290]



134c **149** **150**

Compounds **149** and **150** are white crystalline substances stable at room temperature and soluble in MeCN. Their structures were established on the basis of ^{19}F, ^{13}C and ^{129}Xe NMR spectral data and chemical transformations.

The salts **149** and **150** react with the bromide anion or benzene in acetonitrile to give products with composition 1-R-1,4-C_6F_7 or 1-R-C_6F_9 (R = Br, Ph), respectively.[296,297] The reaction of the salt **149** with sodium fluoride in acetonitrile results in a ring contraction and the formation of perfluoro-3-methylenecyclopentene (**151**).

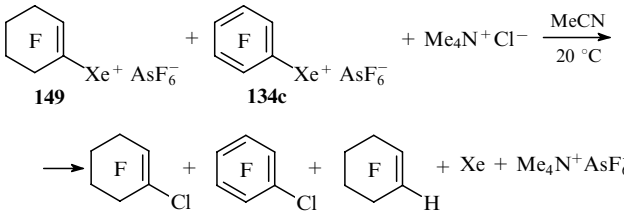


149 **152** **153** **151**

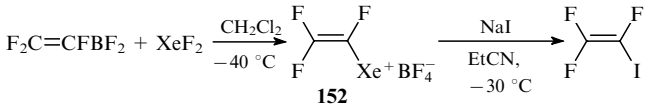
The diene **151** was the main product in the reaction mixture and was unambiguously identified on the basis of ^{19}F NMR spectra (see Ref. 291). Its formation can be interpreted in terms of the HSAB concept. Being a hard base, the nucleophilic fluoride

anion predominantly attacks the hard electrophilic centre of C(2) rather than the soft electrophilic centre of xenon(II). Elimination of xenon from the intermediate **152** results apparently in the carbene **153**, which is further transformed into the reaction product **151**.[291]

The relative reactivities of alkenyl- and arylxenon(II) derivatives were studied in a competitive reaction with tetramethylammonium chloride in acetonitrile. The conversion of the salt **149** was 67% and that of the salt **134c** was 19%. These results and the compositions of the reaction products demonstrate the high electrophilicity of the xenon atom linked to the perfluorocyclohexen-1-yl group.[295]

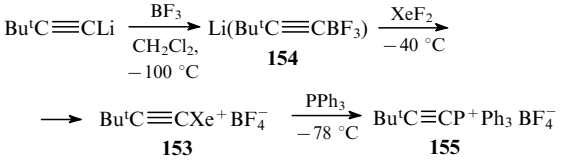


A method for the synthesis of trifluorovinylxenon(II) tetrafluoroborate (**152**) by the reaction of trifluorovinylboron difluoride with XeF_2 in CH_2Cl_2 at −40 °C has been developed recently. The salt **152** is a white solid, which decomposes at temperatures above 0 °C. Its solution in anhydrous HF is stable at 20 °C for several hours but rapidly decomposes in MeCN.[298]



The reaction of the salt **152** with an excess of sodium iodide in EtCN at −30 °C results in trifluoroiodoethylene, which is an indirect proof of the structure of compound **152**.[298]

The alkynylxenon fluoroborate **153** was synthesised using a similar approach.[299] The borofluoride complex **154** generated from lithium *tert*-butylacetylide and BF_3 reacts with XeF_2 in CH_2Cl_2 at −40 °C to give the salt **153** the structure of which was established by NMR and IR spectroscopy. Compound **153** is relatively stable in chloroform at −30 °C, but slowly decomposes at room temperature.[299]



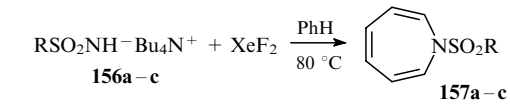
The salt **153** reacts with nucleophiles, *e.g.*, triphenylphosphine, at −78 °C to give the stable phosphonium salt **155**,[299] which confirms its structure.

The attempts to prepare xenon-containing salts from other alkynes were unsuccessful. However, some organoxenon tetrafluoroborates could be detected by ^{129}Xe NMR (see Ref. 299).

VII. Reactions of xenon difluoride with nitrogen-containing compounds

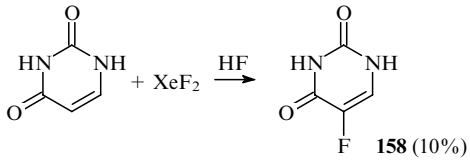
Considerable experience has been gained in the study of reactions of xenon derivatives with nitrogen-containing compounds.

Earlier it was shown[300] that aniline and benzylamine are fluorinated with XeF_2 in the absence of a catalyst without involving the NH-bonds. Unlike benzene derivatives, pyridine easily reacts with XeF_2 in the absence of a catalyst to give 2-fluoro- (35%), 3-fluoro (20%) and 2,6-difluoropyridines (11%).[300] 8-Hydroxyquinoline is converted into 5-fluoro-8-hydroxyquinoline (35%) under the action of XeF_2.[300] On the other hand, imidazo[1,2-*b*]pyridazine is not fluorinated by XeF_2.[301] The reaction of XeF_2 with tetrabutylammonium salts of arenesulfamides **156a–c** in benzene yielded *N*-sulfoazepines **157a–c** presumably formed as a result of generation and subsequent incorporation of nitrene into the benzene ring.[302,303] The yields of the azepines **157a–c** increase as the temperature increases.

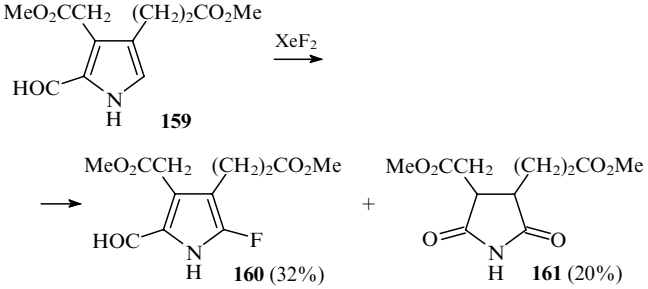


Compound **157**	R	Yield (%)
a	Ph	47
b	Me	41
c	4-MeC_6H_4	42

The reaction of uracil with XeF_2 in hydrofluoric acid or anhydrous hydrogen fluoride results in 5-fluorouracil (**158**) in small yield.[304]

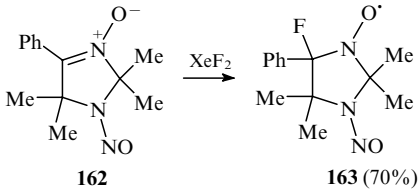


The reaction of the substituted pyrrole **159** with XeF_2 in acetonitrile at 20 °C results in the fluoride **160** and the imide **161**.[305] If the reaction was carried out in dichloromethane, 3-methoxycarbonylmethyl-4-methoxycarbonylethyl-2-formyl-5-chloropyrrole was isolated in 24% yield; its formation is explained by the involvement of the solvent in the reaction.

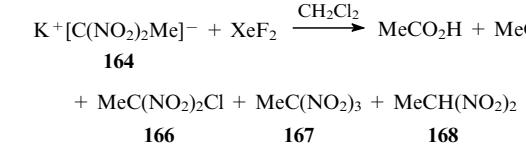


It should be noted that XeF_2 was found to be a most suitable reagent for the fluorination of pyrroles containing electron-withdrawing groups.[305]

The nitrone **162** reacts with XeF_2 to generate a stable nitroxyl radical **163**,[306] which can be converted into an ammonium salt by a reaction with ammonia.



The reaction of aliphatic nitro compounds with xenon difluoride has been studied in detail.[307–313] Thus it was shown that the potassium salt of 1,1-dinitroethane (**164**) reacts with XeF_2 in CH_2Cl_2 to give a mixture of compounds.[307]



When this reaction was carried out in dry dichloromethane, 1,1-dinitro-1-fluoroethane (**165**) was the main product, whereas the chlorodinitro derivative **166** was predominantly formed in

CH_2Cl_2 saturated with water. The addition of nitrogen oxides to the reaction mixture increases the yield of 1,1,1-trinitroethane (**167**) to 22%. When this reaction is carried out in dry CH_2Cl_2, the addition of KCl and Na_2CO_3 does not influence the ratios of the reaction products. However, the yield of compound **166** in aqueous CH_2Cl_2 increases after addition of KCl, whereas 1,1-dinitroethane (**168**) is not formed in the presence of sodium carbonate. Compound **168** does not react with XeF_2 in CH_2Cl_2 at room temperature. As the reaction mixture contains simultaneously 1,1-dinitroethane and its salt, one can anticipate the formation of a self-condensation product of compound **168**, *viz*., 2,5,5-trinitro-3-aza-4-oxa-hex-2-ene, which was in due course detected. The data obtained suggest[307] that this reaction occurs by a radical or a radical-ion mechanism.

The reaction of dinitromethane, trinitromethane and phenyldinitromethane salts with XeF_2 in different solvents (CH_2Cl_2, MeCN, CCl_4) have also been studied.[308, 309] In this case, the formation of fluorination products, *e.g*., fluorodinitromethyl compounds, was accompanied by the formation of reaction products involving solvent molecules, *viz*., dinitromethyl compounds in CH_2Cl_2 (CH-form) and chlorodinitromethyl compounds (in CH_2Cl_2 and CCl_4) Acetonitrile was found to be resistant to XeF_2 and intermediate radical species. The fluorination of 1,1-dinitroethane and phenyldinitromethane in acetonitrile occurs with high selectivity.[308]

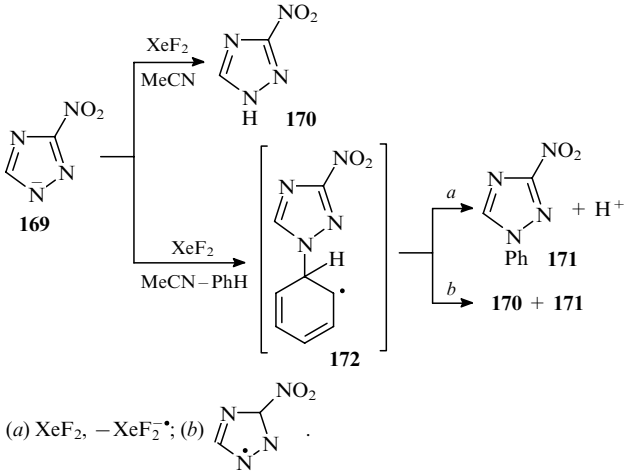
The reaction of the potassium salt of nitroform with XeF_2 in acetonitrile containing 50 vol.% of benzene or THF is accompanied by the formation of a complex mixture of products.[309]

$$^{-}C(NO_2)_3 + XeF_2 \xrightarrow[MeCN]{PhH} FC(NO_2)_3 + HC(NO_2)_3 + PhNO_2 + PhC(NO_2)_3 + PhF + PhPh + FCH(NO_2)_2 + PhC(NO_2)_2F$$

$$^{-}C(NO_2)_3 + XeF_2 \xrightarrow[MeCN]{THF} FC(NO_2)_3 + HC(NO_2)_3 + FCH(NO_2)_2 + \text{O-ring-}C(NO_2)_3 + \text{O-ring-}CF(NO_2)_2$$

It is of note that the side fluorination products of anions of dinitromethyl compounds with XeF_2 in various solvents are similar to the reaction products of dinitromethyl radicals, generated by electrochemical oxidation of polynitroalkane anions, with solvents. This similarity can be explained by the identity of the intermediate species.[309]

Xenon difluoride can play the role of a single-electron oxidant with respect to both 1,1-dinitrocarbanions and the difficultly oxidisable nitroazole anions.[310] Thus the reaction of the potassium salt of 3-nitro-1,2,4-triazole (**169**) with XeF_2 in acetonitrile results in the non-ionised 3-nitro-1,2,4-triazole (**170**) (yield 70%–80%). A 3:2 mixture of 3-nitro- (**170**) and 1-phenyl-3-nitro-1,2,4-triazoles (**171**) is formed in the MeCN–PhH system.



(*a*) XeF_2, $-XeF_2^{-\bullet}$; (*b*)

Presumably, compound **171** is formed as a result of generation of the radical **172**. The latter can be rearomatised by two equally probable routes, *viz*., by single-electron oxidation and deprotonation (route *a*) and by abstraction of the hydrogen atom by the 3-nitro-1,2,4-triazole radical (route *b*).[310] However, the latter route is less probable, since benzene has a much higher oxidation potential ($E_{1/2}$ = 2.02 V[314]) than the triazole anion [$E_{1/2}$ = 1.77 V (see Ref. 315)].

The reactions of potassium salts of 1,1-dinitrobut-2-enonitrile (**173a**) and the respective amide (**173b**) with XeF_2 were studied in order to compare the reactivities of the dinitromethyl group and the double bond. These reactions give the fluorination products **174a**,**b** in high yields.[311]

$$[RCH{=}CHC(NO_2)_2]^{-}K^{+} + XeF_2 \xrightarrow{MeCN} \underset{\mathbf{173a,b}}{} \longrightarrow RCH{=}CHCF(NO_2)_2 + KF + Xe$$

174a,**b**

R = CN (**a**), $CONH_2$ (**b**).

Selective fluorination of the dinitromethyl anion without affecting the double bond can be explained by the absence of a catalyst (HF), since the reaction was carried out in a vessel made of ordinary silicate glass which is known to be an effective chemical acceptor of HF. According to ^{1}H NMR and GLC data, this reaction gives < 5% admixtures. When the fluorination was performed in a reactor made of a fluoropolymer resistant to HF, this resulted in a mixture of products, which can be assigned to the occurrence of HF-catalysed side reactions, *e.g*., the fluorination of the double bond.[311]

The kinetics of fluorination of salts of dinitromethyl compounds by XeF_2 has been studied.[312, 313] The kinetics is described by second-order equations, first-order with respect to each reagent. The nature of the cation in the salt does not influence the value of the fluorination rate constant in the concentration range from 10^{-3} to 10^{-5} mol litre^{-1}. The thermodynamic activation parameters ($\Delta H^{\neq}_{298}$ = 30–60 kJ mol^{-1}, $\Delta S^{\neq}_{298}$ = -60 to -130 J mol^{-1} K^{-1}) lie in the range characteristic of an S_N2 reaction.

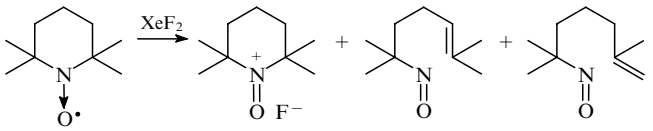
A mechanism of the reaction of dinitro compounds with XeF_2 has been proposed.[307, 309, 310, 313] Its first step probably includes single-electron oxidation of the dinitro compound anion by XeF_2. The reaction products result from the reaction of the solvent molecules with the radical species formed in the first step. The CH_2Cl_2 molecules serve as the source of chlorine and hydrogen atoms, whereas the radical of the original dinitro compound serves as the source of NO_2.

$$R\dot{C}(NO_2)_2 + F^{-} \longrightarrow [RC(NO_2)_2F]^{-\bullet} \xrightarrow{XeF_2\,(\dot{X}eF)} RC(NO_2)_2F$$

$$[RC(NO_2)_2]^{-} + \dot{N}O_2 \longrightarrow [RC(NO_2)_3]^{-\bullet} \xrightarrow{XeF_2\,(\dot{X}eF)} RC(NO_2)_3$$

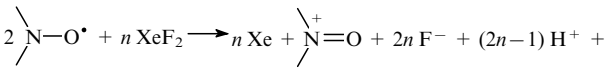
The rates of the reaction of XeF_2 with salts of *ortho*-, *meta*- and *para*-substituted aryldinitromethanes in MeCN were measured by spectrophotometric methods.[313] The relationship between the structures of the substrates and their reactivities with respect to XeF_2 is described by linear free energy equations using inductive, resonance and steric constants of the substituents. For the overwhelming majority of dinitromethyl compounds, it was found that the rate of fluorination of the corresponding dinitrocarbanion decreases with the increase in the CH-acidity.

Xenon difluoride acting as a single-electron oxidant converts the nitroxyl radicals **175** into the oxoammonium fluorides **176**, nitroso compounds **177** and **178** and the products of more profound oxidation.[316]



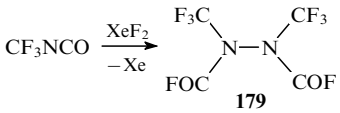
175 **176** **177** **178**

The general stoichiometric equation for the oxidation was derived from the kinetic data.[316]

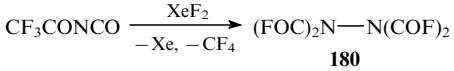


P are reaction products.

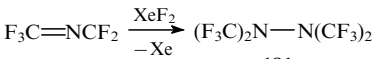
A convenient procedure for the synthesis of fluorocarbonyl-substituted hydrazines **179** and **180** in the reaction of XeF_2 with isocyanates has been developed.[317] The reaction of XeF_2 with perfluoroazapropene yields tetrakis(trifluoromethyl)hydrazine **181**.[317]



179

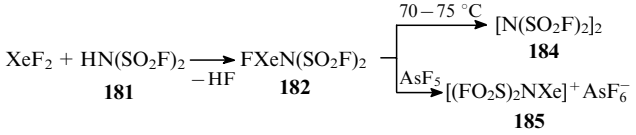


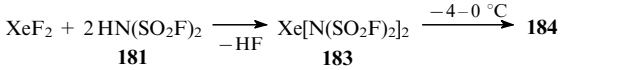
180



181

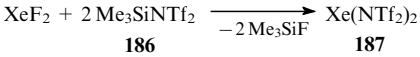
A compound containing the Xe–N bond was first synthesised by the reaction of XeF_2 with di(fluorosulfuryl)imide (**181**).[318–320]





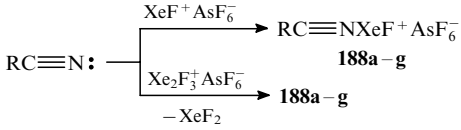
Mono- (**182**) or bis[*N*,*N*-di(fluorosulfuryl)imido]xenon fluorides **183** can be obtained depending on the reagent ratio. The structures of compounds **182** and **183** were confirmed by X-ray diffraction analysis.[321–323] The magnitude of the angle C–Xe–N (174.5°) corresponds to the structure of a distorted trigonal bipyramid with the substituents in the axial positions. The length of the Xe–C bond (2.092 Å) is comparable with that of the C–I bond.[153] The coordinate bond Xe–N (2.681 Å) in compounds **134a**,**b** is much longer than the covalent bond Xe–N.[323, 324] The decomposition of compounds **182** and **183** is accompanied by the formation of the dimer **184**. The intermediate radical $^{\bullet}N(SO_2F)_2$ was detected by EPR. The reaction of compound **182** with AsF_5 gives the salt **185**.[319, 322, 324]

N-Trimethylsilyl(trifluoromethylsulfonyl)amine (**186**) was used as the starting material for the preparation of bis[bis(trifluoromethylsulfonyl)imido]xenon (**187**), which is a stable compound and decomposes only at 72 °C to generate the radical $^{\bullet}N(SO_2CF_3)_2$.[325]



186 **187**

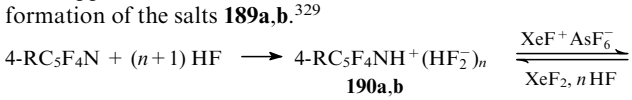
The attempt to prepare compounds containing a Xe–C bond by the reaction of HCN with XeF_2 was unsuccessful. However, the fact that xenon-containing cations manifest the properties of Lewis acids[326] made it possible to synthesise xenon derivatives containing the Xe–N bond from HCN.[327–330] The first adiabatic ionisation potential of HCN (13.80 eV) was determined from photoionisation data.[331] The electron affinity of the XeF^+ cation is 10.9 eV. It may therefore be assumed that HCN will be resistant to the oxidative attack of XeF^+, and $HC{\equiv}NXeF^+$ should manifest satisfactory thermal stability. Indeed, compounds **188a–g** containing covalent Xe–N bonds were synthesised by the reaction of $XeF^+AsF_6^-$ or $Xe_2F_3^+AsF_6^-$ with HCN or nitriles.[327–330]

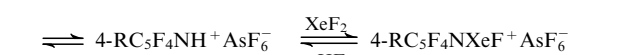


R = H (**a**), Me (**b**), CH_2F (**c**), Et (**d**), C_2F_5 (**e**), C_3F_7 (**f**), C_6F_5 (**g**).

Compounds **188a–g** were characterised by spectral methods.[328] The reaction product with hydrogen cyanide (**188a**) is a white crystalline substance stable below −60 °C. The derivatives **188e–g** containing perfluoroalkyl radicals are even less stable; they were characterised by spectral methods without being isolated from the reaction mixtures. The nature of the bond in the cation $HC{\equiv}NXeF^+$ has been discussed.[328] It is of note that the corresponding fluorokrypton salts were synthesised by an analogous scheme in the reaction of the cation KrF^+ with nitriles (the electron affinity of the cation KrF^+ is 13.2 eV).[330, 332]

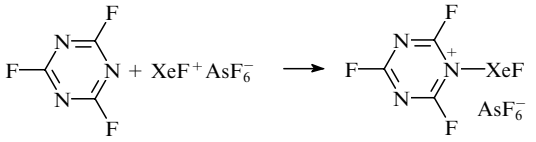
Equimolar amounts of $XeF^+AsF_6^-$ and perfluoropyridine (I_p = 10.08 eV) react in anhydrous HF at −20 to −30 °C to give the salts **189a**,**b** containing the Xe–N bond. Removal of the solvent (HF) at −50 °C leads to the formation of a white solid substance which represents a mixture of XeF_2 with the salts **190a**,**b** and **191a**,**b** containing no xenon (data from the Raman spectra). BrF_5 appeared to be a more suitable solvent than HF in the formation of the salts **189a**,**b**.[329]





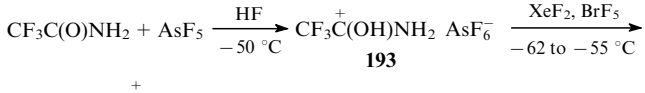
R = F (**a**), CF_3 (**b**).

