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The preparation and properties of polyfluoro aromatic and heteroaromatic compounds

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Abstract

This review is concerned with ring systems formally recognised as "aromatic" and possessing a large proportion of fluorine atoms directly attached to the carbon skeleton. These include derivatives of the following: benzene and polynuclear benzenoid systems; pyridine, diaza- and triazabenzenes and some of their fused six-membered ring compounds; and a wide variety of fused ring carbocycles and heterocycles. Some highly fluorinated non-benzenoid aromatic compounds obeying the Hückel $4n+2$ π electron rule, as well as antiaromatic $4n$ π electron systems, are included in the survey. The wide variety of methods used for synthesising these highly fluorinated compounds, which enabled them to be regarded no longer as mere chemical curiosities, is presented. The chemical behaviour of polyfluoro aromatic and heteroaromatic compounds, at the fluorinated ring, forms the major proportion of this review: reactions with nucleophiles and a rationalisation of orientation reactions; reactions with electrophiles, free radicals, carbenes and nitrenes; the formation of stable salts of radical cations; photochemical reactions and the formation of valence isomers; and rearrangement reactions. Organometallic derivatives of polyfluorinated compounds have been extensively used in organic synthesis.

Keywords: Polyfluoroaromatics; Polyfluoroheterocyclics; Nucleophilic substitution; Orientation reactions; Electrophilic addition; Radical cations; Radical anions; Valence isomers

Contents

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1. Introduction

Over 40 years have elapsed since the first serious study of the chemistry of hexafluorobenzene began [1]. The vision ahead was the exploration of a vast new area of chemistry with fluorine as the principal substituent in all types of aromatic and heteroaromatic compounds, and the potential of commercial exploitation for the benefit of mankind.

This review is concerned with the methods which have been developed to synthesise polyfluoro aromatic and heteroaromatic compounds, and the chemistry which has been carried out on the rings. The very large volume of work that had been published up to the end of 1995 has meant that some selectivity has been necessary. Numerous reviews and textbooks have been consulted in the preparation of the present review [2].

2. Synthesis

The pyrolysis of $CFBr_3$ provided the first relatively simple route to hexafluorobenzene (Eq. (1)) [3–5], but it was clear that other methods were needed for routine access to other ring systems.

$$6CFBr_3 \xrightarrow[630-640°C]{Pt} C_6F_6+9Br_2 \qquad (1)$$

Important routes to fluorinated aromatic and heteroaromatic compounds have used the perchloro analogues, or the simple hydrocarbons or their saturated analogues as starting materials. Formation of the perfluoro compounds may involve the direct replacement of the halogen or hydrogen by a fluorinating agent, or an initial conversion to a saturated or partially saturated intermediate which is aromatised either by dehydrohalogenation or by dehalogenation, or by a combination of both these processes.

2.1. Saturation–rearomatisation by dehalogenation (halogen = Cl, Br, F)

Historically, the first reported synthesis of hexafluorobenzene started with hexachlorobenzene. The two-step bromofluorination to the saturated cyclohexane derivative was followed by a mild dehalogenation reaction to give a low yield of the fluorocarbon accompanied by chloropentafluorobenzene in a complex product (Eq. (2)) [6].

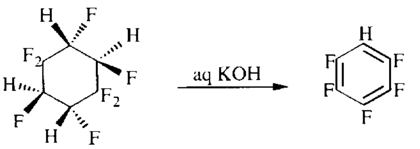
$$C_6Cl_6 + BrF_3 \rightarrow [C_6Br_2Cl_4F_6]_{av} \xrightarrow{SbF_5} C_6BrCl_4F_7 \qquad (2)$$

$$\xrightarrow[EtOH]{Zn} C_6F_6 + C_6F_5Cl$$

Elemental fluorine [7,8] and chlorine trifluoride [9] have been used as alternatives to produce intermediate chlorofluorocyclohexanes from C_6Cl_6 for dehalogenation with iron at 330°C.