The reaction of trifluoro-*s*-triazine (I_p = 11.50 eV) with $XeF^+AsF_6^-$ (1 : 1) for 4 h at room temperature gives the crystalline compound **192** which is stable at room temperature; this compound was characterised by spectral methods.[330]

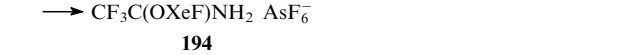


192

The reaction of the salt **193**, prepared by the reaction of trifluoroacetamide (I_p = 10.77 eV) with AsF_5, with xenon difluoride resulted in the organoxenon compound **194**.[333] The salt **193** was isolated in the crystalline state. At 0 °C, it rapidly decomposes to give gaseous products.

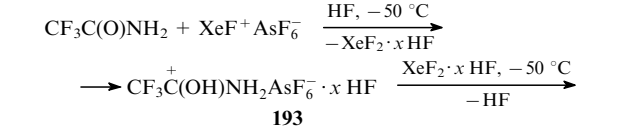


193



194

Rapid removal of HF from a solution containing $XeF^+AsF_6^-$ and $CF_3C(O)NH_2$ at −50 °C affords a white precipitate of composition identical to that of compound **195**; the salt **194** was not detected.[333]



193

$$\longrightarrow CF_3\overset{+}{C}(OH)NH_2AsF_6^- \cdot XeF_2 \cdot x\,HF$$
195

A detailed study of the reaction of xenon difluoride with HN_3, NaN_3 and NaOCN in H_2O, anhydrous HF and SO_2ClF has been published.[334] An analysis of reaction products made it possible to suggest the formation of $FXeN_3$ (**196**) and FXeNCO (**197**) as intermediates, which react according to the following schemes:

$$[FXeN_3] \xrightarrow[-HF,\ -Xe]{H_2O} [HON_3] \xrightarrow{-N_2} [HON] \xrightarrow{-N_2}$$
196

$$\longrightarrow HON{=}NOH \xrightarrow[-H_2O]{} N_2O,$$

$$[FXeNCO] \xrightarrow[-HF,\ -Xe]{H_2O} [HONCO] \xrightarrow{2\,H_2O} HONH_2 + H_2O + CO_2.$$
197

Ab initio quantum-chemical calculations of the structural parameters of both intermediates have been made.[334] The data obtained suggest that the Xe–F bond in the intermediates **196** and **197** (2.051 and 2.024 Å, respectively) is longer than that in bis[(difluorosulfuryl)imido]fluoroxenon **182** (1.97 Å) and in XeF_2 (1.977 Å).[318, 320, 322–325, 328] The calculated length of the Xe–N bond (2.21 Å) in compound **197** is comparable with the experimentally determined value (the length of the corresponding bond in compound **182** is 2.20 Å). The Xe–N distance (2.32 Å) in compound **196** is much longer (2.318 Å).[328] The thermodynamic possibility of formation of the intermediates **196** and **197** was demonstrated using an energy cycle for gas-phase reactions. The enthalpies of the reactions were calculated on the basis of the literature data.[334]

$$XeF_2\,(gas) + NH_3\,(gas) \longrightarrow$$
$$\longrightarrow FXeN_3\,(gas) + HF\,(gas)\ (\Delta H^\circ < -12.1\ kcal\ mol^{-1}).$$

$$XeF_2\,(gas) + HNCO\,(gas) \longrightarrow$$
$$\longrightarrow FXeNCO\,(gas) + HF\,(gas)\ (\Delta H^\circ < -12.1\ kcal\ mol^{-1}).$$

The synthesis of $NO^+XeF_5^-$ and $NMe_4^+XeF_5^-$ in the reaction of XeF_4 with NOF or $Me_4N^+F^-$ (see Ref. 335) and the synthesis of $NF_4^+XeF_7^-$ from XeF_6 and $NF_4^+HF_2^-$ were documented.[336]

VIII. Oxidative fluorination of organoelement compounds by xenon difluoride and its derivatives

Oxidative fluorination of organoelement compounds by xenon difluoride and its derivatives presents theoretical and practical interest. The first reports on the feasibility of oxidative fluorination of iodine to IF_5 (see Ref. 29) and of SO_2 to SO_2F_2 (see Refs. 29 and 337) appeared in the late 1960's to early 1970's. Later, the reactions of other elements, their oxides, halides and carbonyls with XeF_2 were also studied, which demonstrated convincingly the high potentials of the oxidative fluorination.[338]

The transformations of organoelement compounds under the action of XeF_2 are extremely diverse and depend on the structures of the radicals linked to the heteroatom, the degree of oxidation of the heteroatom, the reaction conditions, the nature of the solvent, *etc*. The examples of the application of XeF_2 for fluorination of the majority of classes of organoelement compounds are now available.

1. Reactions of XeF_2 with Group VII organoelement compounds

a. Reactions of organoiodine compounds with XeF_2

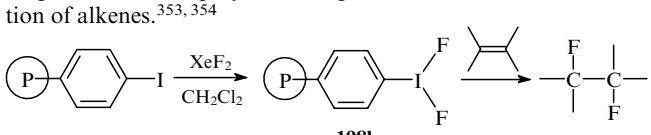
Organoiodine compounds are among the first to have been subjected to oxidative fluorination by XeF_2. These studies were aimed at a search for convenient methods for the preparation of difluoro-λ^3-iodanylalkenes (arenes) used for fluorination of unsaturated compounds.[339–342] The first report on the oxidative fluorination of methyl iodide by XeF_2 was published in the early 1970's. The difluoro-λ^3-iodanylalkene synthesised (**198a**)[339] was rather unstable and could only be characterised by spectral methods. However, despite its low stability this compound was used for iodofluorination of alkenes.[343–346]

Later, this method of the synthesis of difluoro-λ^3-iodanylalkanes (arenes) was extended to a vast variety of alkyl- and aryl iodides. Iodobenzene,[347] substituted aryl iodides[348] as well as perfluoroalkyl- and perfluoroaryl iodides[349] are easily fluorinated by XeF_2. In the case of 1-iodo-3,5-dichlorobenzene and iodopentafluorobenzene, the excess of XeF_2 converts difluoro-λ^3-iodanylarenes into tetrafluoro-λ^5-iodanylarenes in quantitative yields,[349] while the reaction of difluoro-λ^3-iodanylbenzene (**198b**) with XeF_2 results in the fluorination of the aromatic nucleus and the formation of tetrafluoro-λ^5-iodanylbenzene.[349, 350]

$$RI + XeF_2 \xrightarrow{20\ ^\circ C} RIF_2 + Xe$$
198a–k

R = Me (**a**), Ph (**b**), CF_3CH_2 (**c**), C_6F_5 (**d**), 3,5-$Cl_2C_6H_3$ (**e**), 2-$CF_3C_6H_4$ (**f**), 3-$MeOC_6H_4$ (**g**), 4-$MeOC_6H_4$ (**h**), 3-ClC_6H_4 (**i**), 4-ClC_6H_4 (**j**), 3-$NO_2C_6H_4$ (**k**).

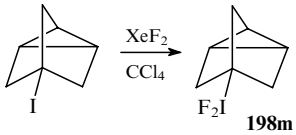
Difluoro-λ^5-iodanylbenzene (**198l**) immobilised on a polymeric support was synthesised using XeF_2 as a soft fluorinating reagent.[351, 352] The polymeric reagent was used for the fluorination of alkenes.[353, 354]



198l

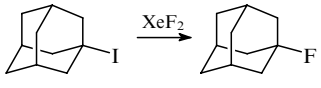
(P) is polymeric support.

In the majority of cases, (difluoro-λ^3-iodanyl)alkanes are unstable.[339] However, treatment of a solution of 4-iodotricyclene in tetrachloromethane with a sixfold excess of XeF_2 and subsequent removal of the solvent and the excess of XeF_2 yield a light-yellow solid stable product **198m**.[355]

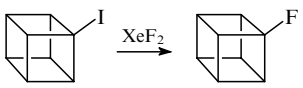


198m

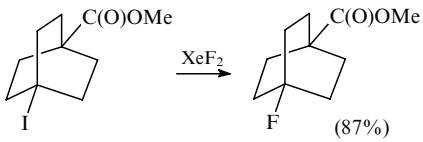
In some cases, the reaction of iodoalkanes with XeF_2 results in the substitution of fluorine for iodine instead of oxidation. This takes place in the reaction of XeF_2 with polycyclic bridged iodides. Fluorinated bicycloalkanes and polycycloalkanes are formed in high yields.[240, 356]



(85%)



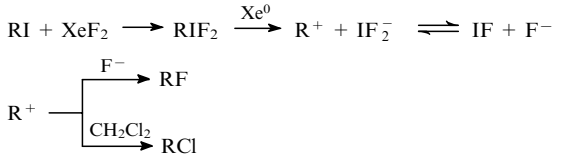
(80%)



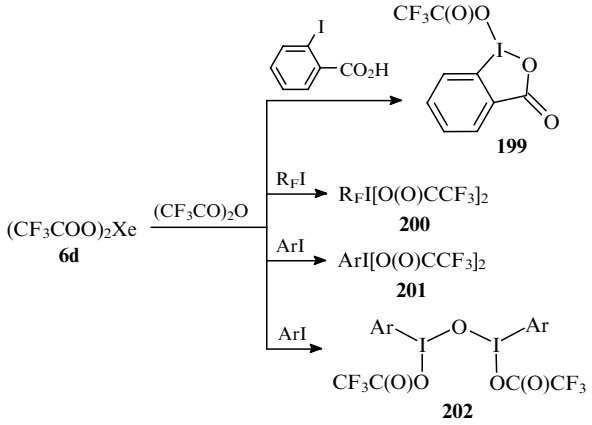
(87%)

It is assumed that this reaction occurs by a carbocationic mechanism. Initially, the difluoro-λ^3-iodanylalkanes generated undergo heterolytic cleavage of the C–I bond to give IF_2^- and the carbocations containing a cationic centre at the head of the bridge.[343] The carbocation can further react either with the fluoride anion to give a fluoride or with CH_2Cl_2 to give a chloride.

Stable cations usually generate fluorides, whereas highly reactive cations, such as cubyl or norbornyl cations, react nonselectively to give chlorides. Their content in the reaction mixture correlates with the calculated values of the carbocation energies.[356]

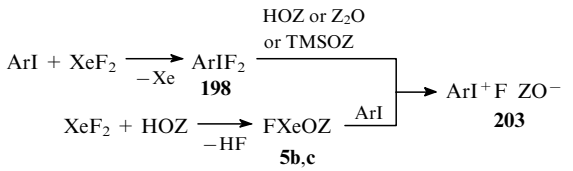


Recently, divalent xenon derivatives other than XeF_2, *e.g.*, xenon bis(trifluoroacetate) (**6d**),[89–91] xenon fluoro(triflate) (**5b**)[89] and xenon fluoro(mesylate) (**5c**),[89] came into use. Thus the reagent (**6d**) obtained *in situ* from XeF_2 and trifluoroacetic acid in the presence of trifluoroacetanhydride reacts with aryl iodides to give bis(trifluoroacetoxy)-λ^3-iodanylarenes **199**–**201**.[357] In the absence of trifluoroacetanhydride, this reaction affords μ-oxobis-[trifluoroacetato(aryl)] iodides (**202**) the structure of which was established by X-ray diffraction analysis.[357, 358]



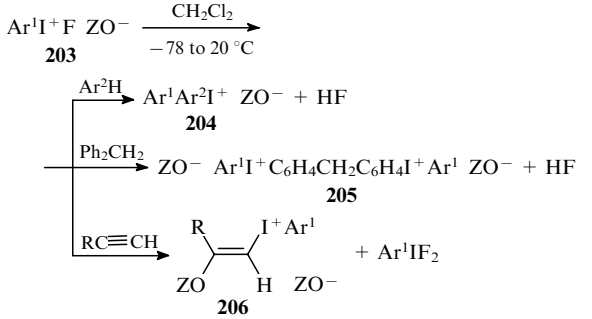
Ar = Ph, 4-MeC_6H_4, 2-MeC_6H_4, 4-PhC_6H_4, 4-[$MeC(O)O]C_6H_4$, 4-$NO_2C_6H_4$, 3-$NO_2C_6H_4$, 2-Me-4-$NO_2C_6H_3$; R_F = C_3F_7, C_4F_9.

A one-step procedure for the generation of iodanylarenes directly from aryl iodides[359–367] is based on their oxidation by xenon fluorosulfonate which gives salts of the type **203**.



Z = Tf (**b**), Ms = SO_2Me (**c**); TMS = Me_3Si.

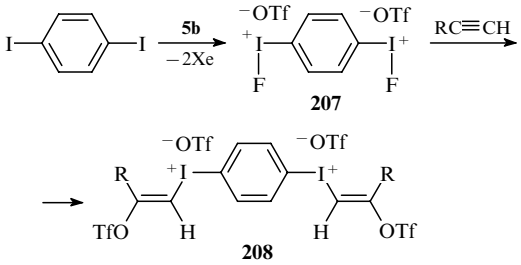
The interest in the sulfonates **203** is due to the fact that they can react with aromatic compounds and terminal alkynes to give the corresponding diaryliodonium (**204**, **205**) and alkenyl(aryl)-iodonium salts **206**.[359, 363, 365]



Z = Tf, Ms; Ar^1, Ar^2 = Ph, 4-MeC_6H_4, 2-MeC_6H_4, 4-$NO_2C_6H_4$;
R = H, Pr^n, Bu^n, n-C_8H_{17}, CH_2OH, CH_2OMe, CH_2Cl, $(CH_2)_2OH$.

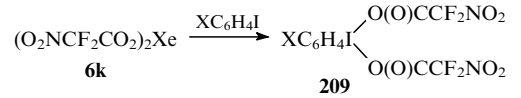
It is noteworthy that in earlier studies the alkenyl(aryl)iodonium sulfonates **206** were obtained by electrophilic addition of [PhIO–HOTf] to alkynes.[368–373] The use of xenon derivatives **5b**,**c** for the synthesis of the salts **203** allows one-pot synthesis of β-functionalised vinyliodonium salts from iodobenzene and terminal acetylenes.

The reagent **5b** oxidises 1,4-diiodobenzene resulting in the bistriflate **207** which reacts with terminal alkynes to yield (*p*-phenylene)alkenyliodonium salts **208**.[364, 365]



R = H, Me, Et, Ph, Pr^n, n-C_8H_{17}, CH_2Cl.

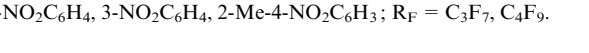
The oxidation of iodoarenes by bis(nitrodifluoroacetoxy)xenon (**6k**) yields the iodonium salts **209** in 65%–80% yields.[374, 375]



X = H, 4-Me, 4-F, 4-MeO, 3-CF_3, 4-NO_2, 4-Cl.

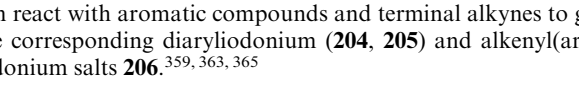
The reaction of $XeF^+AsF_6^-$ with HI in solution has been studied.[376]

According to *ab initio* calculations, the enthalpy of the reaction of XeF_2 with HI is equal to -63.4 kcal mol^{-1} (see Ref. 376).



b. Reactions of organobromine compounds with XeF_2

Nesmeyanov *et al.*[377] have demonstrated that bromine can in principle be oxidised in mononuclear bromoarenes. However, this is possible only with XeF_2. The difluorides **210** formed react with different arenes in the presence of boron trifluoride etherate to give the diarylbromonium salts **211**, their structures were confirmed by independent syntheses, *viz.*, by decomposition of arenediazonium tetrafluoroborates in the presence of the corresponding bromoarenes. In some cases, the formation of bromonium salts could be detected using ^{19}F NMR spectra. The yields of the salts **211** do not exceed 5%. Fluorination and oxidation of aromatic nuclei is the main route of this reaction even at -70 °C.



Ar^1 = 4-FC_6H_4, 4-ClC_6H_4, 4-MeC_6H_4, 2-$MeO_2CC_6H_4$;
Ar^2 = Ph, 4-FC_6H_4, 4-ClC_6H_4, 4-MeC_6H_4.

2. Reactions with Group VI organoelement compounds

a. Reactions of organosulfur compounds with XeF_2

Owing to the high oxidation potential of XeF_2, its reaction with sulfur-containing compounds occurs vigorously at low temperatures. Oxidative fluorination of sulfur-containing compounds, *viz.*, methyl phenyl sulfide, tetrahydrothiopyrones and thiochromanone, by XeF_2 was carried out for the first time in 1976 by Zupan.[378] The reaction of XeF_2 with diaryl or alkyl aryl sulfides results in the formation of sulfur(IV) and sulfur(VI) compounds;

the structures of the original sulfides influence the direction of the reaction. The nature of substituents at the α-carbon atom is the most important factor. The sulfides containing no α-hydrogen atoms are smoothly converted into difluorosulfuranes.[379] The presence of Me, CH_2 and CH fragments vicinal to the sulfur atom results in the formation of α-fluoro sulfides. For example, methyl phenyl sulfide is oxidised to fluoromethyl- (**212**) or difluoromethyl phenyl sulfide (**213**) depending on the amount of XeF_2 used.[378, 379]

$$PhSMe + XeF_2 \xrightarrow[25\ ^\circ C]{HF,\ CH_2Cl_2} \underset{\mathbf{212}\ (67\%)}{PhSCH_2F} \xrightarrow[25\ ^\circ C]{XeF_2\cdot HF,\ CH_2Cl_2} \underset{\mathbf{213}\ (58\%)}{PhSCHF_2}$$

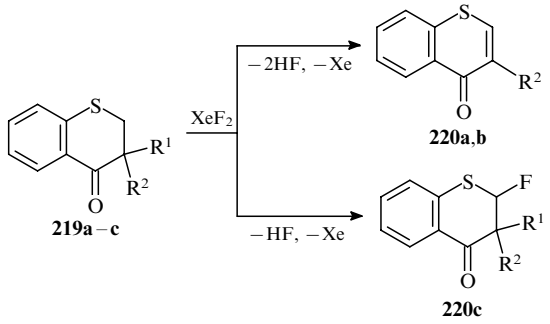
Sometimes, the reaction of alkyl aryl sulfides with XeF_2 gives unsaturated sulfides. This is due to the low stability of α-fluoroalkyl sulfides and their proneness to eliminate HF. Thus the reaction of isopropyl phenyl sulfide with XeF_2 at −10 °C gave the fluorination product **214**, whereas isopropenyl phenyl sulfide (**215**) was obtained at 0 °C.[379]

$$PhSCHMe_2 \xrightarrow{XeF_2} \begin{cases} \xrightarrow[-10\ ^\circ C,\ 30\ min]{MeCN} \underset{\mathbf{214}\ (>90\%)}{PhSCFMe_2} \\ \xrightarrow[0\ ^\circ C,\ 2\ min]{MeCN} \underset{\mathbf{215}\ (>90\%)}{PhSC(Me)=CH_2} \end{cases}$$

The reaction of XeF_2 with diphenyl sulfide and subsequent hydrolysis of the reaction products afford diphenyl sulfoxide or sulfone. Presumably, diphenyldifluoro- (**216**), diphenyldifluorooxo-λ⁴-sulfanes (**217**) and diphenyltetrafluoro-λ⁴-sulfane (**218**) are formed as the intermediate products.[380]

$$Ph_2S \xrightarrow[HF]{XeF_2} \underset{\mathbf{216}}{[Ph_2SF_2]} \begin{cases} \xrightarrow{OH^-} Ph_2SO \xrightarrow[HF]{XeF_2} \underset{\mathbf{217}}{Ph_2S(O)F_2} \xrightarrow{OH^-} Ph_2SO_2 \\ \xrightarrow[HF]{XeF_2} \underset{\mathbf{218}}{Ph_2SF_4} \xrightarrow{OH^-} Ph_2SO_2 \end{cases}$$

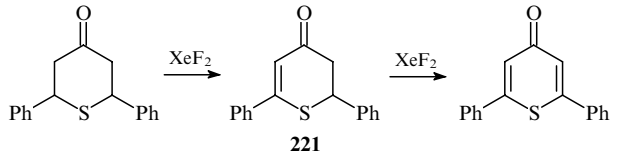
The fluorination of thiochroman-4-one (**219a**) or its 3-bromo derivative (**219b**) results in thiochromen-4-ones (**220a**,**b**), whereas the reaction of 3,3-dibromothiochroman-4-one (**219c**) gives 3,3-dibromo-2-fluorothiochroman-4-one (**220c**).[378, 380]



219a–c **220a**,**b** **220c**

R^1, R^2 = H (**a**); R^1 = H, R^2 = Br (**b**); R^1 = R^2 = Br (**c**).

The reaction of thio-4-pyrone with XeF_2 gives dihydro-2,6-diphenylthio-4-pyrone (**221**) which is dehydrogenated by XeF_2.[378]



221

The reaction of dimethyl sulfide with XeF_2 has been studied in detail. In the absence of a solvent, this reaction is explosive. Dilution of the reaction mixture with trichlorofluoromethane results in FCH_2SMe which further reacts with the excess of dimethyl sulfide to give the salt **222**.[381] It is of note that the reaction of dimethyl sulfide with XeF_2 in the presence of BF_3 or AsF_5 is not accompanied by fluorination of the methyl group but the salts **223** are formed instead.

$$Me_2S \xrightarrow{XeF_2} MeSCH_2F \xrightarrow[HF]{Me_2S} \underset{\mathbf{222}}{[Me_2SCH_2SMe]^+[F(HF)_n]^-}$$

$$Me_2S \xrightarrow[A]{XeF_2} \underset{\mathbf{223}}{[Me_2SF]^+[AF]^-}$$

A = BF_3, AsF_3.

The intermediate formation of the salts **223** in this reaction was confirmed by ^{19}F NMR spectral data and independent synthesis. The cation $[Me_2SCH_2SMe]^+$ is generated only in the presence of a protic acid. It is suggested[381] that $R_2S^+X^-$ or $R_2S^+XeFX^-$ are formed as intermediates. The latter are used[382] for the fluorination of carbanions.

The reactions of sodium derivatives of diethyl malonate or of substituted malonates with XeF_2 in CH_2Cl_2 result in the dimers **224**. The fluorination products **225** were isolated in the presence of $BF_3\cdot Et_2O$. The methylthio derivatives of the malonates **226** are formed along with the fluorination products **225** after addition of dimethyl sulfide to the reaction mixture.[382] It is interesting to note that the reaction of diethyl nitromalonate with XeF_2 gives only a dimer of the type **224**.

$$RC^-(CO_2Et)_2Na^+ \xrightarrow[CH_2Cl_2]{XeF_2} \underset{\mathbf{224}}{\left[\begin{array}{c}(EtO_2C)_2C\\|\\R\end{array}\right]_2}$$

$$RC^-(CO_2Et)_2Na^+ \xrightarrow[CH_2Cl_2,\ BF_3\cdot Et_2O]{XeF_2} \underset{\mathbf{225}}{\begin{array}{c}RC(CO_2Et)_2\\|\\F\end{array}}$$

$$RC^-(CO_2Et)_2Na^+ \xrightarrow[BF_3\cdot Et_2O,\ Me_2S]{XeF_2,\ CH_2Cl_2,} \mathbf{225} + \underset{\mathbf{226}}{\begin{array}{c}RC(CO_2Et)_2\\|\\SMe\end{array}}$$

R = H, Me, Et, C_5H_{11}, Bn, NO_2.

The highest yields of the reaction products are obtained for equimolar ratios of the reagents and at low temperatures (−78 °C).[382]

The reaction of XeF_2 with fluorinated sulfides generated easily hydrolysable aryl trifluoromethyl difluorosulfuranes **227**.[383]

$$4\text{-}RC_6H_4SCF_3 + XeF_2 \xrightarrow{HF} \underset{\mathbf{227}}{4\text{-}RC_6H_4SF_2CF_3} + Xe$$

R = H, Cl, NO_2.

Thus, the reaction of sulfides with XeF_2 affords three main types of reaction products, *viz*., α-fluoroalkyl sulfides, dehydrofluorination products and sulfoxides or sulfones. A mechanism of this reaction has been proposed.[384]

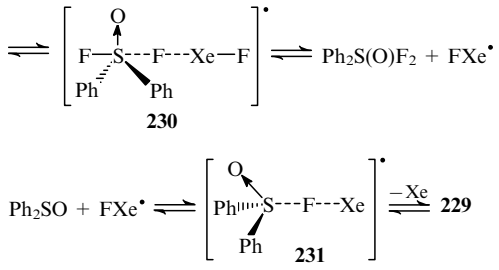
The reaction of Ph_2SO with XeF_2 in the presence of ~1% solution of Et_4NCl in CH_2Cl_2 at 20 °C results in the difluoride **217** in quantitative yield.[385]

$$Ph_2SO + XeF_2 \xrightarrow[CH_2Cl_2]{Et_4NCl} \underset{\mathbf{217}}{Ph_2S(O)F_2} + Xe$$

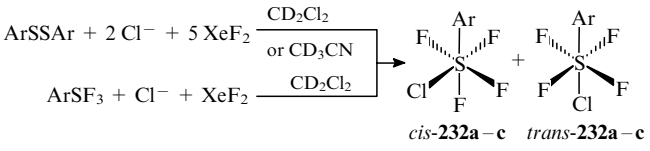
In the absence of Cl^-, the reaction is sluggish (2–6 days). Apparently, the chloride anion promotes the generation of the fluoride anion, which behaves as a strong base in CH_2Cl_2 in the absence of HF.[386, 387] The reaction mechanism proposed by Ou and Janzen[385] which includes the formation of the anion **228** and its oxidation to the radicals **229**–**231** is corroborated experimentally by the identification of the radical XeF• (spectroscopic data).[388]

$$2Cl^- + XeF_2 \longrightarrow 2F^- + Cl_2 + Xe$$

$$Ph_2SO \underset{}{\overset{F^-}{\rightleftharpoons}} \underset{\mathbf{228}}{Ph_2S(O)F^-} \overset{e^-}{\rightleftharpoons} \underset{\mathbf{229}}{Ph_2S(O)F^\bullet} \overset{XeF_2}{\rightleftharpoons}$$

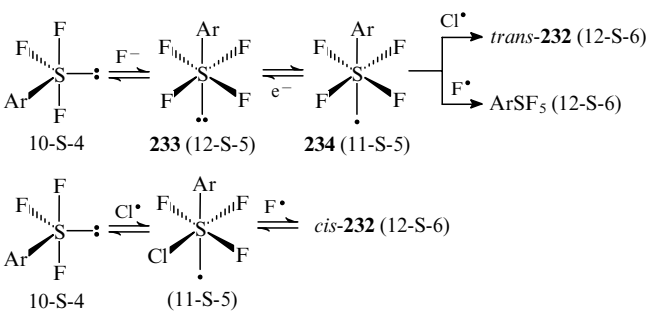


Compounds **232a–c** (*cis*- and *trans*-isomers) were synthesised in the reaction of XeF_2 with ArSSAr or $ArSF_3$ in the presence of a chloride anion source, *viz*., Et_4NCl.[389] Individual isomers can be obtained by varying the reaction conditions and the ratios of the reagents. The maximum yield of the *trans*-**232a** (89%) is achieved for the $Ph_2S_2 : Et_4NCl : XeF_2$ ratio of 1 : 2 : 8, that of the *cis*-**232c** (83%), for the $(4\text{-}O_2NC_6H_4)_2S_2 : Et_4NCl : XeF_2$ ratio of 1 : 2 : 6. In each case, the formation of side products ($ArSF_5$ and $ArSOF_3$) and fluorination of the solvent took place.

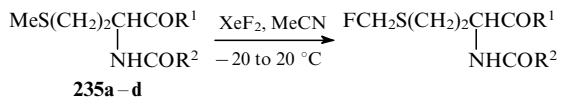


Ar = Ph (**a**), 4-MeC_6H_4 (**b**), 4-$O_2NC_6H_4$ (**c**).

A scheme with the nomenclature N-X-L (where X is the central atom, N is the number of valent electrons and L is the number of ligands)[390] illustrates the mechanism of this reaction which includes the formation of the anion **233**, its oxidation to the radical **234**[391] and subsequent recombination.[389] With a decrease in the content of the radical Cl•, the concentration of $ArSF_5$ should increase, which was confirmed experimentally.[389]



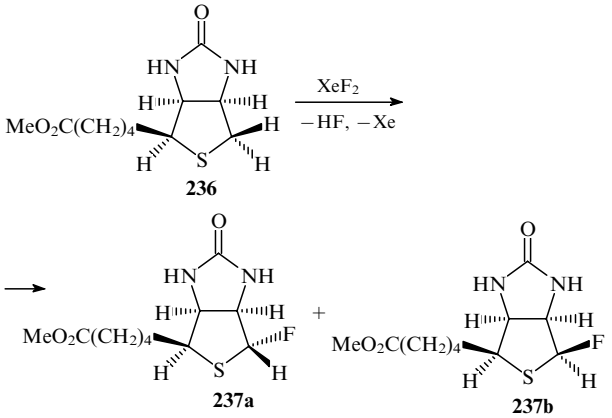
The highly selective oxidative fluorination of sulfides by XeF_2 was used for incorporating one or two fluorine atoms into the carbon chains of biologically active substances. For example, the fluorination of the methionine derivatives **235a–d** by XeF_2 (−20 to 20 °C) occurs regiospecifically and involves the MeS group.[392, 393]



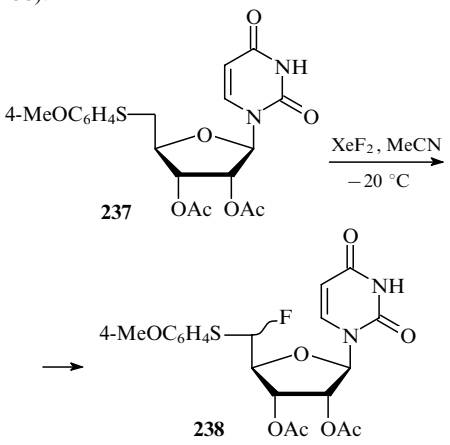
235a–d

R^1 = OMe, R^2 = CF_3 (**a**); R^1 = $OC_6H_4NO_2$-4, R^2 = OBu^t (**b**);
R^1 = $OC_6H_4NO_2$-4, R^2 = CF_3 (**c**); R^1 = $NHCH_2C(O)OEt$,
R^2 = OCH_2Ph (**d**).

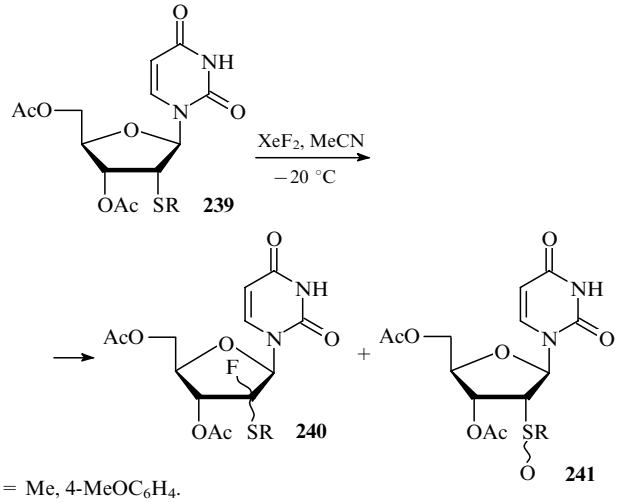
The reaction of XeF_2 with methyl ester of β-biotin (**236**) results in the diastereomers of 6-fluorobiotin methyl ester **237a**,**b**.[394]



The reaction of 2′,3′-di-*O*-acetyl-5′-*S*-(4-methoxyphenyl)-5′-thiouridine (**237**) with XeF_2 yields a mixture of diastereomeric 2′,3′-di-*O*-acetyl-5′-fluoro-5′-*S*-(4-methoxyphenyl)-5′-thiouridines (**238**).[395]



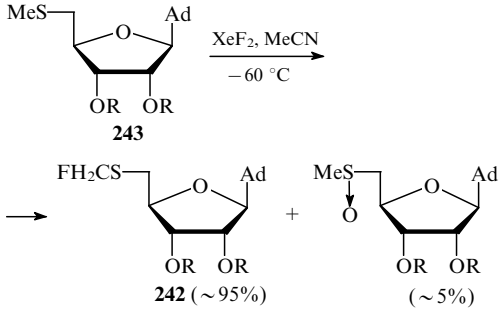
Xenon difluoride was also used for the fluorination of 3′,5′-di-*O*-acetyl-2′-*S*-alkyl(aryl)-2′-thiouridines. Thus the reaction of compound **239** with XeF_2 affords a mixture of diastereoisomeric 3′,5′-di-*O*-acetyl-2′-*S*-alkyl(aryl)-2′-fluoro-2′-thiouridines **240** in 22% yield.[396] This reaction is accompanied by partial oxidation of the sulfur atom in the initial sulfides **239** and the formation of the sulfoxides **241**.



R = Me, 4-$MeOC_6H_4$.

A convenient method for the synthesis of 5′-(fluoromethylthio)adenosine derivatives (**242**) (yield 70%) by regioselective fluorination of 5-methylthioadenosine derivatives **243** by XeF_2 has been proposed.[397] In this case, as in the fluorination of the

5′-arylthioadenosine,[398] methionine [392] and biotin derivatives,[394] the reaction occurs at the least substituted carbon atom.



R = Bz, Ac; Ad is 9-adenine.

In contrast to sulfides, thiols and thiophenols are not fluorinated by XeF_2, but are usually oxidised to disulfides in quantitative yields. The structure of the radical at the sulfur atom and the thiol : XeF_2 ratio do not influence the direction of this reaction.[379]

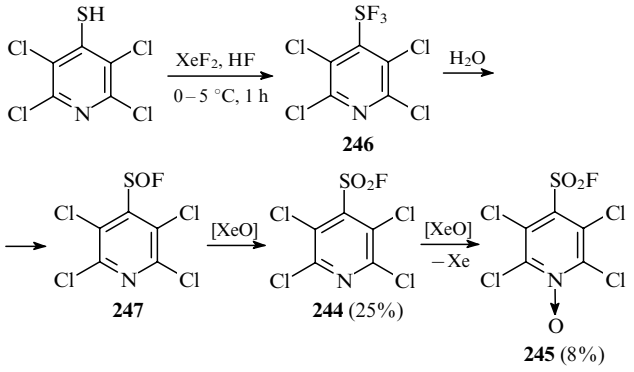
$$2\,RSH + XeF_2 \longrightarrow RSSR + 2\,HF + Xe$$

R = Me, Pr^i, Bu^t, Ph.

Under drastic conditions, disulfides also react with XeF_2. Thus, fusion of bis(pentafluorophenyl) disulfide with XeF_2 at 85 °C in a sealed tube for 3 h yields a mixture of $C_6F_5SF_3$ and C_6F_5SOF which are identified by their ^{19}F NMR spectra (see Ref. 20).

$$C_6F_5SSC_6F_5 + XeF_2 \xrightarrow[-Xe]{} C_6F_5SF_3 \xrightarrow{H_2O} C_6F_5S(O)F$$

The use of XeF_2 in reactions with polychloropyridinethiols allowed one to develop new methods for perfluoroalkylation and oxyfluorination of thiol groups as well as for the oxidation of polychloropyridines to *N*-oxides. Thus the reaction of 2,3,5,6-tetrachloropyridine-4-thiol with XeF_2 in HF gave 4-fluorosulfonyl-2,3,5,6-tetrachloropyridine (**244**) and 4-fluorosulfonyl-2,3,5,6-tetrachloropyridine *N*-oxide (**245**).[399,400] This reaction is accompanied by oxidation of the original thiol into bis(2,3,5,6-tetrachloro-4-pyridyl) disulfide.



A reaction scheme which allows one to get insight into the mechanism of formation of the fluorosulfonyl fragment has been suggested.[400] Initially, the thiol group is fluorinated by XeF_2 in the presence of HF to the derivative **246** which is easily hydrolysed to the sulfoxide **247** and the sulfonylfluoride **244**. The latter can be converted into compound **245** by oxidation with [XeO] species formed in the hydrolysis of XeF_2 (the bonding energy of Xe—O is 7 kcal mol^{-1} which corresponds to the weakly bound atomic oxygen).[62–64]

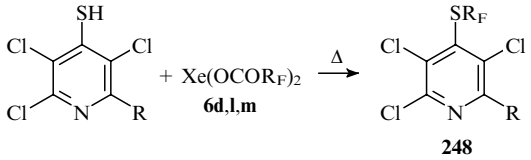
A new method for perfluorination of polychloropyridinethiols which is based on the thermolysis of the xenon bisperfluorocarboxylates **6d**,**l**,**m** in the presence of thiols has been described.[242, 399–404]

Table 2. Perfluoroalkylation of pyridinethiols.

Reagent (method of generation)	Compound **248**	R	R_F	Yield (%)	Ref.
6d (A)	**a**	Cl	CF_3	66	242
6d (B)	**a**	Cl	CF_3	36.5	242, 399
6d (A)	**b**	CCl_3	CF_3	45	242
6d (A)	**c**	CN	CF_3	50	242
6l (B)	**d**	Cl	C_3F_7	85	242, 399
6m (B)	**e**	Cl	C_2F_5	85	404

Thermolysis is carried out either using the preformed reagents **6d**,**l**,**m** (method A) or with the simultaneous *in situ* generation of the xenonates **6d**,**l**,**m** (method B).

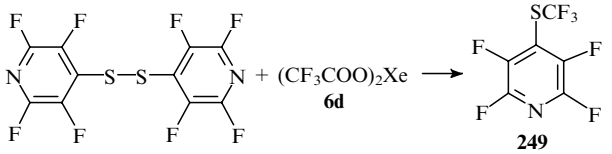
This reaction yields the polychloroperfluoroalkylthiopyridines **248**; their yields depend on the mode of generation of the xenonates **6d**,**l**,**m** (Table 2). It was found that the reactivity of the thiol group decreases with an enhancement of the acceptor properties of the substituent R.[242, 399–404]



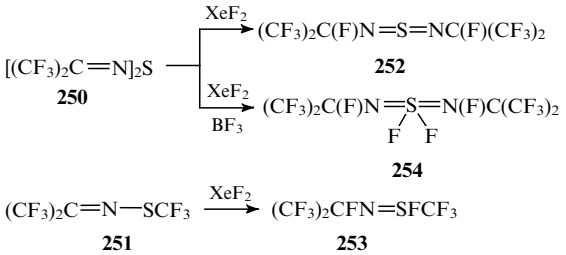
R_F = CF_3 (**d**), C_2F_5 (**l**), C_3F_7 (**m**).

This method allows direct perfluoroalkylation of thiols including those containing substitution-sensitive groups.[405]

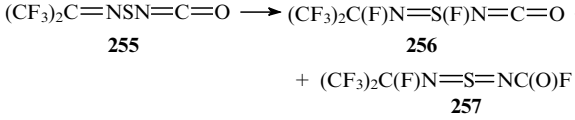
4-Trifluoromethyl-2,3,5,6-tetrafluorothiopyridine (**249**) is formed upon the *in situ* generation of the xenonate **6d** in the presence of di(1,3,5,6-tetrafluoro-4-pyridyl) disulfide with simultaneous thermolysis at 50–60 °C (yield 41%).[242, 406]

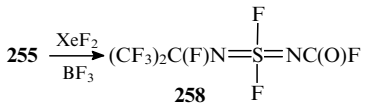


Xenon difluoride selectively oxidises the sulfur atom in compounds containing the S—N bond and the S—N bond is retained. Thus the S(IV) derivatives **252** and **253** containing the imidosulfenyl group are formed from compounds **250** and **251** in the absence of a catalyst, whereas compound **252** is further oxidised into S(VI) compound **254,** when BF_3 is used as a catalyst.[407]

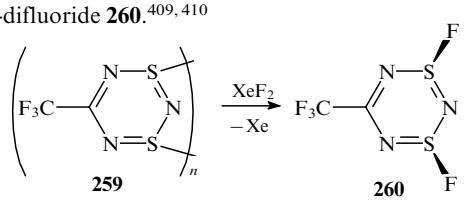


The pseudo-triene system of the isocyanate **255** undergoes 1,3- and 1,5-difluorination by XeF_2 in the absence of a catalyst resulting in compounds **256** and **257**. The N^1-(heptafluoroisopropyl)-N^2-(fluorocarbonyl)-*S*,*S*-difluorosulfodiimide (**258**) is formed in the presence of BF_3.[408]





The oligomeric di-λ^4-thiatriazine **259** is easily fluorinated by XeF_2 with the preservation of the ring and the formation of the *cis*-difluoride **260**.[409,410]



N-Sulfinylperfluoroalkylamines **261** are converted into *N*-perfluoroalkyl-*S*,*S*-difluorosulfoximides **262** by XeF_2 in perfluorodecalin.[411]

$$\underset{\mathbf{261}}{R_FNSO} + XeF_2 \xrightarrow[-Xe]{20\ ^\circ C} \underset{\mathbf{262}}{R_FNSOF_2}$$

R_F = CF_3 (54%), C_2F_5 (50%).

The synthesis of sulfonyl fluorides from sulfonyl chlorides is effected by direct substitution of fluorine for chlorine. For example, the reaction of XeF_2 with methane-, benzene-, *p*-toluene- and pentafluorobenzenesulfonyl chlorides affords the corresponding sulfonyl fluorides as the main products upon heating for 4–10 h (yields 20%–80%). This reaction is carried out in acetonitrile or without the solvent. In some cases, fluorination of the aromatic nucleus takes place.[412]

$$RSO_2Cl \xrightarrow{XeF_2} RSO_2F$$

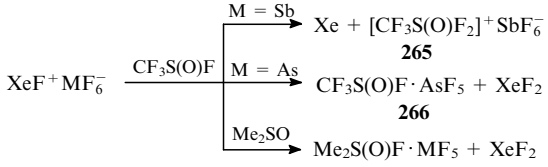
R = Me, Ph, C_6F_5, *p*-MeC_6H_4.