2.2. Saturation–rearomatisation by dehydrofluorination

The reaction of benzene with cobalt trifluoride gave a complex mixture of polyfluorocyclohexanes which have been sources of polyfluorobenzenes. For example, the dehydrofluorination of the 1*H*,4*H*/2*H*-nonafluoro derivative $C_6F_9H_3$ with aqueous KOH gave hexafluorobenzene [1], while a similar reaction with the octafluorocyclohexane (**1**) gave pentafluorobenzene among the products (Eq. (3)) [10].



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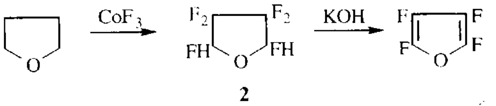
Treatment of tetrahydrofuran with CoF_3 [11,12] and of thiophene with $KCoF_4$ [13,14] gave intermediates (**2**) and (**3**) having different patterns of fluorination which were dehydrofluorinated to the unstable tetrafluorofuran and to tetrafluorothiophene, respectively (Eqs. (4) and (5)).



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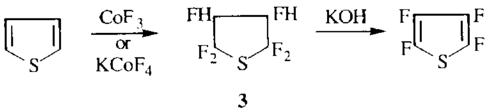

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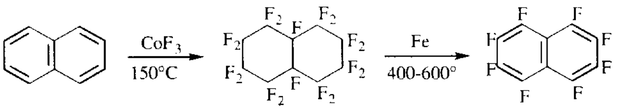
2.3. Saturation (partial saturation)–rearomatisation by defluorination

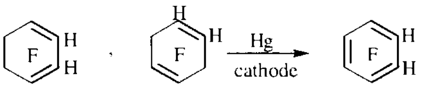
A general route to aromatic fluorocarbons was published in 1959 [15] involving complete fluorination of the hydrocarbon followed by defluorination under vigorous conditions over iron, nickel or Fe_2O_3. Thus, perfluoro-toluene, -ethylbenzene, -diphenyl [15], -*ortho*- and -*para*-xylenes [16], -*meta*-xylene [17] and -mesitylene [18] were prepared by this method. Eq. (6) shows the first synthesis of octafluoronaphthalene [15].



(6)

Other condensed ring compounds prepared include perfluoroanthracene, perfluoroacenaphthylene, perfluoroacenaphthene, perfluoroindane, perfluoropyrene [19], perfluorochrysene [20] and perfluorofluoranthene [21]. Improved syntheses of perfluoro-pyrene and -phenanthrene were obtained using $KCoF_4$ in the first stages of the syntheses [22].

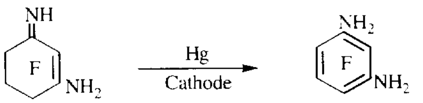
Defluorinations have been carried out at high temperatures with iron on perfluoro-1,3- and -1,4-cyclohexadienes and on polyfluoro-cyclohexenes, and -1,3- and -1,4-cyclohexadienes bearing hydrogen on a double bond, to give hexa-, penta-, 2,3,5,6-tetra- and 2,3,4,6-tetrafluorobenzene [23,24]. A mild electrochemical defluorination procedure at a mercury cathode with the 1,3- and 1,4-cyclohexadienes (**4**) and (**5**) gave o-$C_6F_4H_2$ [25] (Eq. (7)),



(7)

4 **5**

and the process has been applied to a substituted derivative (**6**) [26] (Eq. (8)).



(8)

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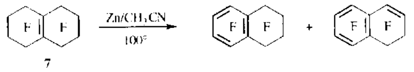
Tetralin and CoF_3 at 250°C gave the perfluoroalkene (**7**) among the products [27], which has been partially defluorinated under mild conditions with zinc in polar aprotic solvents (Eq. (9)) [28].



(9)

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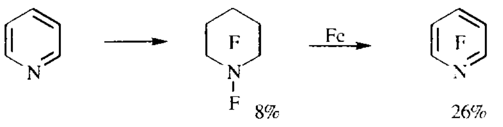
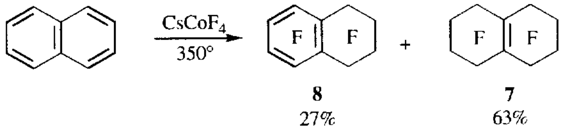
Pentafluoropyridine was prepared for the first time in low overall yield by defluorination of perfluoropiperidine, obtained via the electrochemical fluorination of pyridine or piperidine (Eq. (10)) [29–31]. Perfluoro-2-, -3- and -4-methylpyridines have been prepared by the same methodology [32].