Recent reports suggest the use of $XeF^+MF_6^-$ salts (M = As, Sb) as the oxidants. It was shown in particular that $XeF^+MF_6^-$ reacts with the sulfides R^1SR^2 ($R^1 = R^2 = C_6F_5$;[413] $R^1 = CF_3$, $R^2 = Me$;[414,415] $R^1 = R^2 = Me$[381,414,415]) and thiols RSH [R = Me, CF_3 (see Ref. 416)] to give the fluorosulfonium cations of the type $R^1R^2S^+(F)MF_6^-$ and with disulfides R^1SSR^2 [$R^1 = R^2 = CF_3$; $R^1 = Me$, $R^2 = CF_3$; $R^1 = R^2 = Me$;[417] $R^1 = R^2 = Cl$ (see Ref. 418)] to give the sulfonium salts $[R^1SS(F)R^2]^+MF_6^-$. The reaction of the λ^4-sulfanes **263** with $XeF^+MF_6^-$ (M = As, Sb) gives the corresponding fluorosulfonium salts **264** and XeF_2[418] which cannot convert S(IV) into S(VI) due to its lower oxidation capacity in comparison with the cation XeF^+ (see Ref. 326).

$$\underset{\mathbf{263}}{R_nSF_{4-n}} + XeF^+MF_6^- \longrightarrow \underset{\mathbf{264}}{R_nS^+F_{3-n}MF_6^-} + XeF_2$$

R = CF_3; n = 0, 1, 2; M = As, Sb.

It should be noted that in the case of the λ^4-sulfanes **263**, $XeF^+MF_6^-$ salts behave as Lewis acids rather than oxidants. Their oxidative properties are manifested in the reaction with trifluoromethane sulfinyl fluoride. The S–F bond in $CF_3S(O)F$ is relatively strong as can be judged from its length (1.591 Å).[419] Depending on the nature of the element, this reaction affords either (trifluoromethyl)difluorosulfinyl hexafluoroantimonate (**265**) or the adduct **266**.[419] The reaction with dimethyl sulfoxide gives similar adducts.[419]



M = As, Sb.

The reaction of bis(trifluoromethyl) sulfoxide with $XeF^+SbF_6^-$ yields the salt **267** which was identified by spectral methods.[419,420] It is assumed that its first step involves a cationic attack of the sulfoxide oxygen atom by XeF^+, whereas the second step consists in the intramolecular migration of the fluoride anion to the sulfur atom. The second step seems to be hindered by steric shielding of the reaction centre by two CF_3 groups.[327]

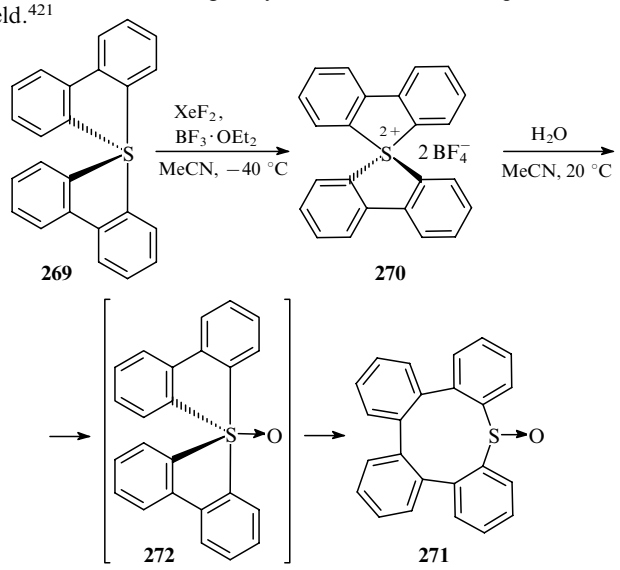
$$(CF_3)_2SO + XeF^+SbF_6^- \longrightarrow \underset{\mathbf{267}}{[(CF_3)_2SOXeF]^+SbF_6^-}$$

The reaction of thionyl chloride with $XeF^+MF_6^-$ is accompanied by the elimination of Xe and the formation of the salt **268**.[419]

$$2OSCl_2 + 3XeF^+MF_6^- \longrightarrow \underset{\mathbf{268}}{2[OSClF_2]^+MF_6^-} + Cl_2 + MF_5 + 3Xe$$

M = As, Sb.

The reaction of bis(2,2′-biphenylyl)-λ^4-sulfane **269** with 1 equiv. of XeF_2 in the presence of $BF_3 \cdot OEt_2$ gives the bis(tetrafluoroborate) **270** which reacts with excess water or a dilute solution of an alkali to give cyclic sulfoxide **271** in a quantitative yield.[421]



The formation of the sulfoxide **271** is associated with the C–C ligand coupling in the oxide **272**.[422]

The first compound containing the Xe–S bond, *viz*., HXeSH, was studied by spectral methods.[423,424] It was generated by photolysis of H_2S in a xenon matrix at 7.5 K and represents a particular case of a compound with the general formula HXY, where X = Xe, Kr, and Y is the fragment with a higher electron affinity (H, Cl, Br, I, CN, NC).[425–428]

b. Reactions of organoselenium compounds with XeF_2

For selenium, the transition into a four-coordinated state occurs much easier than for sulfur. Aryl trifluoromethyl selenides form more stable fluorides with XeF_2 than the corresponding sulfides. Thus compounds **273** react with XeF_2 in the presence of HF to give aryl trifluoromethyl difluoro-λ^4-selanes **274** in quantitative yields.[429] Bis(pentafluorophenyl) diselenide forms the pentafluorophenyl trifluoro-λ^4-selane (**275**) with XeF_2.

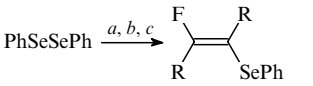
$$\underset{\mathbf{273}}{4\text{-}RC_6H_4SeCF_3} \xrightarrow[HF]{XeF_2} \underset{\mathbf{274}}{4\text{-}RC_6H_4SeF_2CF_3}$$

R = H, Cl, NO_2.

$$C_6F_5SeSeC_6F_5 \xrightarrow[HF]{XeF_2} \underset{\mathbf{275}}{C_6F_5SeF_3}$$

An efficient procedure for vicinal fluoroselenenation of alkynes by addition of synthetic equivalents of the selanyl fluoride

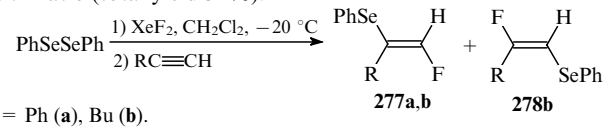
RSeF generated *in situ* from XeF_2, diaryl, dibenzyl or dialkyl diselenides has been developed.[430] The direction of this reaction depends on the structures of the alkyne and the diselenide. Thus symmetric dialkylacetylenes react smoothly with XeF_2 and diphenyl diselenide to give the vicinal (fluoroalkenyl)phenyl selenides **276** in high yields.[430]



276 (72% – 87%)

R = Me, Et, Pr, Bu; (*a*) XeF_2, CH_2Cl_2, −20 °C, 15 min;
(*b*) RC≡CR, −20 °C, 0.5 h, (*c*) 20 °C, 1 h.

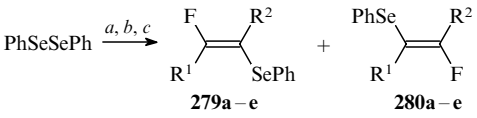
Terminal alkynes do not react with PhSeBr and AgF (sonication);[431] phenylacetylene forms the adduct **277a** with XeF_2 and diphenyl diselenide in 27% yield. Under these conditions, hex-1-yne affords a mixture of *E*-isomers of the adducts **277b** and **278b** in a 3 : 1 ratio (total yield 31%).[430]



277a,**b** **278b**

R = Ph (**a**), Bu (**b**).

The reaction of asymmetrical inner alkynes with XeF_2 and $(PhSe)_2$ also results in the vicinal fluoroselenenation products **279a**–**e** and **280a**–**e** (total yield 26% – 83%).[430]

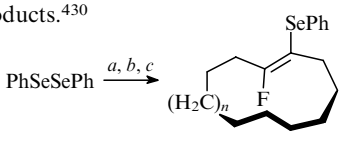


279a–**e** **280a**–**e**

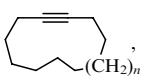
R^1 = Ph, R^2 = Me (**a**); R^1 = Bu, R^2 = Me (**b**); R^1 = Bu, R^2 = Et (**c**);
R^1 = Bu, R^2 = Pr^i (**d**); R^1 = Bu, R^2 = Bu^t (**e**);
(*a*) XeF_2, CH_2Cl_2, −20 °C, 15 min;
(*b*) $R^1C{\equiv}CR^2$, −20 °C, 0.5 – 2 h; (*c*) 20 °C, 1 – 2.5 h.

Compounds **279** or a mixture of the selenides **279** and **280** are exclusively formed depending on the nature of the substituent in the alkyne. Thus 1-phenylpropyne and the sterically hindered 2,2-dimethyloct-3-yne react with XeF_2 and $(PhSe)_2$ to give exclusively the isomers **279a**,**e**, while hept-2-yne and oct-3-yne give a mixture of the isomeric selenides **279b**,**c** and **280b**,**c** in a *ca.* 1 : 1 ratio. The proportion of the isomer **279d** increases significantly in the case of 2-methyloct-3-yne.[430]

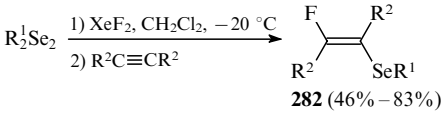
It can be expected that cycloalkynes will behave similarly in reactions with XeF_2 and $(PhSe)_2$. However, it was found that only cycloundecyne and cyclododecyne react selectively to give the adducts **281a**,**b** (yields 68% and 80%, respectively), whereas cyclooctyne and cyclodecyne yield a mixture of non-identified products.[430]



281a,**b**

n = 1 (**a**), 2 (**b**); (*a*) XeF_2, CH_2Cl_2, −20 °C, 15 min; (*b*) , −20 °C, 1 h; (*c*) 20 °C, 1 h.

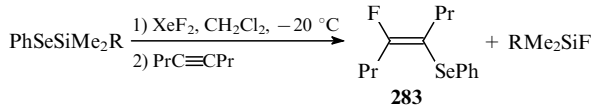
The reactions of other diselenides with XeF_2 and alkynes including functionally substituted ones have been studied.[432] These reactions resulted in the adducts **282**.[430, 432]



282 (46% – 83%)

R^1 = Me, Et, Pr^i, Bn, Bu^t, 2-$NO_2C_6H_4$, $CH_2CH(OMe)_2$, $(CH_2)_3CO_2Et$, $(CH_2)_3CO_2H$, $(CH_2)_2NMe_2$, CH_2SiMe_3; R^2 = Me, Et, Pr, Bu.

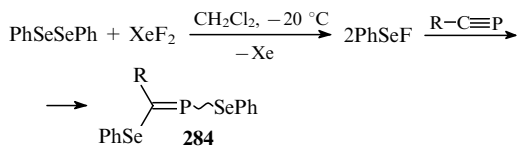
Trimethylphenylselanylsilane and *tert*-butyldimethylphenylselanylsilane react with oct-4-yne under analogous conditions to give the adducts **283** (yields 73% and 82%, respectively). Contrary to expectations, alkynes do not react with the PhSeNCO – XeF_2 system.[430]



283

R = Me, Bu^t.

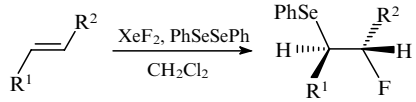
The fluorophenylselenenation of various phosphaalkynes resulting in the adducts **284** has been studied.[433]



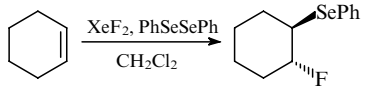
284

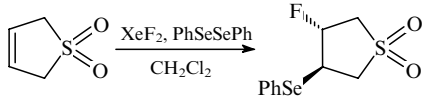
R = Bu^t, adamantyl.

Alkenes also react with XeF_2 and $(PhSe)_2$ in CH_2Cl_2 to give readily hydrolysable vicinal phenylselanylfluoroalkanes. The yields of the products depend on the reaction conditions and decrease dramatically with an increase in temperature.[434]



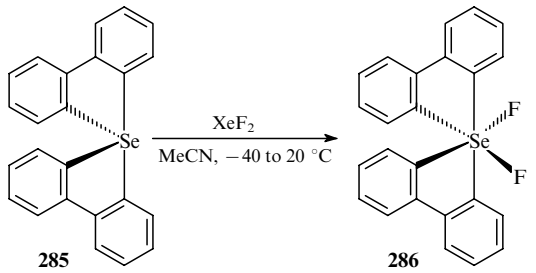
R^1 = H, Me, Bu, CH_2CN; R^2 = H, CH_2CN, CO_2Me, SO_2Ph.





The *in situ* generated PhSeF is more reactive than PhSeCl or PhSeBr; it reacts even with electron-deficient alkenes and 2,5-dihydrothiophene 1,1-dioxide. Since the Se – F bond is more polar than the Se – Cl and Se – Br bonds, the PhSe fragment in PhSeF bears a higher positive charge than that in PhSeBr and PhSeCl and is therefore more electrophilic. Indirect evidence in favour of this assumption was obtained from spectral data.[434]

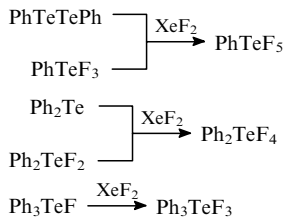
Bis(2,2′-biphenylene)-λ^4-selane (**285**) reacts with XeF_2 in acetonitrile at −40 °C to give the bis(2,2′-biphenylene)difluoro-λ^6-selane (**286**) in 54% yield.[435]



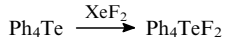
285 **286**

c. Reactions of organotellurium compounds with XeF_2

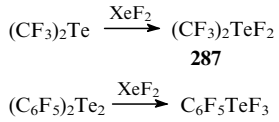
Organotellurium compounds react smoothly with XeF_2 to give derivatives of Te(IV) and Te(VI). XeF_2 was successfully used for the synthesis of a vast variety of aryltellurium(VI) fluorides from diaryl tellurides or Te(IV) derivatives.[389, 436]



X = F, Cl, Br.



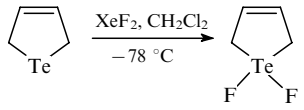
Bis(trifluoromethyl)tellurium difluoride **287** was synthesised by fluorination of bis(trifluoromethyl) telluride by XeF_2 in an acetonitrile–Freon-11 mixture.[437] Bis(pentafluorophenyl) ditelluride reacts with XeF_2 to give the pentafluorophenyltellurium trifluoride (**288**) with the cleavage of the Te–Te bond and the oxidation of Te(II) to Te(IV).[429]



287

288

The oxidative fluorination of 2,5-dihydrotellurophene by xenon difluoride results in 2,5-dihydrotellurophene 1,1-difluoride (**289**).[438]



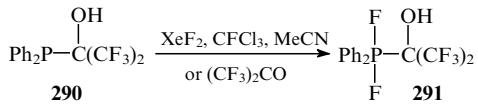
289

Special mention should be made of an unsuccessful attempt at the fluorotellurination of oct-4-yne by the Ph_2Te_2–XeF_2 or $PhTeSiMe_3$–XeF_2 systems.[430]

3. Reactions of XeF_2 with Group V organoelement compounds

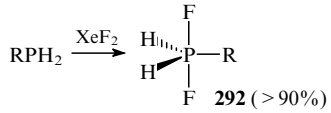
a. Reactions of organophosphorus compounds with XeF_2

Xenon difluoride smoothly oxidises phosphorus(III) to phosphorus(V) in various phosphorus derivatives. Under these conditions, other functional groups present in the molecule are not involved as a rule. Thus the oxidation of (1-hydroxyhexafluoroisopropyl)diphenylphosphine (**290**) yields the pentavalent phosphorus derivative **291**.[439]

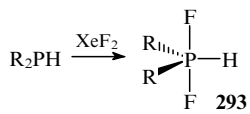


290 **291**

High selectivity is also observed in the oxidation of compounds containing a P–H bond. Thus the reaction of primary and secondary phosphines with XeF_2 gives the corresponding difluorides **292** and **293** in high yields.[347, 440]



292 (>90%)



293

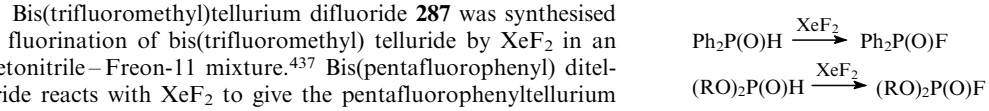
R = Ph, CH_2CH_2CN.

Oxidative fluorination also takes place in reactions with arylchlorophosphines **294** where it occurs simultaneously with the substitution of fluorine for chlorine. Triphenylphosphine (**294d**) is quantitatively converted into triphenyldifluorophosphorane **295d**,[347] whereas the chlorine-containing phosphines **294a**–**c** react with XeF_2 to give the fluoro-substituted phosphoranes **295a**–**c** in quantitative yields. No intermediate formation of chlorofluorophosphoranes was detected.[353]

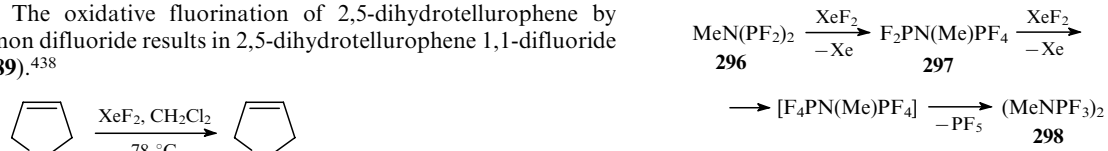


n = 0 (**a**), 1 (**b**), 2 (**c**), 3 (**d**).

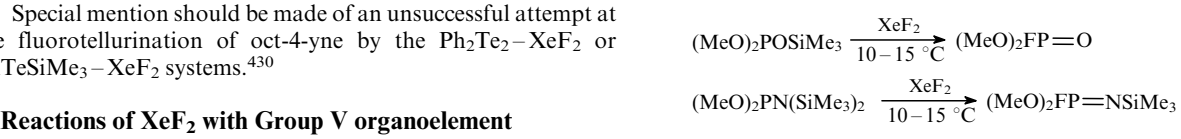
The fluorination of four-coordinated phosphorus derivatives containing P–H bonds results in fluorides.[441]



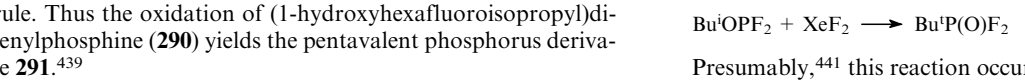
The oxidation of organic derivatives of phosphorus(III) containing P–N, P–S or P–O bonds is complicated due to easy elimination of PF_5 which is accompanied by the formation of compounds containing a P = X fragment (X = N, O, S). For example, the fluorination of bis(difluorophosphino)methylamine (**296**) by XeF_2 gives difluorophosphino(tetrafluorophosphoranyl)methylamine (**297**), which undergoes dimerisation to give compound **298**.[442]



Silyl esters and silyl-substituted amides of trivalent phosphorus acids are oxidised by XeF_2 to dialkylphosphofluoridates or dialkyl fluorophosphazenes, respectively.[441]



An unusual reaction takes place on the interaction of isobutyl phosphodifluoridite with catalytic amounts of XeF_2. In this case, the *tert*-butylphosphonic difluoride was isolated as the main product in 50% yield.[441, 443]



Presumably,[441] this reaction occurs through the formation of alkoxytetraphenylphosphorane, which disproportionates with the formation of the isobutyl cation.[443] The latter undergoes isomerisation and reacts with the original phosphite to afford the final product.

b. Reactions of organoarsenic derivatives with XeF_2

The reactions of XeF_2 with organoarsenic derivatives were studied in the single example.[351]



It is quite probable that in other cases the behaviour of As(III) compounds in the reaction with XeF_2 will also not be different from that of P(III) derivatives.

c. Reactions of organoantimony compounds with XeF_2

To date, reactions of XeF_2 with antimony derivatives have been studied relatively little.

Xenon difluoride fluorinates aromatic derivatives of trivalent antimony in quantitative yields under mild conditions. Trifluorodiphenylantimony and difluorotriphenylantimony were prepared from fluorodiphenylstibine (or trifluorodiphenylacetoxystibine) and triphenylstibine, respectively.[444] Tris(pentafluoro-

phenyl)stibine yields difluoro tris(pentafluorophenyl)antimony in its reaction with XeF_2.[262]

$$Sb(C_6F_5)_3 \xrightarrow{XeF_2} Sb(C_6F_5)_3F_2 + Xe$$

d. Reactions of organobismuth compounds with XeF_2

Oxidative fluorination of triphenylbismuth with XeF_2 is the most convenient and available method for the preparation of trisubstituted bismuth difluoride[445] which is interesting as a fluorinating reagent.[446, 447]

$$Ar_3Bi + XeF_2 \longrightarrow Ar_3BiF_2 + Xe$$

Ar = Ph, C_6F_5.

However, tris(trifluoromethyl)bismuth yields the bismuth trifluoride, CF_4 and Xe even at −60 °C. Their formation is attributed either to the trifluoromethylation of the XeF^+ intermediate or the degradation of the pentavalent bismuth derivative.[445]

$$Bi(CF_3)_3 + 3\,XeF_2 \longrightarrow BiF_3 + 3\,CF_4 + 3\,Xe$$

The reactions of XeF_2 or $XeF^+MF_6^-$ (M = As, Sb, Ta) with tris(pentafluorophenyl)bismuth have been studied.[448] In both cases, $(C_6F_5)_3BiF_2$ was isolated from the reaction mixture with trace amounts of pentafluorobenzene which provides indirect support for the formation of xenon compounds, such as C_6F_5XeF or $C_6F_5Xe^+MF_6^-$.[262]

4. Reactions of XeF_2 with Group IV organoelement compounds

a. Reactions of organosilicon compounds with XeF_2

Reactions of organosilicon compounds with XeF_2 were studied for compounds containing Si−Cl, Si−H, Si−C, Si−O, Si−S and Si−N bonds.

The reactions of XeF_2 with chlorosilanes are completed within several minutes. However, the yields of fluorosilanes depend on the number of chlorine atoms to be substituted in the original molecule. Mono- and dichlorosilanes are easily fluorinated to give fluoro- and difluorosilanes.[440]

$$2R_3SiCl + XeF_2 \xrightarrow{MeCN} 2R_3SiF + Xe + Cl_2$$

$$Me_2SiCl_2 + XeF_2 \xrightarrow{MeCN} Me_2SiF_2 + Xe + Cl_2$$

R = Me, Et, Ph.

If the molecule contains a hydrogen atom, difluorosilanes are formed in satisfactory yields. A stepwise mechanism of this reaction which includes initial fluorination of the Si−H bond has been proposed.[440]

$$R_2SiHCl \xrightarrow{XeF_2} R_2SiHF \xrightarrow{Cl_2} R_2SiClF \xrightarrow{XeF_2} R_2SiF_2$$

R = Ph, Me.

Triarylchlorosilanes yield products of more profound conversions.[440]

The reaction of allylchlorodimethylsilane with XeF_2 is accompanied by the cleavage of the Si−C bond to afford difluorodimethylsilane in a quantitative yield.[440]

Compounds containing alkoxy groups at the silicon atom react with XeF_2 at a very slow rate (within 4–5 days).[399] On the other hand, the reaction of XeF_2 with *tert*-butylthiotrimethylsilane in acetonitrile occurs easily and affords di-*tert*-butyl disulfide and flurotrimethylsilane in high yields.[347]

$$Me_3SiSBu^t + XeF_2 \xrightarrow{MeCN} Bu^tSSBu^t + Me_3SiF + Xe$$

Bu^tSSSBu^t and Bu^tSH are formed as side products. In the absence of a solvent, this reaction yields a mixture of products.[347]

The reaction of XeF_2 with nitrogen-containing silanes is accompanied by the cleavage of Si−N bonds resulting in the formation of fluorotrimethylsilane in > 90% yield. Presumably, this reaction occurs by a radical mechanism. The formation of $FXeNR_2$ (see Ref. 423) and FXeSR (see Refs. 318–321) as intermediate products was proposed.

$$Me_3SiNR_2 + XeF_2 \xrightarrow{MeCN} Me_3SiF + Xe + R_2\dot{N}$$

$$R_2\dot{N} \xrightarrow{R = Me} MeN{=}CH_2 \longrightarrow \text{polymer}$$

$$R_2\dot{N} \xrightarrow{MeCN} R_2NH$$

The ability of XeF_2 to cleave smoothly the Si−N bonds in polyfunctional compounds was used in the synthesis of the hexamethyltriamido-*N*-fluorophosphazene (**299**) from hexamethyltriamido-*N*-trimethylsilylphosphazene (**300**).[449]

$$\underset{\mathbf{300}}{(Me_2N)_3P{=}NSiMe_3} + XeF_2 \xrightarrow[-15\ ^\circ C]{MeCN} \underset{\mathbf{299}}{(Me_2N)_3P{=}NF} + Me_3SiF + Xe$$

An attempt to synthesise a compound containing the Xe−N bond by the reaction of XeF_2 with $Me_3SiN{=}C(CF_3)_2$ was unsuccessful. This reaction gave Xe, Me_3SiF and $(CF_3)_2C{=}NH$.[347]

It was found that trimethylpentafluorophenylsilane (**301a**) does not react with XeF_2 in acetonitrile at 20 °C. However, the addition of a catalytic amount of anhydrous CsF to the reaction mixture results in the formation of pentafluorobenzene and decafluorobiphenyl in 58% and 11% yields, respectively. In acetonitrile, this reaction is completed within 15–20 min, but in $CFCl_3$ or SO_2FCl trimethylpentafluorophenylsilane (**301a**) does not react with XeF_2 even in the presence of CsF, apparently due to the low solubility of the latter.[450–452]

$$\underset{\mathbf{301a-d}}{ArSiMe_3} + XeF_2 \xrightarrow[10-20\ ^\circ C]{CsF,\ MeCN} ArH + ArAr + Xe + Me_3SiF$$

Ar = C_6F_5 (**a**), 4-$CF_3C_6F_4$ (**b**), 4-C_5F_4N (**c**), 4-$CF_3C_6H_4$ (**d**).

Arylsilanes **301a**,**b** react similarly with XeF_2 in the presence of anhydrous KF and RbF.[450]

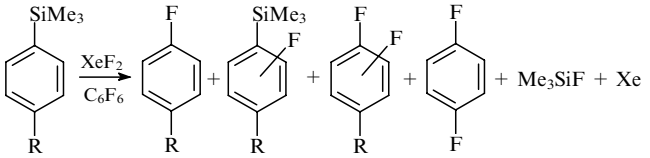
Trimethyl-4-tetrafluoropyridylsilane (**301c**) reacts with XeF_2 very slowly in the absence of a catalyst and within several minutes in the presence of CsF.[450]

In contrast to fluorinated arylsilanes, their hydrocarbon analogues (phenyl-, 4-tolyltrimethylsilane, tetraphenylsilane) do not enter into the reaction with XeF_2 and CsF even on heating at 40–60 °C for several hours.[451] The presence of the electron-withdrawing CF_3 group in (4-trifluoromethylphenyl)trimethylsilane (**301d**) increases its reactivity in comparison with trimethylphenylsilane. It reacts with XeF_2 to give benzotrifluoride and 4,4′-bis(trifluoromethyl)biphenyl, although the conversion is low.[450]

^{19}F CIDNP was used to establish a radical mechanism of the Si−C bond cleavage.[450] This reaction seems to be convenient for generating polyfluoroaryl and polyfluorohetaryl radicals under mild conditions. Chemical reactions occurring in the arylsilane–XeF_2–CsF system and the CIDNP data offer the most probable mechanism for this reaction.

$$C_6F_5SiMe_3 \overset{F^-}{\rightleftharpoons} \left[C_6F_5SiFMe_3\right]^- \xrightarrow[-XeF^{\bullet}, -F^{\bullet}]{XeF_2} \left[C_6F_5SiFMe_3\right]^{\bullet} \xrightarrow[-Me_3SiF]{} [C_6F_5]^{\bullet} \longrightarrow C_6F_5H + C_{12}F_{10}$$

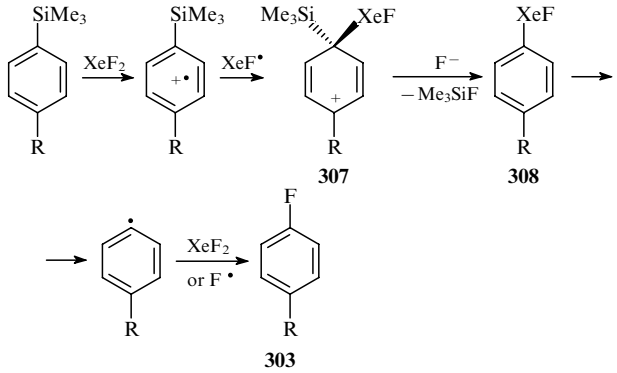
A radical mechanism has also been proposed for the reaction of aryltrimethylsilanes **302a**–**d**.[453] It was shown that compounds **302a**–**d** react with two equivalents of XeF_2 to give the *para*-fluoro derivatives **303**. Moreover, this reaction gives the isomeric monofluoroarylsilanes **304**, the difluorides **305** and 1,4-difluorobenzene (**306**) as is the case with the reaction involving acetyl hypofluorite, the well-known radical fluorinating agent.[453]



302a–d **303a–d** **304a–d** **305a–d** **306**

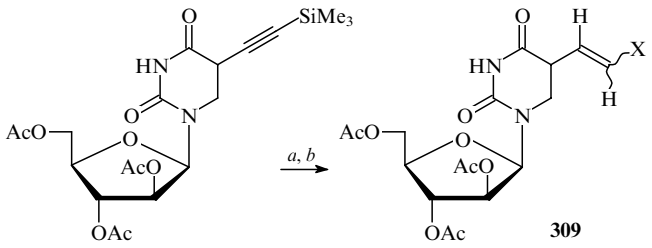
Compounds **302**	R	Yield (%)			
		303	**304**	**305**	**306**
a	H	65	0	0	35
b	Bu^t	86	8	6	0
c	OMe	61	39	0	0
d	Cl	82	12	6	0

This reaction occurs through the formation of the cationoid intermediate **307**, which is stabilised not only due to the β-effect of the silyl substituent but also due to the interaction of the cationic centre with the non-bonding molecular orbital of the hypervalent xenon.[453]



The subsequent reaction with the fluoride anion results in the intermediate **308** (see Section VI) which further yields the aryl fluorides **303a–d**.

Xenon difluoride is a convenient reagent for converting vinyl silanes into vinyl halides. This reaction was used in particular in the synthesis of 5-(2-halovinyl) derivatives of the pyrimidine nucleosides **309**.[454]



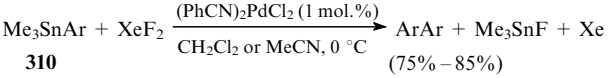
X = $SiMe_3$, I, Br, Cl;

(*a*) $Pd/CaCO_3$, , AcOEt; (*b*) XeF_2, MX (MX = LiCl, LiBr, NaI), PhH.

b. Reactions of organotin compounds with XeF_2

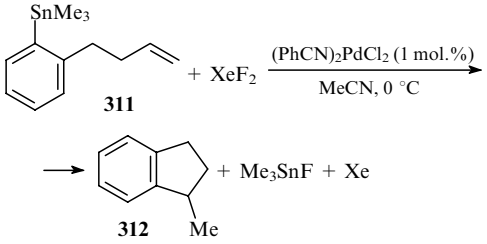
Aryltrimethylstannanes react with XeF_2 with cleavage of the C–Sn bond and can be used for the generation of aryl radicals. Thus trimethyl(phenyl)stannane reacts with XeF_2 rather slowly, *viz*., the conversion of the original compound reaches 80% after 12 h. In the presence of $BF_3 \cdot Et_2O$ as the catalyst, this reaction is strongly accelerated but yields a complex mixture of products.[455]

XeF_2 reacts with aryltrimethylstannanes more selectively in the presence of catalytic amounts of a palladium benzonitrile complex. Thus biaryls are formed in good yields from the aryltrimethylstannanes **310**; the yields of side products (benzene, chlorobenzene) do not exceed 1%–2%.[455]

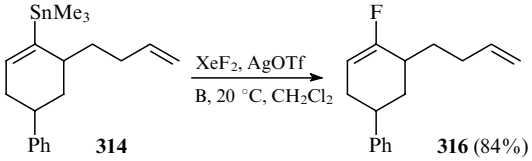


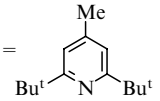
Ar = Ph, 1-naphthyl.

If a molecule contains a functional group which can react with the radical, cascade reactions may be triggered. Thus the reaction of 2-trimethylstannyl(but-3-enyl)benzene (**311**) with XeF_2 in the presence of a Pd complex results in 1-methylindan (**312**) in a satisfactory yield. In this case, no homocoupling reaction occurs.[455]



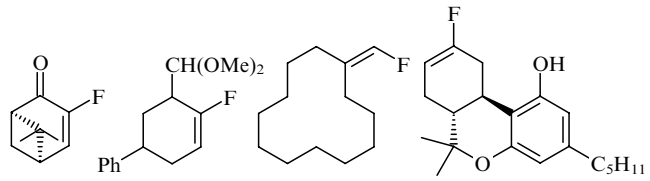
Organotin compounds can be used for the synthesis of organofluorine derivatives.[456–462] Thus the reaction of the vinylstannanes **313** and **314** with XeF_2 in the presence of silver triflate (~1:1.5) and a catalytic amount of 2,6-di-*tert*-butyl-4-methylpyridine in dichloromethane results in the vinyl fluorides **315** and **316**.



B = .

It should be noted that in contrast to compound **311**, the stannane **314** does not undergo cyclisation.[463]

Diverse functional groups in the vinylstannane molecule do not inferfere with this reaction. Thus this approach was used for the synthesis of the vinyl fluorides **317–320**.[460–462]



317 (20%) **318** (53%) **319** (70%) **320** (52%)

5. Reactions of XeF_2 with organoaluminium compounds

The oxidation of organoaluminium compounds (OAC) by XeF_2 is an exothermic reaction. Any contact of even small amounts of the reagents in the absence of a solvent brings about an explosion. Oxidation in solutions (toluene appeared to be the most suitable one) is associated with chemiluminescence,[261] which is similar to that observed on oxidation of OAC by oxygen.[464] It was found that this reaction involves exclusively the C–Al or the H–Al bond. The reactions of Et_3Al, $(EtO)_2AlEt$, Et_2AlCl and Bu^i_2AlH with XeF_2 gave Et_2AlF, $(EtO)_2AlF$, EtAlClF and Bu^i_2AlF (yields 95%, 97%, 80% and 79%, respectively). In addition to the above-mentioned products, Xe and C_2H_6 are formed as the main products, while C_2H_4 and C_4H_{10} are formed as admixtures. The AOC : XeF_2 ratio of 2:1 ensures the reaction of XeF_2 with the

most reactive substituent (H, Alk, Cl) bound to Al. The reactivities of the substituents decrease in the following order: H > Alk > Cl.[465]

The mechanism of the reaction of OAC with XeF_2 in toluene was studied in the example of a model compound $(EtO)_2AlEt$ containing only one non-oxidised Al–C bond.[465,466] The redox reaction begins with the formation of the intermediate complex **321** in which the electron is transferred from the OAC to the electrophilic XeF_2.[467] The reactive intermediates, *viz*., $^{\bullet}C_2H_5$ radicals, are converted through three main routes, *viz*., they react with each other to give ethane, ethylene and butane; they attack toluene at the side chain to give bibenzyl or at the aromatic ring to give ethyl-, diethyltoluenes and bitolyls. Chemiluminescence is evoked as a result of excitation and generation of the $^{\bullet}XeF$ radicals formed in the reaction of polarised ethyl radicals with XeF_2.[466,467]

$$\text{Al}{-}C_2H_5 + XeF_2 \longrightarrow \left[\text{Al}{-}C_2H_5\cdot XeF_2\right] \longrightarrow$$

321

$$\longrightarrow \left[\text{Al}{-}C_2H_5^{+\bullet}\,XeF_2^{-\bullet}\right] \longrightarrow \text{Al}{-}F + \dot{X}eF + \dot{C}_2H_5$$

The effects of luminescence activators, *viz*., 9,10-dibromoanthracene, pyrene, *p*-terphenyl and the $[Ru(bipy)_3Cl_2\cdot(OAC)_n]$ complex (bipy is 2,2′-bipyridyl) on the chemiluminescence of the reaction of $(EtO)_2AlEt$ with XeF_2 in solution have been studied.[468] It was shown that enhanced luminescence is a result of involvement of the activator in the oxidation–reduction process.[468]

6. Reactions of XeF_2 with Group II organoelement compounds

a. Reactions of organomagnesium compounds with XeF_2

The direction of the reactions of the Grignard reagents **322a–c** with XeF_2 in diethyl ether at 20 °C depends on the structure of the substrate. Thus decylmagnesium bromide reacts with XeF_2 to give 2-ethoxydecane (**323a**), decane (**324a**) and eicosane (**325a**) in a total yield 98%. In the case of benzylmagnesium bromide, the total yield of the three main reaction products **323b–325b** is 80%; benzyl bromide was detected among side products. The composition of the reaction mixture is even more complicated in the reaction of phenylmagnesium bromide with XeF_2. In this case, the main products **323c–325c** are formed in a total yield 70% (the side products include bromobenzene, bromophenyl, mono- and dibromoacetophenone, *etc*.).[469]

$$\underset{\textbf{322a–c}}{RMgBr} + XeF_2 \xrightarrow{Et_2O} \underset{\textbf{323a–c}}{RCHOEt\ (Me)} + \underset{\textbf{324a–c}}{RH} + \underset{\textbf{325a–c}}{RR}$$

R = n-$C_{10}H_{21}$ (**a**), Bn (**b**), Ph (**c**).

A method for incorporating a trifluoromethyl group into the molecules of aromatic compounds has been proposed[470,471] which includes the conversion of aryl halides (more preferably, bromides) into the corresponding Grignard reagents and their subsequent reaction with carbon disulfide and XeF_2.

$$ArX \xrightarrow[3)\ XeF_2]{1)\ Mg,\ Et_2O;\ 2)\ CS_2} ArCF_3$$

Ar = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 3-$CF_3C_6H_4$, ; X = Cl, Br.

b. Reactions of organomercury compounds with XeF_2

The C–Hg bond in the reaction of XeF_2 with the mercury derivatives R_2Hg is cleaved to yield a mixture of products, such as RHgF (or RHgF + HgF_2), RF, RR, *etc*.[260,472]

$$R_2Hg + XeF_2 \longrightarrow RHgF\ (HgF_2) + RR + RF + Xe$$

R = 4-$MeOC_6H_4$, 4-$Me_2NC_6H_4$, Bn, 4-$EtO_2CC_6H_4$, PhC≡C.

This reaction is carried out in an argon atmosphere to avoid the formation of oxygen-containing products. In the case of di(phenylethynyl)mercury, PhC≡CF is unstable and could not therefore be detected in the reaction mixture. However, indirect evidence for the formation of this compound was obtained upon treatment of the reaction mixture with tetraethylammonium bromide after complete liberation of xenon eventually resulting in PhC≡CBr in 43% yield.[472]

The efficiency of this reaction is judged by the temperature at which the liberation of xenon occurs. The reactivities of R_2Hg were found to decrease in the following order depending on R: $PhCH_2$ > *p*-$Me_2NC_6H_4$ > PhC≡C > *p*-$MeOC_6H_4$ > *p*-EtO_2C–C_6H_4. Hence, XeF_2 acts as an electron acceptor, while R_2Hg acts as an electron donor. Presumably, this reaction is a radical process involving an initial transfer of an electron from R_2Hg to XeF_2. The absence of R_2Hg fluorination products in the reaction mixture suggests that the C–Hg bond is cleaved by XeF_2 more easily than the C–H or C–C bond.[260,472]

$$R_2Hg + XeF_2 \longrightarrow \left[R_2Hg\cdot XeF_2\right] \longrightarrow \left[R_2Hg^{+\bullet}\,XeF_2^{-\bullet}\right] \longrightarrow$$

$$\longrightarrow RHgF + R^{\bullet} + X + F^{\bullet}$$

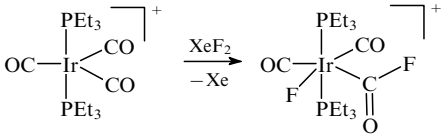
$$2\,R^{\bullet} \longrightarrow RR$$

$$R^{\bullet} + F^{\bullet} \longrightarrow RF$$

It should be noted that XeF_2 also reacts readily with mercury dihalides to give mercury difluoride in a quantitative yield. This reaction occurs especially easily with HgI_2.[472]

7. Reactions of other organometallic compounds with XeF_2

Many metals, *e.g*., iridium, react with XeF_2 to yield metal fluorides.[473] The high oxidation potential of XeF_2 allows the oxidation of carbonyl complexes of some metals. Thus the cationic complex tricarbonylbis(triethylphosphine)iridium(I) **326** reacts with XeF_2 to give the complex **327**.[474]



326 **327**

This approach can be used for preparing fluorinecarbonyl complexes of other metals.

The reactions of $[M_2(CO)_{10}]$ (M = Mn, Re) with $Xe(OTeF_5)_2$ at −78 °C in CH_2Cl_2,[475] and the reactions of $[Os_3(CO)_{12}]$,[476] $[Ir_4(CO)_{12}]$[421,477,478] and $[Ru_3(CO)_{12}]$[479] with XeF_2 in the presence of HF have been studied.

IX. Miscellaneous reactions

It was shown that the fluorination of polyethylene with XeF_2 in liquid media follows a radical mechanism.[480] The oxidation of methane by XeF_2 in aqueous media at 10–25 °C gives a mixture of MeOH (8%), MeF (2%) and CO_2 (50%).[481] The reaction of $CF_3COOXeF$ and $(CF_3COO)_2Xe$ with adamantane and its 1-halogeno (Cl, Br) derivatives results in a mixture of isomeric trifluoroacetoxyadamantanes.[482] The use of a new reagent, *viz*., I_2–XeF_2, has been documented recently.[483] Its application allows one to convert terminal alkenes into geminal difluorides.[484–486] The hypothetical mechanism of this reaction is discussed.[486]

A new line of research in the chemistry of fullerenes associated with their fluorination has evolved and is developing actively.[487] It was found that noble gas fluorides, particularly xenon difluoride, can be successfully used for the fluorination of fullerenes.[487–489]

* * *

The data discussed in the review provide convincing evidence that xenon chemistry is developing successfully and XeF_2 is applicable to miscellaneous synthetic tasks. The reagents based on the xenon derivatives considered in the review surpass well-known classical reagents and can often replace them.