(10)

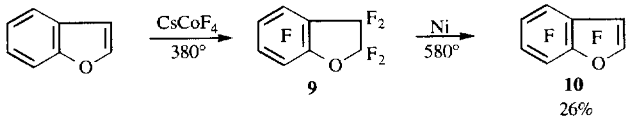
2.4. Direct replacement of hydrogen by fluorine

In principle, this process would be the most convenient route to the target compounds and a number of studies have been carried out using complex metal fluorides. The most effective reagent was $CsCoF_4$, which with benzene at 250°C gave a mixture of products, including C_6F_5H (9%) and C_6F_6 (4%), and was the first direct synthesis of a perfluoro-arene [33]. Octafluorotoluene was formed in 18% yield from benzotrifluoride [34]. Naphthalene gave perfluorotetralin (**8**) and compound (**7**) as the major products (Eq. (11)) [35] and in a similar process with quinoline, the analogue of (**8**) with nitrogen in the aromatic ring was identified in the product [36].



(11)

Low yields of pentafluoropyridine (15%) [37] and octafluoro(4-methylpyridine) [38] were obtained from the corresponding heterocycles. The fluorination of benzo[*b*]furan and defluorination of the product (**9**) resulted in the first synthesis of perfluorobenzo[*b*]furan (**10**) (Eq. (12)) [39].



(12)

Treatment of benzene with CeF_4 at 480°C gave *o*-$C_6F_4H_2$ and *p*-$C_6F_4H_2$ [40].

2.5. Direct replacement of chlorine by fluorine

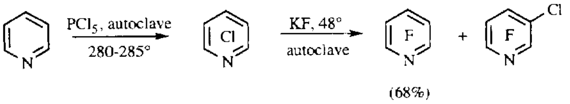
The ready availability of C_6Cl_6 made this compound the prototype for reaction with potassium fluoride. Only a trace of C_6F_6 was formed in the reaction carried out in sulpholane (Eq. (13)), but a good yield (52%) of $C_{10}F_8$ was obtained from octachloronaphthalene [41].

$$C_6Cl_6 \xrightarrow[230-240^\circ]{KF,\ sulpholane} C_6F_6\ (0.4\%) + C_6F_5Cl\ (25\%) + C_6F_4Cl_2\ (24\%) + 1,3,5-C_6F_3Cl_3\ (30\%) \tag{13}$$

In the absence of solvent, Russian workers identified a much more efficient procedure with C_6Cl_6 (Eq. (14)) [42], and with $C_{10}Cl_8$ [43], which has become the standard procedure for making nitrogen-containing perfluoroheteroaromatic systems.

$$C_6Cl_6 \xrightarrow[450-500^\circ C]{KF,\ autoclave} C_6F_6\ (21\%) + C_6F_5Cl\ (20\%) + C_6F_4Cl_2\ (14\%) + C_6F_3Cl_3\ (12\%) \tag{14}$$

The remarkable fact is that perchloroazabenzenoid compounds, in general, can readily be prepared by the further chlorination of partially chlorinated compound (obtained by a standard Friedel–Crafts reaction) with phosphorus pentachloride. Pentachloropyridine was formed from PCl_5 alone and gave high yields of pentafluoropyridine with KF [44,45] (Eq. (15)). The preparation of heptafluoroquinoline (**11**) [353] by the general procedure is given in Eq. (16).



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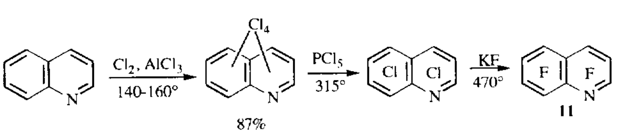
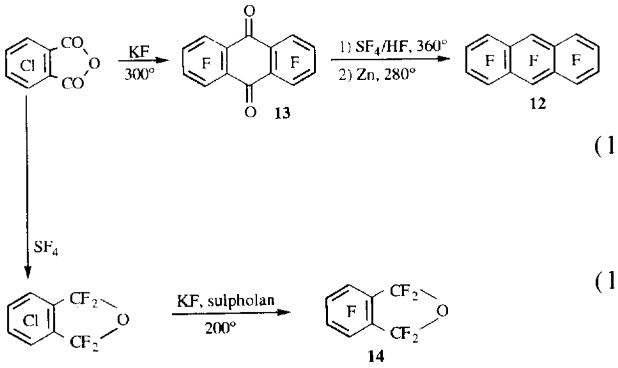


(16)

The syntheses of other perfluoroheteroaromatic compounds can be found in the references cited in Table 5 which deals with their reactions with nucleophiles. Methods have been developed for the polychlorination and subsequent fluorination of benzonitrile [46] and 2-cyanopyridine [47] with retention of the CN group. The syntheses of perfluoroheteroaromatic compounds have been reviewed [48,49].

Tetrachlorophthalic anhydride has been used as the starting material for an alternative synthesis of decafluoroanthracene (**12**) [50] (Eq. (17)) via octafluoroanthraquinone (**13**) [51], and of octafluoro-1,3-dihydrobenzo[*c*]furan (**14**) (Eq. (18)) [52a].



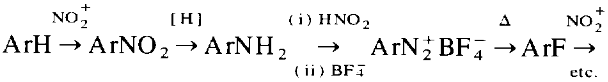
(17)

(18)

2.6. Replacement of –N_2^+ by fluorine: the Balz–Schiemann reaction

This classical reaction [52b], which involves the pyrolysis of aryldiazonium tetrafluoroborates, was used to make

p-$C_6F_4H_2$ from m-$C_6H_4F_2$ via the sequence of reactions of the type shown below [52c]. However, the limitations of the procedure had been reached at that time, since the nitration of the tetrafluoro compound was unsuccessful (see Section 3.3.2).



$$ArH \xrightarrow{NO_2^+} ArNO_2 \xrightarrow{[H]} ArNH_2 \xrightarrow[(ii)\ BF_4^-]{(i)\ HNO_2} ArN_2^+BF_4^- \xrightarrow{\Delta} ArF \xrightarrow[etc.]{NO_2^+}$$

2.7. Non-benzenoid aromatic compounds

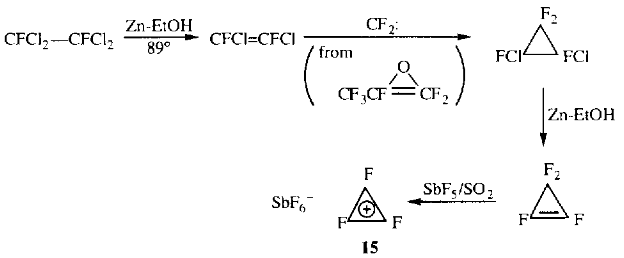
According to the Hückel rule, cyclic systems containing $4n+2$ π electrons are formally considered to be "aromatic". Three ionic species, fully fluorinated, have been prepared which fit into this category:

(i) The trifluorocyclopropenyl cation (**15**) was prepared by the following sequence of reactions (Scheme 1) and showed a single resonance absorption in its ^{19}F NMR spectrum [53].

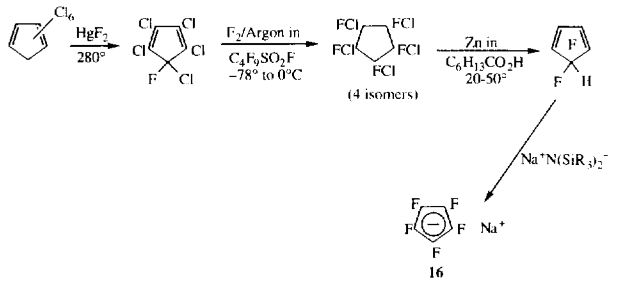
(ii) The pentafluorocyclopentadienyl anion (**16**), as its sodium salt, was stable in THF/18-crown-6. Its ^{19}F NMR spectrum was a singlet. The synthesis is shown in Scheme 2 [54].