References

1. N Bartlett *Proc. Chem. Soc.* 218 (1962)
2. V Zemva, R Hagiwara, W J Casteel, K Lutar, A Jesih, N Bartlett *J. Am. Chem. Soc.* **112** 4846 (1990)
3. D Schröder, J N Harvey, M Arschi, H Schwarz *J. Phys. Chem.* **108** 8446 (1998)
4. D R Brown, M J Clegg, A J Downs, R C Fowler, A R Minihan, J R Norris, L Stein *Inorg. Chem.* **31** 5041 (1992)
5. L Stein, W W Henderson *J. Am. Chem. Soc.* **102** 2856 (1980)
6. R Cipollini, F Grandinetti *J. Chem. Soc., Chem. Commun.* 773 (1995)
7. M Attina, F Bernardi, F Cacace, I Rossi *Chem. Eur. J.* **5** 1186 (1999)
8. R Hoppe, W Dähne, H Mattauch, K-M Rödder *Angew. Chem., Int. Ed. Engl.* **1** 599 (1962)
9. H H Claassen, H Selig, J G Malm, *J. Am. Chem. Soc.* **84** 3593 (1962)
10. K Lutar, A Smalc, B Zemva, S A Kinkead *Inorg. Synth.* **29** 4 (1992)
11. R D LeBlond, D D DesMarteau *J. Chem. Soc., Chem. Commun.* 555 (1974)
12. C T Goetschel, K R Loos *J. Am. Chem. Soc.* **94** 3018 (1972)
13. L J Turbini, R E Aikman, R J Lagow *J. Am. Chem. Soc.* **101** 5833 (1979)
14. A V Eletskii, S N Spirin, E V Stepanov, B B Chaivanov *Eksperimental'noe i Teoreticheskoe Issledovanie Protsessov Vzaimodeistviya Atomarnogo Ftora s Kristallicheskim Ksenonom* (Experimental and Theoretical Investigations of Processes of Interaction of Atomic Fluorine with Crystalline Xenon) Preprint of Institute of Nuclear Energy, No. 3836/13, Moscow, 1983
15. J H Holloway *J. Fluorine Chem.* **33** 149 (1986)
16. J H Holloway *Chem. Br.* **23** 658 (1987)
17. N Bartlett *The Chemistry of the Noble Gases* (Amsterdam: Elsevier, 1971)
18. D T Hawkins, W E Falconer, N Bartlett *Noble Gas Compounds. A Bibliography: 1962–1976* (New York: Plenum, 1978)
19. P Laszlo, G J Schrobilgen *Angew. Chem.* **100** 495 (1988)
20. V V Bardin, Yu L Yagupol'skii, in *Ftoriruyushchie Reagenty v Organicheskom Sinteze* (Fluorinating Agents in Organic Synthesis) (Ed L S German, S M Zemskov) (Novosibirsk: Nauka, 1987) p. 63
21. J H Holloway *Noble Gas Chemistry* (London: Methuen, 1968)
22. A B Neiding, V B Sokolov *Usp. Khim.* **43** 2146 (1974) [*Russ. Chem. Rev.* **43** 1043 (1974)]
23. R E banks (Ed.) *Fluorine Chemistry at the Millennium: Fascinated by Fluorine* (Amsterdam: Elsevier, 2000)
24. O Bostrup *Dan. Kemi* **76** 35 (1995)
25. M R C Gerstenberger, A Haas *Angew. Chem., Int. Ed. Engl.* **20** 647 (1981)
26. G Resnati *Tetrahedron* **49** 9385 (1993)
27. G A Olah, R D Chambers, G K Surya Prakash (Eds) *Synthetic Fluorine Chemistry* (New York: Wiley, 1992)
28. M Hudlicky, A E Pavlath (Eds) *Chemistry of Organic Fluorine Compounds (ACS Monograph. Ser.)* Vol. 187 (Washington, DC: American Chemical Society, 1995)
29. V A Legasov, V N Prusakov, B B Chaivanov *Reaktsii Okislitel'nogo Ftorirovaniya Diftorida Ksenona* (Reactions of Oxidative Fluorination of Xenon Difluoride) Preprint of Institute of Nuclear Energy, No. 2185, Moscow, 1972
30. R Filler *Isr. J. Chem.* **17** 71 (1978)
31. M Zupan, in *The Chemistry of Functional Groups, Supplement D: The Chemistry of Halides, Pseudo-Halides, and Azides* Parts 1, 2 (Eds S Patai, Z Rappoport) (Chichester: Wiley, 1983) p. 657
32. J A Wilkinson *Chem. Rev.* **92** 505 (1992)
33. M A Tius *Tetrahedron* **51** 6605 (1995)
34. V V Zhdankin *Izv. Akad. Nauk, Ser. Khim.* 1849 (1993) [a]
35. V K Brel, N S Zefirov, in *Chemistry of Hypervalent Compounds* (Ed. Kin-ya Akiba) (New York: Wiley-VCH, 1999) p. 389
36. F Sladky *Allg. Prakt. Chem.* **22** 213 (1971)
37. T Cleveland, C R Landis *J. Am. Chem. Soc.* **118** 6020 (1996)
38. V A Legasov, A S Marinin *Zh. Neorg. Khim.* **27** 2408 (1972) [b]
39. W W Dukat, J H Holloway, E G Hope, P J Townson, R L Powell. *J. Fluorine Chem.* **62** 293 (1993)
40. C L Chernick, J G Malm *Inorg. Synth.* **8** 258 (1966)
41. W E Falconer, W A Sunder *J. Inorg. Nucl. Chem.* **29** 1380 (1967)
42. J G Malm, E H Appelman *At. Energy Rev.* **7** 3 (1969)
43. F Schreiner, G N McDonald, C L Chernick *J. Phys. Chem.* **72** 1162 (1968)
44. J L Weeks, C L Chernick, M S Matheson *J. Am. Chem. Soc.* **84** 4612 (1962)
45. L V Streng, A G Streng *Inorg. Chem.* **4** 1370 (1965)
46. S M Williamson *Inorg. Synth.* **11** 147 (1968)
47. J H Holloway *J. Chem. Sos., Chem. Commun.* 22 (1966)
48. M-Sh Liao, Q-E Zhang *J. Phys. Chem. A* **102** 10 647 (1998)
49. V N Mit'kin, S V Zemskov *Izv. Akad. Nauk SSSR, Ser. Neorg. Mater.* **17** 1897 (1981) [c]
50. J B Nielsen, S A Kinkead, J D Purson, P G Eller *Inorg. Chem.* **29** 1779 (1990)
51. H Dang, L Huag, Q Xu, R Yang, B Zhang, D Wang, Z Lu *Wuji Huaxue Xuebao* **12** 18 (1996); *Chem. Abstr.* **125** 24 976 (1996)
52. A V Eletskii, V A Legasov, S N Spirin, E V Stepanov, B B Chaivanov *Dokl. Akad. Nauk SSSR* **280** 909 (1985) [d]
53. D R MacKenzie, R H Wiswall, in *Noble Gas Compounds* (Chicago; London: University of Chicago Press, 1963) p. 81.
54. A D Kirshenbaum, L V Streng, A G Sreng, A V Grosse *J. Am. Chem. Soc.* **85** 360 (1963)
55. J H Holloway *Educ. Chem.* **10** 140 (1973)
56. C R Bieler, K C Janda *J. Am. Chem. Soc.* **112** 2033 (1990)
57. K Seppelt *Angew. Chem.* **91** 199 (1979)
58. A Filippi, A Troiani, M Speranza *J. Phys. Chem. A* **101** 9344 (1997)
59. E H Appelman *J. Am. Chem. Soc.* **90** 1900 (1968)
60. A Schneer-Ergey, K Kozmutza *Magy. Kem. Foly.* **78** 486 (1972)
61. I Feher, M Semptey *Magy. Kem. Foly.* **76** 141 (1970)
62. A A Goncharov, Yu N Kozlov, A P Purmal' *Zh. Fiz. Khim.* **52** 2870 (1978) [e]
63. A A Goncharov, Yu N Kozlov *Zh. Fiz. Khim.* **52** 945 (1978) [e]
64. A A Goncharov, Yu N Kozlov, A P Purmal' *Zh. Fiz. Khim.* **55** 1633 (1981) [e]
65. D F Smith *Science* **140** 899 (1963)
66. K O Christe, W W Wilson *Inorg. Chem.* **27** 2714 (1988)
67. C L Chernick, H H Claassen, J G Malm, P L Plurien, in *Noble Gas Compounds* (Chicago; London: University of Chicago Press, 1963) p. 287
68. K Seppelt, H H Rupp *Z. Anorg. Allg. Chem.* **409** 331 (1974)
69. W W Wilson, K O Christe *Inorg. Chem.* **26** 916 (1987)
70. K O Christe, W W Wilson *Inorg. Chem.* **27** 1296 (1988)
71. K O Christe, W W Wilson *Inorg. Chem.* **27** 3763 (1988)
72. H P A Mercier, G J Schrobilgen *Inorg. Chem.* **32** 145 (1993)
73. J B Nielsen, S A Kinkead, P G Eller *Inorg. Chem.* **29** 3621 (1990)
74. H Selig *Inorg. Chem.* **5** 183 (1966)
75. G J Moody, H Selig *Inorg. Nucl. Chem. Lett.* **2** 319 (1966)
76. G J Schrobilgen, D Martin-Rovet, P Charpin, M Lance *J. Chem. Soc., Chem. Commun.* 894 (1980)
77. J H Holloway, V Kaučič, D Martin-Rovet, D R Russell, G J Schrobilgen, H Selig *Inorg. Chem.* **24** 678 (1985)
78. K O Christe, D A Dixon, J C P Sanders, G J Schrobilgen, S Tsai, W W Wilson *Inorg. Chem.* **34** 1868 (1995)
79. K O Christe, E C Curtis, D A Dixon, H P Mercier, J C P Sanders, G J Schrobilgen *J. Am. Chem. Soc.* **113** 3351 (1991)
80. A Ellern, K Seppelt *Angew. Chem., Int. Ed. Engl.* **34** 1586 (1995)
81. J Foropoulos Jr, D D DesMarteau *Inorg. Chem.* **21** 2503 (1982)
82. L D Shustov, N S Tolmacheva, Sh Sh Nabiev, E K Il'in, V D Klimov, V P Ushakov *Zh. Neorg. Khim.* **34** 1673 (1989) [b]
83. V K Isupov, A V Oleinik, N N Aleinikov *Zh. Neorg. Khim.* **34** 2080 (1989) [b]
84. N N Aleinikov, S A Kashtanov, I A Pomytkin, A M Sipyagin *Izv. Akad. Nauk, Ser. Khim.* 184 (1995) [a]
85. Yu M Kiselev, N E Fadeeva, A I Popov, M V Korobov, V V Nikulin, V I Spitsyn *Dokl. Akad. Nauk SSSR* **295** 378 (1987) [d]
86. V A Legasov *Vestn. Akad. Nauk SSSR* (12) 3 (1976) [f]
87. N Bartlett, M Wechsberg, F O Sladky, P A Bulliner, G R Jones, R D Burbank *J. Chem. Soc., Chem. Commun.* 703 (1969)
88. M Eisenberg, D D DesMarteau *Inorg. Nucl. Chem. Lett.* **6** 29 (1970)

89. M Wechsberg, P A Bulliner, F O Sladky, R Mews, N Bartlett *Inorg. Chem.* **11** 3063 (1972)
90. F O Sladky *Monatsh. Chem.* **101** 1571 (1970)
91. J I Musher *J. Am. Chem. Soc.* **90** 7371 (1968)
92. M Eisenberg, D D DesMarteau *Inorg. Chem.* **11** 1901 (1972)
93. R G Syvret, G J Schrobilgen *J. Chem. Soc., Chem. Commun.* 1529 (1985)
94. R G Syvret, G J Schrobilgen *Inorg. Chem.* **28** 1564 (1989)
95. K Seppelt *Angew. Chem., Int. Ed. Engl.* **11** 723 (1972)
96. K Seppelt, D Lentz, G Kloeter *Inorg. Synth.* **24** 27 (1986)
97. F O Sladky *Monatsh. Chem.* **101** 1559 (1970)
98. H P A Mercier, J C P Sanders, G J Schrobilgen *J. Am. Chem. Soc.* **116** 2921 (1994)
99. F O Sladky *Inorg. Synth.* **24** 33 (1986)
100. V K Brel, A S Koz'min, V I Uvarov, N S Zefirov, V V Zhdankin, P J Stang *Tetrahedron Lett.* 5225 (1990)
101. B Cremer-Lober, H Butler, D Naumann, W Tyrra *Z. Anorg. Allg. Chem.* **607** 34 (1992)
102. K Seppelt, D Lentz, in *Progress in Inorganic Chemistry* Vol. 29 (New York: Wiley, 1982) p. 167
103. T Birchall, R D Myers, H DeWaard, G J Schrobilgen *Inorg. Chem.* **21** 1068 (1982)
104. L Turowsky, K Seppelt *Inorg. Chem.* **29** 3226 (1990)
105. R G Syvret, K M Mitchell, J C P Sanders, G J Schrobilgen *Inorg. Chem.* **31** 3381 (1992)
106. D Lentz, K Seppelt *Angew. Chem., Int. Ed. Engl.* **17** 356 (1978)
107. E Jacob, D Lentz, K Seppelt, A Simon *Z. Anorg. Allg. Chem.* **472** 7 (1981)
108. L Turowsky, K Seppelt *Z. Anorg. Allg. Chem.* **609** 153 (1992)
109. D Lentz, K Seppelt *Angew. Chem., Int. Ed. Engl.* **18** 66 (1979)
110. G A Schumacher, G J Schrobilgen *Inorg. Chem.* **23** 2923 (1984)
111. T-C Shieh, N C Yang, C L Chernick *J. Am. Chem. Soc.* **86** 5021 (1964)
112. T C Shieh, E D Feit, C L Chernick, N C Yang *J. Org. Chem.* **35** 4020 (1970)
113. S A Shakelford, R R McGuire, J L Pflug *Tetrahedron Lett.* 363 (1977)
114. M Zupan, A Pollak *J. Chem. Soc., Chem. Commun.* 845 (1973)
115. M Zupan, A Pollak *Tetrahedron* **33** 1017 (1977)
116. A Gregorčič, M Zupan *J. Org. Chem.* **44** 4120 (1979)
117. A Gregorčič, M Zupan *J. Org. Chem.* **44** 1255 (1979)
118. M Zupan, A Pollak *J. Org. Chem.* **41** 4002 (1976)
119. S Stavber, M Zupan *J. Fluorine Chem.* **10** 271 (1977)
120. D F Shellhamer, M L Ragains, B T Gipe, V L Heasley, G E Heasley *J. Fluorine Chem.* **20** 13 (1980)
121. M Zupan, B Šket *J. Org. Chem.* **43** 696 (1978)
122. A Gregorčič, M Zupan *J. Org. Chem.* **49** 333 (1984)
123. M Zupan, A Pollak *J. Org. Chem.* **42** 1559 (1977)
124. B Šket, M Zupan *J. Chem. Soc. Perkin Trans. 1* 2169 (1977)
125. M Zupan, A Gregorčič, A Pollak *J. Org. Chem.* **42** 1562 (1977)
126. S A Shakelford *Tetrahedron Lett.* 4265 (1977)
127. S A Shakelford *J. Org. Chem.* **44** 3485 (1979)
128. A Gregorčič, M Zupan *Bull. Chem. Soc. Jpn.* **53** 1085 (1980)
129. A Gregorčič, M Zupan *J. Fluorine Chem.* **24** 291 (1984)
130. R A Hildreth, M L Druelinger, S A Shakelford *Tetrahedron Lett.* **23** 1059 (1982)
131. A Gregorčič, M Zupan *Tetrahedron* **33** 3243 (1977)
132. D F Shellhamer, R J Conner, R E Richardson, V L Heasley, G E Heasley *J. Org. Chem.* **49** 5015 (1984)
133. S Rozen, R Filler *Tetrahedron* **41** 1111 (1985)
134. T B Patrick, R Mortezania *J. Org. Chem.* **53** 5153 (1988)
135. G S Garrett, T J Emge, S C Lee, E M Fischer, K Dyehouse, J M McIver *J. Org. Chem.* **56** 4823 (1991)
136. B Zajc, M Zupan *J. Chem. Soc., Chem. Commun.* 759 (1980)
137. G L Cantrell, R Filler *J. Fluorine Chem.* **27** 35 (1985)
138. B Zajc, M Zupan *J. Org. Chem.* **47** 573 (1982)
139. T Tsushima, K Kawada, T Tsuji *Tetrahedron Lett.* **23** 1165 (1982)
140. E Differding, G M Ruegg *Tetrahedron Lett.* **32** 3815 (1991)
141. M Zupan, A Pollak *J. Org. Chem.* **39** 2646 (1974)
142. W Korytnyk, S Valentekovic-Horvath, C R Petrie III *Tetrahedron* **38** 2547 (1982)
143. W Korytnyk, S Valentekovic-Horvath *Tetrahedron Lett.* **21** 1493 (1980)
144. C C Geilen, N Loch, W Reutter, K Seppelt, F Oberdorfer *Tetrahedron Lett.* **33** 2435 (1992)
145. N N Aleinikov, I A Pomytkin, S A Kashtanov, O N Efimov, A F Zueva *Izv. Akad. Nauk SSSR, Ser. Khim.* 2850 (1988) [a]
146. F O Sladky, P A Bulliner, N Bartlett *J. Chem. Soc., A* 2179 (1969)
147. N S Zefirov, V V Zhdankin, A A Gakh, P J Stang *Izv. Akad. Nauk SSSR, Ser. Khim.* 1196 (1990) [a]
148. N S Zefirov, A A Gakh, V V Zhdankin, P J Stang *J. Org. Chem.* **56** 1416 (1991)
149. V K Brel, V I Uvarov, N S Zefirov *J. Fluorine Chem.* **54** 34 (1991)
150. V K Brel, A A Gakh, V V Zhdankin, N S Zefirov, A S Koz'min, A A Korkin, T G Kutateladze, R Caple, S A Lermontov, I G Plokhikh, S O Safronov, P J Stang, N G Chovnikova *Dokl. Akad. Nauk SSSR* **313** 1131 (1990) [d]
151. V I Uvarov, V K Brel *Izv. Akad. Nauk, Ser. Khim.* 764 (1994) [a]
152. A L Henne, E C Ladd *J. Am. Chem. Soc.* **58** 402 (1936)
153. A Varvoglis *Hypervalent Iodine in Organic Synthesis* (London: Academic Press, 1997)
154. P J Stang, V V Zhdankin *Chem. Rev.* **96** 1123 (1996)
155. N Sh Pirkuliev, V K Brel, N S Zefirov *Usp. Khim.* **69** 118 (2000) [*Russ. Chem. Rev.* **69** 105 (2000)]
156. V V Zhdankin, R Tykwinski, B Berglund, M Mullikin, R Caple, N S Zefirov, A S Koz'min *J. Org. Chem.* **54** 2609 (1989)
157. V V Zhdankin, M Mullikin, R Tykwinski, B Berglund, R Caple, N S Zefirov, A S Koz'min *J. Org. Chem.* **54** 2605 (1989)
158. N S Zefirov, T M Kasumov, A S Koz'min, V D Sorokin, V R Polishchuk *Zh. Org. Khim.* **30** 321 (1994) [g]
159. N S Zefirov, V V Zhdankin, Yu V Dan'kov, V D Sorokin, V N Semerikov, A S Koz'min, R Caple, B A Berglund *Tetrahedron Lett.* **27** 3971 (1986)
160. N S Zefirov, N Sh Samsoniya, T G Kutateladze, V V Zhdankin *Zh. Org. Khim.* **27** 220 (1991) [g]
161. N S Zefirov, V V Zhdankin, Yu V Dan'kov, V V Samoshin, A S Koz'min *Zh. Org. Khim.* **20** 444 (1984) [g]
162. V V Zhdankin, P J Stang *Tetrahedron* **54** 10927 (1998)
163. N S Zefirov, V V Zhdankin, A S Koz'min *Tetrahedron Lett.* **27** 1845 (1986)
164. D F Shellhamer, C M Curtis, D R Hollingsworth, M L Ragains, R E Richardson, V L Heasley, G E Heasley *Tetrahedron Lett.* **23** 2157 (1982)
165. D F Shellhamer, C M Curtis, R H Dunham, D R Hollingsworth, M L Ragains, R E Richardson, V L Heasley, S A Shackelford, G E Heasley *J. Org. Chem.* **50** 2751 (1985)
166. D F Shellhamer, S L Carter, R H Dunham, S N Graham, M P Spitsbergen, V L Heasley, R D Chapman, M L Druelinger *J. Chem. Soc., Perkin Trans. 2* 159 (1989)
167. D F Shellhamer, S L Carter, M C Chiaco, T E Harris, R D Henderson, W S C Low, B T Metcalf, M C Willis, V L Heasley, R D Chapman *J. Chem. Soc. Perkin Trans. 2* 401 (1991)
168. M L Druelinger, D F Shellhamer, R D Chapman, S A Shackelford, M E Riner, S L Carter, R P Callahan, C R Youngstrom *J. Chem. Soc. Perkin Trans. 2* 787 (1997)
169. M Zupan, M Metelko, S Stavber *J. Chem. Soc. Perkin Trans. 1* 2851 (1993)
170. S Rozen, E Mishani, M Kol *J. Am. Chem. Soc.* **114** 7643 (1992)
171. D F Shellhamer, M J Horney, A L Toth, V L Heasley *Tetrahedron Lett.* **33** 6903 (1992)
172. D F Shellhamer, M J Horney, B J Pettus, T L Pettus, J M Stringer, V L Heasley *J. Org. Chem.* **64** 1094 (1999)
173. S Stavber, T Sotler, M Zupan, R G Syvret, J M Dobrolsky Jr, A Popovič *J. Org. Chem.* **59** 5891 (1994)
174. Ch A Ramsden, R G Smith *J. Am. Chem. Soc.* **120** 6842 (1998)
175. D R MacKenzie, J Fajer *J. Am. Chem. Soc.* **92** 4994 (1970)
176. M J Shaw, H H Hyman, R Filler *J. Am. Chem. Soc.* **91** 1563 (1969)
177. M J Shaw, H H Hyman, R Filler *J. Am. Chem. Soc.* **92** 6498 (1970)
178. M Ya Turkina, I P Gragerov *Zh. Org. Khim.* **11** 340 (1975) [g]
179. US P. 3 833 581; *Ref. Zh. Khim.* 12 N 136P (1975)
180. M J Shaw, H H Hyman, R Filler *J. Org. Chem.* **36** 2917 (1971)
181. S Stavber, M Zupan *J. Org. Chem.* **48** 2223 (1983)
182. M Zupan *Chimia* **30** 305 (1976)
183. B Šket, M Zupan *J. Org. Chem.* **43** 835 (1978)
184. B Šket, M Zupan *Bull. Chem. Soc. Jpn.* **54** 279 (1981)
185. S P Anand, L A Quarterman, P A Christian, H H Hyman, R Filler *J. Org. Chem.* **40** 3796 (1975)