(iii) Octafluorocycloheptatriene (**17**) is a potential source of 6π-electron systems. Two syntheses have been described, one starting from C_6F_6 [55], the other from cycloheptatriene or cycloheptane [56] which is shown in Scheme 3. (Complex mixtures resulted in the earlier stages: only the relevant intermediates are given.) Treatment of (**17**) with BF_3 gave the heptafluorotropylium cation (**18**); its ^{19}F NMR spectrum showed one sharp singlet [55].

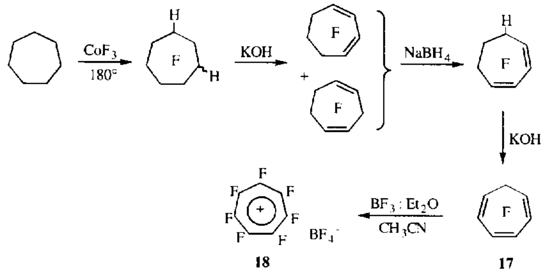
The tropylidene (**17**) was readily hydrolysed by atmospheric moisture to the hexafluorotropone (**19**), which in turn with very dilute NaOH gave the 2-, 3- and 4-hydroxy derivatives (**20**) (Scheme 4) [57]. X-ray crystallographic data showed that there was no significant delocalisation in (**19**) and only a small amount in the 2-tropolone derivative [58].



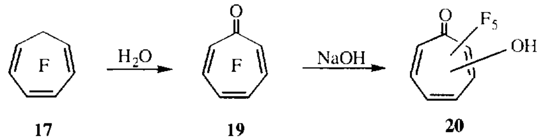
Scheme 1.



Scheme 2.



Scheme 3.



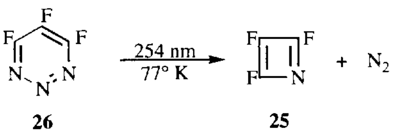
Scheme 4.

The octafluorocyclooctatetraene radical anion $C_8F_8^{\bullet-}$, generated by γ-irradiation of its solid solution in 2-methyltetrahydrofuran at 77 K, has an ESR spectrum at 145 K consistent with a planar aromatic structure. It was argued that, despite the negative charge, in terms of the $4n+2$ rule it was electron deficient and could be compared to the radical cations of fluorinated aromatic molecules [59].

2.8. Non-benzenoid antiaromatic compounds

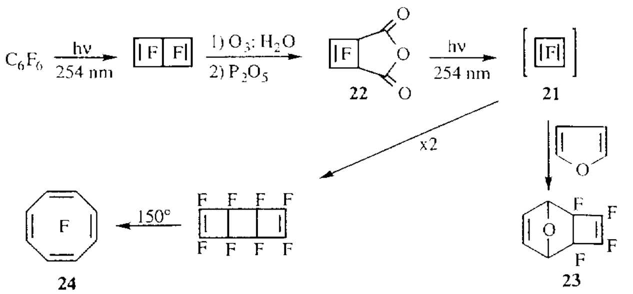
Cyclic conjugated compounds possessing $4n$ π electrons, are usually considered alongside those with $4n+2$ π electrons in general discussions about aromaticity. The simplest of these formally antiaromatic systems in fluorine chemistry is tetrafluorocyclobutadiene C_4F_4 (**21**). The successful generation of this highly reactive, short-lived species from (**22**) was demonstrated by trapping it with furan to give (**23**), and identifying the product of its dimerisation by conversion to cyclo-C_8F_8 (**24**) (Scheme 5) [60].

Direct evidence (mass spectrometry, infrared data and mass spectrometry on the adduct with furan) was obtained for the formation of trifluoroazete (**25**) via the photochemical decomposition of trifluoro-1,2,3-triazine (**26**) (Eq. (19)) [61].

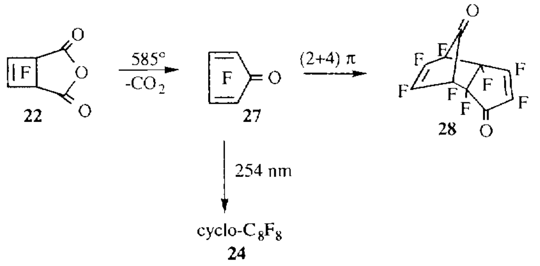


(19)

Tetrafluorocyclopentadienone (**27**), a 4π-electron system, which could be manipulated at room temperature as an orange vapour, was obtained by the thermolysis of compound (**22**). Its identity was determined from its dimerisation product (**28**) and photolysis to cyclo-C_8F_8 (**24**), probably via cyclo-C_4F_4 (**21**) (Scheme 6) [62].

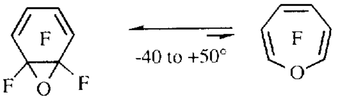


Scheme 5.



Scheme 6.

Hexafluorooxepin (**29**), formally an antiaromatic system with 8 π electrons, was deduced to be present in a dynamic equilibrium with hexafluorobenzene oxide (**30**), though it was not independently observed during variable low temperature ^{19}F NMR studies (Eq. (20)) [63].

 (20)

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3. The chemistry of polyfluoro aromatic and heteroaromatic compounds

Hexafluorobenzene began to become available in quantity in the 1950s and an early report [3] indicated that it was unreactive towards electrophiles, the reagents used to bring about substitution of hydrogen in "traditional" benzenoid species. Electrophilic substitution would require the elimination of F^+, so that from energetic considerations it is not surprising that the process did not occur. Russian workers later discovered that addition reactions to polyfluoroaromatic compounds can occur very readily under appropriate circumstances and opened up a new field of chemistry. This work is considered in Section 3.4.

It was soon established that C_6F_6 was reactive towards nucleophiles [1,10,64,65], substitution reactions taking place with fluoride ion being eliminated, and it is inevitable that this area of chemistry has been intensively studied. In this review it is the starting point for looking at the chemistry of polyfluoro-aromatic and -heteroaromatic compounds; their interaction with electrophiles, free radicals and carbenes and a host of other reactions involving the aromatic ring are covered in later sections.

3.1. Nucleophilic aromatic substitution of fluorine

The wide range of reagents which have been used to form C_6F_5X derivatives from hexafluorobenzene are shown in Table 1. However, the further reaction of these compounds with nucleophiles presented the same intriguing question encountered in the more familiar reactions of benzene derivatives, C_6H_5X, with electrophiles: namely, the choice of three sites of attack, ortho, meta and para to the group X. The general pattern of directive effects for nucleophilic substitutions in compounds C_6F_5X was soon established [82,117,110]. The major product in most cases (but not all) was the para isomer, 1,4-YC_6F_4X. In the very early work, orientations were established by relationship to 1,2,4,5-tetrafluorobenzene [52c] and to tetrafluoro-*p*-benzoquinone [201,243], and ^{19}F NMR spectroscopy could be used thereafter [82]. In later work, further nucleophilic replacements in tetrafluoro-substituted benzenes were investigated [249,250,311]. There were also orientational questions to be addressed in the cases of perfluoro-polycyclic aromatic compounds and in perfluoro- and polyfluoro-heteroaromatic systems. Tables 2–5 show some of the results of these investigations. In the following sections the major highlights of these studies are presented.

3.1.1. Metallation reactions

Carbanionic reagents feature strongly in the reactions with C_6F_6 to form C_6F_5–C derivatives (Table 1), but they are conspicuously absent in reactions with C_6F_5H (Table 2). Treatment of pentafluorobenzene with Grignard reagents followed by carbonation showed that metallation of the ring had taken place rather than fluorine substitution (Eq. (21)) [68].