186. M Rabinovitz, I Agranat, H Selig, C-H Lin *J. Fluorine Chem.* **10** 159 (1977)
187. I Agranat, M Rabinovitz, H Selig, C-H Lin *Chem. Lett.* **32** 1271 (1975)
188. M Zupan, A Pollak *J. Org. Chem.* **40** 3794 (1975)
189. E D Bergmann, H Selig, C-H Lin, M Rabinovitz, I Agranat *J. Org. Chem.* **40** 3793 (1975)
190. I Agranat, M Rabinovitz, H Selig, C-H Lin *Experientia* **32** 417 (1976)
191. M T Stephenson, H J Shine *J. Org. Chem.* **46** 3139 (1981)
192. S Stavber, M Zupan *J. Chem. Soc., Chem. Commun.* 969 (1978)
193. S Stavber, M Zupan *J. Org. Chem.* **46** 300 (1981)
194. V V Bardin, G G Furin, G G Jakobson *Zh. Org. Khim.* **18** 604 (1982) [g]
195. V V Bardin, G G Furin, G G Jakobson, in *Tez. Dokl. Vsesoyuz. Konf. Pamyati A E Favorskogo, Leningrad, 1980* (Abstracts of Reports of the All-Union Conference on A E Favorskii Memory, Leningrad, 1980) p. 110
196. G G Jakobson, V V Bardin, G G Furin, in *The IIIrd Regular Meeting of Soviet-Japanese Fluorine Chemists, Tokyo, 1983* p. 14.1
197. B Zajc, M Zupan *Bull. Chem. Soc. Jpn.* **55** 1617 (1982)
198. S P Anand, L A Quarterman, H H Hyman, K G Migliorese, R Filler *J. Org. Chem.* **40** 807 (1975)
199. A A Goncharov, Yu N Kozlov, A P Purmal' *Zh. Fiz. Khim.* **51** 2839 (1977) [e]
200. H Koudstaal, C Olieman *Recl. Trav. Chim. Pays-Bas* **100** 246 (1981)
201. M Zupan, A Pollak *J. Fluorine Chem.* **7** 443 (1976)
202. L N Nikolenko, T I Yurasova, A A Man'ko *Zh. Obshch. Khim.* **40** 938 (1970) [h]
203. A A Avramenko, V V Bardin, A I Karelin, V A Krasil'nikov, P P Tushin, G G Furin, G G Jakobson *Zh. Org. Khim.* **21** 822 (1985) [g]
204. V V Bardin, I V Stennikova, G G Furin, G G Jakobson, in *Stroenie i Reaktsionnaya Sposobnost' Kremniiorganicheskikh Soedinenii (Tez. Dokl. 3-go Vsesoyuz. Simpoziuma), Irkutsk, 1985* [Structure and Reactivity of Organosilicon Compounds (Abstracts of Reports of the 3rd All-Union Symposium), Irkutsk, 1985] p. 133
205. V V Bardin, I V Stennikova, G G Furin, G G Jakobson *Zh. Org. Khim.* **21** 458 (1985) [g]
206. G Firnau, R Chirakal, S Sood, S Garnett *Can. J. Chem.* **58** 1449 (1980)
207. G Firnau, R Chirakal, S Sood, S Garnett *J. Labelled Compd. Radiopharm.* **18** 7 (1981)
208. Z Planinsek, S Stavber, M Zupan *J. Fluorine Chem.* **45** 141 (1989)
209. S Stavber, Z Koren, M Zupan *Synlett* 265 (1994)
210. B Zajc, M Zupan *J. Org. Chem.* **55** 1099 (1990)
211. S Stavber, B Šket, B Zajc, M Zupan *Tetrahedron* **45** 6003 (1989)
212. S Stavber, M Zupan *Tetrahedron Lett.* **34** 4355 (1993)
213. V A Nikanorov, V I Rozenberg, V G Kharitonov, D Yu Antonov, V A Mikul'shina, M V Galakhov, D P Krut'ko, N S Kopelev, V N Guryshev, V P Yur'ev, O A Reutov *Dokl. Akad. Nauk SSSR* **315** 1388 (1990) [d]
214. I Takemoto, K Yamasaki *Biosci. Biotechnol. Biochem.* **58** 594 (1994)
215. T Umemoto, S Fukami, G Tomizawa, K Harasawa, K Kawada, K Tomita *J. Am. Chem. Soc.* **112** 8563 (1990)
216. G G Furin, A A Fainzilberg *Usp. Khim.* **68** 725 (1999) [*Russ. Chem. Rev.* **68** 653 (1999)]
217. S A Kashtanov, N N Aleinikov, F I Dubovitskii *Izv. Akad. Nauk SSSR, Ser. Khim.* 2678 (1987) [a]
218. G B Shul'pin, M M Kats, Yu N Kozlov *Izv. Akad. Nauk SSSR, Ser. Khim.* 2654 (1988) [a]
219. M M Kats, Yu N Kozlov, G B Shul'pin *Zh. Obshch. Khim.* **61** 1835 (1991) [h]
220. D F Shellhamer, B C Jones, B J Pettus, T L Pettus, J M Stringer, V L Heasley *J. Fluorine Chem.* **88** 37 (1998)
221. M Zupan, J Iskra, S Stavber *J. Org. Chem.* **63** 878 (1998)
222. V V Bardin, L N Shchegoleva, H J Frohn *J. Fluorine Chem.* **77** 153 (1996)
223. L N Nikolenko, L D Shustov, T N Bocharova, T N Yurasova, V A Legasov *Dokl. Akad. Nauk SSSR* **204** 1369 (1972) [d]
224. L D Shustov, T N Bocharova, T I Yurasova, N G Marchenkova, V A Legasov, L N Nikolenko *Zh. Obshch. Khim.* **43** 841 (1973) [h]
225. T N Bocharova, N G Marchenkova, L D Shustov, T Yu Prokof'eva, L N Nikolenko *Zh. Obshch. Khim.* **43** 1325 (1973) [h]
226. L D Shustov, T D Tel'kovskaya, L N Nikolenko *Zh. Org. Khim.* **11** 2137 (1975) [g]
227. L D Shustov, T D Tel'kovskaya, L N Nikolenko *Zh. Obshch. Khim.* **44** 2564 (1974) [h]
228. L D Shustov, M N Semenova, L N Nikolenko *Zh. Obshch. Khim.* **48** 1903 (1978) [h]
229. T B Patrick, K K Johri, D H White *J. Org. Chem.* **48** 4158 (1983)
230. T B Patrick, K K Johri, D H White, W S Bertrand, R Mokhtar, M R Kilbourn, M J Welch *Can. J. Chem.* **64** 138 (1986)
231. G J Schrobilgen, G Firnau, R Chirakal *J. Chem. Soc., Chem. Commun.* 198 (1981)
232. D I Davies, C Waring *J. Chem. Soc., C* 1865 (1968)
233. J W Wilt, in *Free Radicals* Vol. 1 (Ed. J K Kochi) (New York: Wiley, 1973) p. 333
234. C V Wilson *Org. React.* **9** 332 (1957)
235. L Kaplan, in *Free Radicals* Vol. 2 (Ed. J K Kochi) (New York: Wiley, 1973) p. 372
236. J K Kochi *J. Am. Chem. Soc.* **87** 2500 (1965)
237. R A Sheldon, J K Kochi *Org. React.* **19** 179 (1972)
238. T B Patrick, S Khazaeli, S Nadji, K Hering-Smith, D Reif *J. Org. Chem.* **58** 705 (1993)
239. D P Curran, E Bosch, J Kaplan, M Newcomb *J. Org. Chem.* **54** 1826 (1989)
240. E W Della, N J Head *J. Org. Chem.* **57** 2850 (1992)
241. Y Tanabe, N Matsuo, N Ohno *J. Org. Chem.* **53** 4582 (1988)
242. A M Sipyagin, I A Pomytkin, S V Pal'tsun, N N Aleinikov, V G Kartsev *Dokl. Akad. Nauk SSSR* **311** 1137 (1990) [d]
243. G G Furin *Usp. Khim.* **69** 538 (2000) [*Russ. Chem. Rev.* **69** 491 (2000)]
244. V K Brel, V I Uvarov, N S Zefirov, P J Stang, R Caple *J. Org. Chem.* **58** 6922 (1993)
245. V I Uvarov, V K Brel, I V Martynov, N N Aleinikov, S A Kashtanov *Izv. Akad. Nauk SSSR, Ser. Khim.* 2650 (1988) [a]
246. I V Martynov, V K Brel, V I Uvarov, I A Pomytkin, N N Aleinikov, S A Kashtanov *Izv. Akad. Nauk SSSR, Ser. Khim.* 466 (1988) [a]
247. I V Martynov, V K Brel, V I Uvarov, N N Aleinikov, S A Kashtanov *Izv. Akad. Nauk SSSR, Ser. Khim.* 2639 (1988) [a]
248. V K Brel, A S Koz'min, I V Martynov, V I Uvarov, N S Zefirov, V V Zhdankin, P J Stang *Tetrahedron Lett.* **31** 4799 (1990)
249. Yu L Yagupol'skii, T I Savina *Zh. Org. Khim.* **17** 1330 (1981) [g]
250. L D Shustov, L N Nikolenko *Zh. Obshch. Khim.* **53** 2408 (1983) [h]
251. P Nongkunsarn, Ch A Ramsden *J. Chem. Soc., Perkin Trans. 1* 121 (1996)
252. D Holtz, J L Beauchamp *Science* **173** 1237 (1971)
253. H S Johnston, R Woolfolk *J. Chem. Phys.* **41** 269 (1964)
254. J Berkowitz, W A Chupka, P M Guyon, J H Holloway, R Spohr *J. Phys. Chem.* **75** 1461 (1971)
255. J K Hovey, T B McMahon *J. Am. Chem. Soc.* **108** 528 (1986)
256. T Umemoto *Chem. Rev.* **96** 1757 (1996)
257. H J Frohn, S Jacobs *J. Chem. Soc., Chem. Commun.* 625 (1989)
258. H J Frohn, S Jacobs, G Henkel *Angew. Chem., Int. Ed. Engl.* **28** 1506 (1989)
259. R J Lagow, L J Turbini, R E Aikman, M M Brezinski *J. Fluorine Chem.* **45** 12 (1989)
260. K P Butin, Ya M Kiselev, T V Magdesieva, O A Reutov *Izv. Akad. Nauk SSSR, Ser. Khim.* 716 (1982) [a]
261. R G Bulgakov, G Ya Mastrenko, G A Tolstikov, B N Yakovlev, V P Kazakov *Izv. Akad. Nauk SSSR, Ser. Khim.* 2644 (1984) [a]
262. W Tyrra, D Naumann *Can. J. Chem.* **67** 1949 (1989)
263. D Naumann, W Tyrra *J. Chem. Soc., Chem. Commun.* 47 (1989)
264. W Breuer, H J Frohn, M Giesen, S Jacobs, in *Chemiedozenten–Tagung 1989 (Abstracts of Reports), Bielefeld, 1989* p. 108
265. W Breuer, H J Frohn, M Giesen, S Jacobs, in *The 12th International Symposium on Fluorine Chemistry, 1988* p. 213
266. H J Frohn, S Jakobs, C Rossbach *Eur. J. Solid State Inorg. Chem.* **29** 729 (1992)
267. H Meinert, S Rudiger *Z. Chem.* **9** 35 (1969)
268. C J Jameson, in *Multinuclear NMR* (Ed. J Mason) (New York; London: Plenum, 1987)

269. S Tanaka, M Sugimoto, H Takashima, M Hada, H Nakatsuji *Bull. Chem. Soc. Jpn.* **69** 953 (1996)
270. C I Ratcliffe *Annu. Rep. NMR Spectrosc.* **36** 123 (1998)
271. H Butler, D Naumann, W Tyrra *Eur. J. Solid State Inorg. Chem.* **29** 739 (1992)
272. H J Frohn, A Klose, G Henkel *GIT Fachz. Lab.* **37** 752 (1993)
273. H J Frohn, A Klose, V V Bardin, A J Kruppa, T V Leshina *J. Fluorine Chem.* **70** 147 (1995)
274. H J Frohn, A Klose, V V Bardin *J. Fluorine Chem.* **64** 201 (1993)
275. H J Frohn, A Klose, G Henkel *Angew. Chem., Int. Ed. Engl.* **32** 99 (1993)
276. V M McRae, R D Peacock, D R Russell *J. Chem. Soc., Chem. Commun.* 62 (1969)
277. N Bartlett, M Wechsberg, G R Jones, R D Burbank *Inorg. Chem.* **11** 1124 (1972)
278. L K Templeton, D H Templeton, K Seppelt, N Bartlett *Inorg. Chem.* **15** 2718 (1976)
279. R J Gillepsie, G J Schrobilgen, D R Slim *J. Chem. Soc., Dalton Trans.* 1003 (1977)
280. A F Wells *Structural Inorganic Chemistry* (Oxford: Clarendon Press, 1984) p. 920
281. H J Frohn, C Rossbach *Z. Anorg. Allg. Chem.* **619** 1672 (1993)
282. H J Frohn, S Jakobs, C Rossbach, in *The 13th International Symposium on Fluorine Chemistry, Bochum, 1991* A 8
283. H J Frohn, S Jakobs, C Rossbach *J. Fluorine Chem.* **54** 8 (1991)
284. V V Bardin, H J Frohn *J. Fluorine Chem.* **60** 141 (1993)
285. D Naumann, H Butler, R Gnann, W Tyrra *Inorg. Chem.* **32** 861 (1993)
286. D Naumann, H Butler, R Gnann *Z. Anorg. Allg. Chem.* **618** 74 (1992)
287. S Datsenko, N Ignat'ev, P Barthen, H J Frohn, T Scholten, T Schroer, D Welting *Z. Anorg. Allg. Chem.* **624** 1669 (1998)
288. D Naumann, W Tyrra, R Gnann, D Pfolk *J. Chem. Soc., Chem. Commun.* 2651 (1994)
289. D Naumann, W Tyrra, R Gnann, D Pfolk, T Gilles, K F Teble *Z. Anorg. Allg. Chem.* **623** 1821 (1997)
290. H J Frohn, V V Bardin *J. Chem. Soc., Chem. Commun.* 1072 (1993)
291. H J Frohn, V V Bardin *Mendeleev Commun.* 114 (1995)
292. H J Frohn, V V Bardin *Z. Naturforsch., B Chem. Sci.* **51** 1011 (1996)
293. H J Frohn, V V Bardin *Z. Naturforsch., B Chem. Sci.* **53** 562 (1998)
294. H J Frohn, A Klose, T Schroer, G Henkel, V Buss, D Opitz, R Vahrenhorst *Inorg. Chem.* **37** 4884 (1998)
295. H J Frohn, V V Bardin *Z. Anorg. Allg. Chem.* **622** 2031 (1996)
296. V V Bardin *J. Fluorine Chem.* **89** 195 (1998)
297. A A Avramenko, V V Bardin, G G Furin, A I Karelin, V A Krasil'nikov, P P Tushin *Zh. Org. Khim.* **24** 1443 (1988) [g]
298. H J Frohn, V V Bardin *J. Chem. Soc., Chem. Commun.* 919 (1999)
299. V V Zhdankin, P J Stang, N S Zefirov *J. Chem. Soc., Chem. Commun.* 578 (1992)
300. S P Anand, R Filler *J. Fluorine Chem.* **7** 179 (1976)
301. M Zupan, A Pollak *J. Fluorine Chem.* **8** 275 (1976)
302. S V Kovalenko, V K Brel, N S Zefirov *Izv. Akad. Nauk, Ser. Khim.* 1841 (1994) [a]
303. S V Kovalenko, V K Brel, N S Zefirov, P J Stang *Mendeleev Commun.* 68 (1998)
304. T I Yurasova *Zh. Obshch. Khim.* **44** 956 (1974) [h]
305. J Wang, A I Scott *Tetrahedron* **50** 6181 (1994)
306. I A Grigor'ev, L B Volodarsky, V F Strichenko, I A Kirilyuk *Tetrahedron Lett.* **30** 751 (1989)
307. I V Tselinskii, A A Mel'nikov, L G Varyagina, A E Trubitsin *Zh. Org. Khim.* **21** 2490 (1985) [g]
308. I V Tselinskii, A A Mel'nikov, A E Trubitsin *Zh. Org. Khim.* **23** 1657 (1987) [g]
309. I V Tselinskii, A A Mel'nikov, A E Trubitsin *Zh. Org. Khim.* **24** 688 (1988) [g]
310. A E Trubitsin, A A Mel'nikov, M S Pevzner, I V Tselinskii, M E Niyazymbetov, V A Petrosyan *Izv. Akad. Nauk SSSR, Ser. Khim.* 736 (1989) [a]
311. I V Tselinskii, A A Mel'nikov, A E Trubitsin, G M Frolova *Zh. Org. Khim.* **26** 69 (1990) [g]
312. I V Tselinskii, A A Mel'nikov, A E Trubitsin *Zh. Org. Khim.* **26** 272 (1990) [g]
313. A E Trubitsin, A A Mel'nikov, I V Tselinskii, A M Popov *Zh. Org. Khim.* **26** 2007 (1990) [g]
314. V A Petrosyan, M E Niyazymbetov *Izv. Akad. Nauk SSSR, Ser. Khim.* 368 (1988) [a]
315. M E Niyazymbetov, V A Petrosyan, A A Gakh, A A Fainzil'berg *Izv. Akad. Nauk SSSR, Ser. Khim.* 2390 (1987) [a]
316. V A Golubev, N N Salmina, B L Korsunskii, N N Aleinikov, F N Dubovitskii *Izv. Akad. Nauk, Ser. Khim.* 778 (1978) [a]
317. W Sundermeyer, M Witz *J. Fluorine Chem.* **34** 251 (1986)
318. G J Schrobilgen, J H Holloway, P Granger, C Brevard *Inorg. Chem.* **17** 980 (1978)
319. D D DesMarteau *J. Am. Chem. Soc.* **100** 6270 (1978)
320. D D DesMarteau, R D LeBlond, S F Hossain, D Nothe *J. Am. Chem. Soc.* **103** 7734 (1981)
321. J F Sawyer, G J Schrobilgen, S J Sutherland *J. Chem. Soc., Chem. Commun.* 210 (1982)
322. R Faggiani, D K Kennepohl, C J L Lock, G J Schrobilgen *Inorg. Chem.* **25** 563 (1986)
323. J F Sawyer, G J Schrobilgen, S J Sutherland *Inorg. Chem.* **21** 4064 (1982)
324. G A Schumacher, G J Schrobilgen *Inorg. Chem.* **22** 2178 (1983)
325. J Foropoulos Jr, D D DesMarteau *J. Am. Chem. Soc.* **104** 4260 (1982)
326. H Selig, J H Holloway *Top. Curr. Chem., Inorg. Chem.* **124** 33 (1984)
327. A A A Emara, G J Schrobilgen *J. Chem. Soc., Chem. Commun.* 1644 (1987)
328. A A A Emara, G J Schrobilgen *Inorg. Chem.* **31** 1323 (1992)
329. A A A Emara, G J Schrobilgen *J. Chem. Soc., Chem. Commun.* 257 (1988)
330. G J Schrobilgen *J. Chem. Soc., Chem. Commun.* 1506 (1988)
331. V H Dibeler, S K Liston *J. Chem. Phys.* **48** 4765 (1968)
332. G J Schrobilgen *J. Chem. Soc., Chem. Commun.* 863 (1988)
333. G J Schrobilgen, J M Whalen *Inorg. Chem.* **33** 5207 (1994)
334. A Schulz, T M Klapötke *Inorg. Chem.* **36** 1929 (1997)
335. K O Christe, E C Curtis, D A Dixon, H P Mercier, J C P Sanders, G J Schrobilgen *J. Am. Chem. Soc.* **113** 3351 (1991)
336. K O Christe, W W Wilson *Inorg. Chem.* **21** 4113 (1982)
337. N Bartlett, F O Sladky *J. Chem. Soc., D* 1046 (1968)
338. Yu M Kiselev *Koord. Khim.* **23** 83 (1997) [i]
339. J A Gibson, A F Janzen *J. Chem. Soc., Chem. Commun.* 739 (1973)
340. J Bornstein, M R Borden, F Nunes, H I Tarlin *J. Am. Chem. Soc.* **85** 1609 (1963)
341. W Carpenter *J. Org. Chem.* **31** 2688 (1966)
342. J J Edmans, W B Motherwell *J. Chem. Soc., Chem. Commun.* 881 (1989)
343. M Zupan, A Pollak *J. Org. Chem.* **41** 2179 (1976)
344. S Stavber, M Zupan *J. Fluorine Chem.* **12** 307 (1978)
345. M Zupan *Synthesis* 473 (1976)
346. M Zupan, A Pollak *J. Chem. Soc., Perkin Trans. 1* 1745 (1976)
347. J A Gibson, R K Marat, A F Janzen *Can. J. Chem.* **53** 3044 (1975)
348. M Zupan, A Pollak *J. Fluorine. Chem.* **7** 445 (1976)
349. I I Maletina, V V Orda, N N Aleinikov, B L Korsunskii, L M Yagupol'skii *Zh. Org. Khim.* **12** 1371 (1976) [g]
350. H J Frohn, V V Bardin *Z. Naturforsch., B Chem. Sci.* **51** 1015 (1996)
351. M Zupan, A Pollak *J. Chem. Soc., Chem. Commun.* 715 (1975)
352. M Zupan *Collect. Czech. Chem. Commun.* **42** 266 (1977)
353. K Alam, A F Janzen *J. Fluorine Chem.* **36** 179 (1987)
354. A Gregorčič, M Zupan *Bull. Chem. Soc. Jpn.* **50** 517 (1976)
355. G W Bradley, J H Holloway, H J Koh, D G Morris, P G Watson *J. Chem. Soc., Perkin Trans. 1* 3001 (1992)
356. E W Della, N J Head, W K Janowski, C H Schiesser *J. Org. Chem.* **58** 7876 (1993)
357. A N Chekhlov, T M Kasumov, V K Brel, N S Zefirov *Zh. Strukt. Khim.* **37** 940 (1996) [j]
358. T M Kasumov, V K Brel, Yu K Grishin, N S Zefirov, P J Stang *Tetrahedron* **53** 1145 (1997)
359. T M Kasumov, N Sh Pirguliyev, V K Brel, Yu K Grishin, N S Zefirov, P J Stang *Tetrahedron* **53** 13139 (1997)
360. T M Kasumov, V K Brel, K A Potekhin, E V Balashova, N S Zefirov *Dokl. Akad. Nauk* **351** 644 (1996) [d]
361. T M Kasumov, V K Brel, K A Potekhin, A S Koz'min, E V Balashova, Yu S Struchkov, N S Zefirov *Dokl. Akad. Nauk* **349** 634 (1996) [d]

362. T M Kasumov, V K Brel, K A Potekhin, E V Balashova, N S Zefirov, P J Stang *Dokl. Akad. Nauk* **353** 770 (1997) [d]
363. N Sh Pirkuliev, V K Brel, T M Kasumov, N G Akhmedov, N S Zefirov *Zh. Org. Khim.* **35** 1633 (1999) [g]
364. N Sh Pirguliyev, V K Brel, T M Kasumov, N S Zefirov, P J Stang *Synthesis* 1297 (1999)
365. N Sh Pirkuliev, Candidate Thesis in Chemical Sciences, Moscow State University, Moscow, 1999
366. T M Kasumov, V K Brel, A S Koz'min, N S Zefirov, K A Potekhin, P J Stang *New J. Chem.* **21** 1347 (1997)
367. N Sh Pirguliyev, V K Brel, N S Zefirov, P J Stang *Mendeleev Commun.* 189 (1999)
368. T Kitamura, R Furuki, K Nagata, H Taniguchi, P J Stang *J. Org. Chem.* **57** 6810 (1992)
369. T Kitamura, R Furuki, H Taniguchi, P J Stang *Tetrahedron Lett.* **31** 703 (1990)
370. T Kitamura, R Furuki, H Taniguchi, P J Stang *Tetrahedron* **48** 7149 (1992)
371. P J Stang, V V Zhdankin, N S Zefirov *Mendeleev Commun.* 159 (1992)
372. T Kitamura, R Furuki, H Taniguchi, P J Stang *Mendeleev Commun.* 148 (1991)
373. T Kitamura, R Furuki, K Nagata, L Zheng, H Taniguchi *Synlett* 193 (1993)
374. V I Uvarov, V K Brel *Izv. Akad. Nauk, Ser. Khim.* 1629 (1994) [a]
375. V I Uvarov, V K Brel *Zh. Obshch. Khim.* **64** 2060 (1994) [h]
376. T M Klapötke *Heteroatom. Chem.* **8** 473 (1997)
377. A N Nesmeyanov, I N Lisichkina, A S Kulikov, A N Vanchikov, T P Tolstaya, V A Chertkov *Dokl. Akad. Nauk SSSR* **243** 1463 (1978) [d]
378. M Zupan *J. Fluorine Chem.* **8** 305 (1976)
379. R K Marat, A F Janzen *Can. J. Chem.* **55** 3031 (1977)
380. M Zupan, B Zajc *J. Chem. Soc., Perkin Trans. 1* **9** 965 (1978)
381. A M Forster, A J Downs *J. Chem. Soc., Dalton Trans.* 2827 (1984)
382. T B Patrick, S Nadji *J. Fluorine Chem.* **39** 415 (1988)
383. Yu L Yagupol'skii, T I Savina *Zh. Org. Khim.* **15** 438 (1979) [g]
384. A Gregorčič, B Zajc, M Zupan *Phosphorus Sulfur* **6** 107 (1979)
385. X Ou, A F Janzen *Can. J. Chem.* **74** 2002 (1996)
386. K O Christe, W W Wilson *J. Fluorine Chem.* **47** 117 (1990)
387. J E Gordon *The Organic Chemistry of Electrolyte Solutions* (New York: Wiley, 1975)
388. G Zerza, G Sliwinski, N Schwentner, G J Hoffman, D G Imre, V A Apkarian *J. Chem. Phys.* **99** 8414 (1993)
389. X Ou, G M Bernard, A F Janzen *Can. J. Chem.* **75** 1878 (1997)
390. C W Perkins, J C Martin, A J Arduengo, W Lau, A Alegria, J K Kochi *J. Am. Chem. Soc.* **102** 7753 (1980)
391. X Ou, A F Janzen *Inorg. Chem.* **36** 392 (1997)
392. A F Janzen, P M C Wang, A E Lemire *J. Fluorine Chem.* **22** 557 (1983)
393. K Hatano *Chem. Pharm. Bull.* **46** 1337 (1998)
394. X Huang, B J Blackburn, A F Janzen *J. Fluorine Chem.* **47** 145 (1990)
395. M J Robins, S F Wnuk, K B Mullah, N K Dalley *J. Org. Chem.* **56** 6878 (1991)
396. M J Robins, K B Mullah, S F Wnuk, N K Dalley *J. Org. Chem.* **57** 2357 (1992)
397. G Guillerm, M Gatel *J. Chem. Soc., Perkin Trans. 1* 153 (1994)
398. M J Robins, S F Wnuk, K B Mullah, N K Dalley, C-S Yuan, Y Lee, R T Borchardt *J. Org. Chem.* **59** 544 (1994)
399. A M Sipyagin, I A Pomytkin, N N Aleinikov, S V Pal'tsun, V G Kartsev, in *Tez. Dokl. VI Vsesoyuz. Konf. po Khimii Ftororganicheskikh Soedinenii, Novosibirsk, 1990* (Abstracts of Reports of the VIth All-Union Conference on the Chemistry of Organofluorine Compounds, Novosibirsk, 1990)
400. A M Sipyagin, I A Pomytkin, S V Pal'tsun, N N Aleinikov *Khim. Geterotsikl. Soedin.* 58 (1994) [k]
401. A M Sipyagin, I V Efremov, I A Pomytkin, S A Kashtanov, N N Aleinikov *Khim. Geterotsikl. Soedin.* 1291 (1994) [k]
402. A M Sipyagin, Z G Aliev *Khim. Geterotsikl. Soedin.* 1278 (1994) [k]
403. A M Sipyagin, Z G Aliev *Khim. Geterotsikl. Soedin.* 1495 (1993) [k]
404. A M Sipyagin, I A Pomytkin, S V Pal'tsun, N N Aleinikov *Chem. Heterocycl. Compd.* **30** 52 (1994)
405. V N Boiko, G M Shchupak, N V Ignat'ev, L M Yagupol'skii *Zh. Org. Khim.* **15** 1245 (1979) [g]
406. V S Ershov, S A Kashtanov, I V Efremov, I A Pomytkin, A M Sipyagin, N N Aleinikov *Khim. Geterotsikl. Soedin.* 1703 (1995) [k]
407. J Varwing, R Mews *J. Chem. Res. (S)* 245 (1977)
408. H Steinbeisser, R Mews *J. Fluorine Chem.* **17** 505 (1981)
409. R Maggiulli, R Mews, H Oberhammer, W-D Stohrer *J. Fluorine Chem.* **45** 77 (1989)
410. E Jaudas-Presel, R Maggiulli, R Mews, H Oberhammer, T Paust, W-D Stohrer *Chem. Ber.* **123** 2123 (1990)
411. W Leidinger, W Sundermeyer *Chem. Ber.* **115** 2892 (1982)
412. S A Volkova, Z M Sinyutina, L N Nikolenko *Zh. Obshch. Khim.* **44** 2592 (1974) [h]
413. R Minkwitz, G Nowicki, H Preut *Z. Anorg. Allg. Chem.* **573** 185 (1989)
414. R Minkwitz, A Werner *Z. Naturforsch., B Chem. Sci.* **43** 403 (1988)
415. R Minkwitz, G Nowicki *Z. Naturforsch., B Chem. Sci.* **44** 1343 (1989)
416. R Minkwitz, G Nowicki *Inorg. Chem.* **31** 225 (1992)
417. R Minkwitz, G Nowicki *Inorg. Chem.* **30** 4426 (1991)
418. R Minkwitz, W Molsbeck *Z. Anorg. Allg. Chem.* **612** 35 (1992)
419. A J Downs, G S McGrady, E A Barnfield, D W H Rankin, H E Robertson, J E Boggs, K D Dobbs *Inorg. Chem.* **28** 3286 (1989)
420. R Minkwitz, U Lohmann, H Bormann *Z. Anorg. Allg. Chem.* **622** 889 (1996)
421. S Sato, H Ameta, E Horn, O Takahashi, N Furukawa *J. Am. Chem. Soc.* **119** 12374 (1997)
422. T Kawashima, F Ohno, R Okazaki, H Ikeda, S Inagaki *J. Am. Chem. Soc.* **118** 12455 (1996)
423. M Pettersson, J Lundell, L Khriachtchev, E Isoniemi, M Räsänen *J. Am. Chem. Soc.* **120** 7979 (1998)
424. M Yamanishi, K Hirao, K Yamashita *J. Chem. Phys.* **108** 1514 (1998)
425. M Pettersson, J Lundell, M Räsänen *J. Chem. Phys.* **102** 6423 (1995)
426. M Pettersson, J Lundell, M Räsänen *J. Chem. Phys.* **103** 205 (1995)
427. M Pettersson, J Nieminen, L Khriachtchev, M Räsänen *J. Chem. Phys.* **107** 8423 (1997)
428. M Pettersson, J Lundell, L Khriachtchev, M Räsänen *J. Chem. Phys.* **109** 618 (1998)
429. R Kasemann, D Naumann *J. Fluorine Chem.* **41** 321 (1988)
430. H Poleschner, M Heydenreich, K Spindler, G Haufe *Synthesis* 1043 (1994)
431. Y Usuki, M Iwaoka, S Tomoda *Chem. Lett.* 1507 (1992)
432. H Poleschner, M Heydenreich, U Schilde *Liebigs Ann. Chem.* 1187 (1996)
433. K K Laali, W Fiedler, M Regitz *J. Chem. Soc., Chem. Commun.* 1641 (1997)
434. K Uneyama, M Kanai *Tetrahedron Lett.* **31** 3583 (1990)
435. S Sato, H Arakawa, E Horn, N Furukawa *Chem. Lett.* 213 (1998)
436. K Alam, A F Janzen *J. Fluorine Chem.* **27** 467 (1985)
437. D Naumann, S Herberg *J. Fluorine Chem.* **19** 205 (1982)
438. J Bergman, L Engman *J. Am. Chem. Soc.* **103** 2715 (1981)
439. A F Janzen, O C Vaidya *Can. J. Chem.* **51** 1136 (1973)
440. J A Gibson, A F Janzen *Can. J. Chem.* **49** 2168 (1971)
441. S A Lermontov, A V Popov, S I Zavorin, I I Sukhojenko, N V Kuryleva, I V Martynov, N S Zefirov, P J Stang *J. Fluorine Chem.* **66** 233 (1994)
442. A H Cowley, R C-Y Lee *Inorg. Chem.* **18** 60 (1979)
443. S A Lermontov, A V Popov, V O Zavel'skii, I I Sukhozhenko, N V Kirilova, I V Martynov. *Izv. Akad. Nauk SSSR, Ser. Khim.* 682 (1990) [a]
444. L M Yagupol'skii, V I Popov, N V Kondratenko, B L Korsunskii, N N Aleinikov *Zh. Org. Khim.* **11** 459 (1975) [g]
445. D Naumann, W Tyrra *J. Organomet. Chem.* **334** 323 (1987)
446. I G Rakov, Candidate Thesis in Chemical Sciences, Institute of Physiologically Active Compounds, Russian Academy of Sciences, Chernogolovka, 1997
447. S A Lermontov, D M Rakov, N S Zefirov, P J Stang *Phosphorus Sulfur Silicon Relat. Elem.* **92** 225 (1994)
448. R Minkwitz, B Baeck *ACS Symp. Ser.* **555** 90 (1994)
449. I V Martynov, R G Gafurov, A K Ustinov, N N Aleinikov, S A Kashtanov. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1437 (1987) [a]
450. V V Bardin, I V Stennikova, G G Furin, T V Leshina, G G Jakobson *Zh. Obshch. Khim.* **58** 2580 (1988) [h]

451. V V Bardin, H J Frohn *J. Fluorine Chem.* **90** 93 (1998)
452. A P Lothian, C A Ramsden *Synlett* 753 (1993)
453. G W M Visser, R E Herder, F J J de Kanter, J D M Herscheid *J. Chem. Soc., Perkin Trans. 1* 1203 (1988)
454. M J Robins, S Manfredini *Tetrahedron Lett.* **31** 5633 (1990)
455. S A Klyuchinskii, M-A M Abid-Albaki, V S Zavgorodnii *Zh. Obshch. Khim.* **64** 161 (1994) [h]
456. M A Tius, J K Kawakami *Synth. Commun.* **22** 1461 (1992)
457. M A Tius, J K Kawakami *Synlett* 207 (1993)
458. D P Matthews, S C Miller, E T Jarvi, J S Sarbol, J R McCarthy *Tetrahedron Lett.* **34** 3057 (1993)
459. H F Hodson, D J Madge, D A Widdowson *Synlett* 831 (1992)
460. M A Tius, J K Kawakami *Tetrahedron* **51** 3997 (1995)
461. M A Tius, G S K Kannangara *Tetrahedron* **48** 9173 (1992)
462. M A Tius, G S K Kannangara, M A Kerr, K J S Grace *Tetrahedron* **49** 3291 (1993)
463. A L J Beckwith, D M O'Shea *Tetrahedron Lett.* **27** 4525 (1986)
464. G A Tolstikov, S K Minsker, Z G Bulgakov, G Ya Maistrenko, A V Kuchin, U M Dzhemilev, V P Kazakov *Izv. Akad. Nauk SSSR, Ser. Khim.* 2631 (1979) [a]
465. R G Bulgakov, V N Yakovlev, G Ya Maistrenko, G A Tolstikov, V P Kazakov *Izv. Akad. Nauk SSSR, Ser. Khim.* 490 (1986) [a]
466. R G Bulgakov, V N Yakovlev, R A Sadykov, G Ya Maistrenko, V P Kazakov, G A Tolstikov *Metalloorg. Khim.* **2** 339 (1989) [l]
467. G A Tolstikov, R G Bulgakov, S K Minsker, G Ya Maistrenko, A V Kuchin, U M Dzhemilev, V P Kazakov *Khim. Vys. Energ.* **15** 248 (1981) [m]
468. V P Kazakov, V N Yakovlev, G Ya Maistrenko *Khim. Vys. Energ.* **31** 133 (1997) [m]
469. Z Bregar, S Stavber, M Zupan *J. Fluorine Chem.* **44** 187 (1989)
470. Z Bregar, M Zupan, in *The 8th International Conference on Organic Synthesis (IUPAC), Helsinski, 1990* p. 123
471. M Zupan, Z Bregar *Tetrahedron Lett.* **31** 3357 (1990)
472. K P Butin, Yu M Kiselev, T V Magdesieva, O A Reutov *J. Organomet. Chem.* **235** 127 (1982)
473. R C Burns, I D MacLeod, T A O'Donnell, T E Peel, K A Phillips, A W Waugh *J. Inorg. Nucl. Chem.* **39** 1737 (1977)
474. A J Blake, R W Cockman, E A V Ebsworth, J H Holloway *J. Chem. Soc., Chem. Commun.* 529 (1988)
475. M C Crossman, E G Hope, L J Wootton *J. Chem. Soc., Dalton Trans.* 1813 (1998)
476. S A Brewer, J H Holloway, E G Hope *J. Chem. Soc., Dalton Trans.* 1067 (1994)
477. S A Brewer, A K Brisdon, J H Holloway, E G Hope, L A Reck, P G Watson *J. Chem. Soc., Dalton Trans.* 2945 (1995)
478. S A Brewer, J H Holloway, E G Hope, P G Watson *J. Chem. Soc. Dalton Trans.* 1577 (1992)
479. K S Coleman, J H Holloway, E G Hope *J. Chem. Soc., Dalton Trans.* 11713 (1997)
480. V P Zubov, S D Stavrova, I P Chikhacheva, O A Prudnikova, G A Fedorova, G B Barsamyan, V B Sokolov *Zh. Prikl. Khim.* **71** 848 (1998) [n]
481. Yu N Kozlov, A P Moravskii, A M Uskov, A E Shilov *Kinet. Katal.* **31** 251 (1990) [o]
482. A I Yurtanov, V A Piven', S K Baidildaeva, A V Sliz'kii, V K Brel *Zh. Org. Khim.* **32** 848 (1996) [g]
483. D L Shellhamer, B C Jones, B J Pettus, T L Pettus, J M Stringer, V L Heasley *J. Fluorine Chem.* **88** 37 (1998)
484. T B Patrick, L Zhang *Tetrahedron Lett.* **38** 8925 (1997)
485. T B Patrick, L Zhang, Q Li *J. Fluorine Chem.* **102** 11 (2000)
486. T B Patrick, S Qian *Org. Lett.* **2** 3359 (2000)
487. R Taylor *Izv. Akad. Nauk, Ser. Khim.* 852 (1998) [a]
488. O V Boltalina, A K Abdul-Sada, R Taylor *J. Chem. Soc., Perkin Trans. 2* 981 (1995)
489. L G Bulusheva, A V Okotrub *Rev. Inorg. Chem.* **19** 79 (1999)

[a] — *Russ. Chem. Bull. (Engl. Transl.)*
[b] — *Russ. J. Inorg. Chem. (Engl. Transl.)*
[c] — *Inorg. Mater. (Engl. Transl.)*
[d] — *Dokl. Chem. Technol., Dokl. Chem. (Engl. Transl.)*
[e] — *Russ. J. Phys. Chem. (Engl. Transl.)*
[f] — *Herald Russ. Acad. Sci. (Engl. Transl.)*
[g] — *Russ. J. Org. Chem. (Engl. Transl.)*
[h] — *Russ. J. Gen. Chem. (Engl. Transl.)*
[i] — *Russ. J. Coord. Chem. (Engl. Transl.)*
[j] — *J. Struct. Chem. (Engl. Transl.)*
[k] — *Chem. Heterocycl. Compd. (Engl. Transl.)*
[l] — *Organomet. Chem. (Engl. Transl.)*
[m] — *High Energy Chem. (Engl. Transl.)*
[n] — *Russ. J. Appl. Chem. (Engl. Transl.)*
[o] — *Kinet. Catal. (Engl. Transl.)*