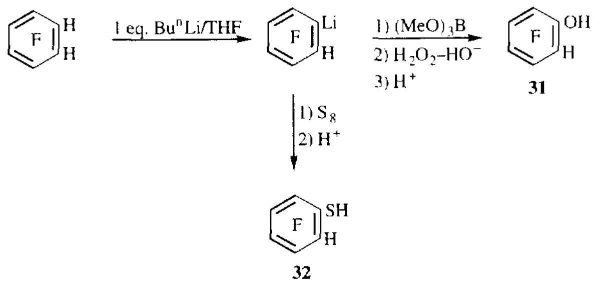
$$C_6F_5H \xrightarrow{\text{EtMgBr}} C_6F_5MgBr \xrightarrow[\text{2) }H^+]{\text{1) }CO_2} \underset{85\%}{C_6F_5CO_2H} \qquad (21)$$

Lithiation with *n*-butyllithium is even more effective and is used routinely: it reacts selectively with *o*- and *p*-$C_6F_4H_2$ [68]. The former compound was converted into the phenol (**31**) and the thiophenol (**32**) derivatives (Scheme 7) [360], precursors for the syntheses of fused ring heterocycles [361,362].

3.1.2. Polyfluoroalkylation and related reactions

Fluoroalkenes react with fluoride ion in aprotic solvents to form carbanions which may be trapped with reactive polyfluoro-aromatic and -heteroaromatic compounds (e.g. Eq. (22));

$$F^- + CF_2{=}CFCF_3 \rightleftharpoons (CF_3)_2CF \overset{\text{ArF}}{\rightleftharpoons} ArCF(CF_3)_2 + F^- \qquad (22)$$



Scheme 7.

the overall process may be regarded as the nucleophilic counterpart of a Friedel–Crafts reaction [2a]. Pentafluoropyridine has been reacted with the largest variety of such polyfluoroalkyl groups (Table 4). Mono- and di-polyfluoroalkylation patterns for $(CF_3)_2CF$ are "normal" (giving 4- and 2,4-derivatives, respectively), but the introduction of a third group into the 5-position is a result of kinetic control. Under more vigorous conditions, the 2,4,5-compound (**33**) rearranges to the thermodynamically more stable 2,4,6-isomer (**34**) and the 2,5-disubstituted compound (**35**) is also

Table 1
Formation of C_6F_5X compounds from C_6F_6

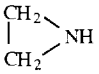
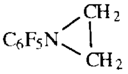
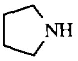
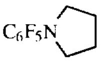
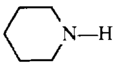
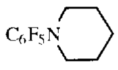
Nucleophile	Product (C_6F_5X)	Ref.
$LiAlH_4$	C_6F_5H	[66]
MeMgI	C_6F_5Me (3%)	[64]
MeLi	C_6F_5Me	[66,67,451c]
EtMgBr	C_6F_5Et	[68,69]
Et_2Mg	C_6F_5Et	[70]
Bu^{n}Li	$C_6F_5Bu^n$	[66,67]
Bu^{n}MgBr	$C_6F_5Bu^n$	[71a]
$CH_2{=}CHCH_2MgBr$	$C_6F_5CH_2CH{=}CH_2$	[68]
$MeSOCH_2Na$	$C_6F_5CH_2SOMe$	[416]
$PhSO_2CH_2Li$	$C_6F_5CH_2SO_2Ph$	[71b]
$CH_2{=}CHLi$	$C_6F_5CH{=}CH_2$	[66]
$MeCH{=}CHLi$	$C_6F_5CH{=}CHMe$	[72]
$CH_2{=}C(Me)Li$	$C_6F_5C(Me){=}CH_2$	[66]
Et_2NCOLi	$C_6F_5CON(Et)_2$	[73]
$Ph_3P{=}CHR$	$Ph_3P{=}C(R)C_6F_5$	[74,75]
$Ph_3As{=}CH_2$	$Ph_3As{=}CHC_6F_5$	[76,136]
$Ph_3P{=}CH–CH{=}CH_2$	$Ph_3P{=}CH–CH{=}CHC_6F_5$	[77]
PhLi	C_6F_5Ph	[66,78]
PhMgBr	C_6F_5Ph	[68]
o-, *m*-, *p*-MeC_6H_4Li	*o*-, *m*-, *p*-C_6F_5–C_6H_4Me	[79]
$R–C{\equiv}CLi$	$C_6F_5C{\equiv}CR$	[80]
$NaCH(CO_2Et)_2$	$C_6F_5CH(CO_2Et)_2$	[81]
$NaCH(CN)_2$	$C_6F_5CH(CN)_2$	[81]
$NaCH(CN)CO_2Et$	$C_6F_5CH(CN)CO_2Et$	[81]
Me_3SiNa	$C_6F_5SiMe_3$	[71]
$NaNH_2$	$C_6F_5NH_2$	[65]
NH_3	$C_6F_5NH_2$	[66,82,83]
$MeNH_2$	C_6F_5NHMe	[66,82]
Me_3CNH_2	$C_6F_5NHCMe_3$	[84]
$PhNH_2/NaH$	C_6F_5NHPh	[85]
$C_6F_5NH_2/NaH$	$(C_6F_5)_2NH$	[85,86]
$(Me_3Si)_2NNa$	$(C_6F_5)_2NH$	[87]
4-$HC_6F_4NH_2/NaH$	4-$HC_6F_4NHC_6F_5$	[86]
$ArNH_2/NaH$	C_6F_5NHAr	[88]
$H_2N(CH_2)_2NH_2$	$C_6F_5NH(CH_2)_2NH_2$	[89]
$HO(CH_2)_2NH_2$ (100–110°C, solvent)	$C_6F_5NH(CH_2)_2OH$	[89–91]
NH_2OH	C_6F_5NHOH	[92]
Me_2NH	$C_6F_5NMe_2$	[66]
$(HOCH_2CH_2)_2NH$	$C_6F_5N(CH_2CH_2OH)_2$	[93]
		[93]
		[94]
		[95]

Table 1 (*continued*)

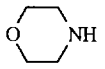
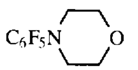
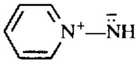
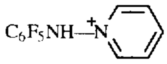
Nucleophile	Product (C_6F_5X)	Ref.
		[93,95]
Ph_2NH/NaH	$C_6F_5NPh_2$	[85]
Ph_2NLi	$C_6F_5NPh_2$	[96]
$C_6F_5\bar{N}Ph$	$(C_6F_5)_2NPh$	[85]
$(C_6F_5)_2\bar{N}$	$(C_6F_5)_3N$	[85]
$PhN(Li)SiMe_3$	$C_6F_5N(Ph)SiMe_3$	[97]
Pr^i_2NLi	$C_6F_5NPr^i_2$	[259]
H_2NH_2	$C_6F_5NHNH_2$	[82,98,99]
		[100a]
$NaNO_2$, DMSO	4-$HOC_6F_4NO_2$	[101]
$(EtO)_2PO^-$	$C_6F_5PO(OEt)_2$	[102]
HO^-/H_2O–Bu_4NOH	C_6F_5OH	[103]
KOH/Bu^tOH	C_6F_5OH	[5,104,105]
KOH/liq. NH_3	C_6F_5OH	[106]
MeONa (also in liq. NH_3)	C_6F_5OMe	[1,64,244]([106])
EtOK	C_6F_5OEt	[5]
CF_3CH_2ONa	$C_6F_5OCH_2CF_3$	[107,108]
$CF_3CH_2OSi(CH_3)_3/CsF$	$C_6F_5OCH_2CF_3$, $C_6(OCH_2CF_3)_6$	[109]
$CF_2H(CF_2)_3CH_2ONa$	$C_6F_5OCH_2(CF_2)_4H$	[108]
$PhCH_2ONa$	$C_6F_5OCH_2Ph$	[66]
$HOCH_2CH_2OH$	$C_6F_5OCH_2CH_2OH$	[89,91]
$HOCH_2CH_2OH$/liq. NH_3	$(C_6F_5OCH_2)_2$	[111]
$NH_2CH_2CH_2ONa$/liq. NH_3	$C_6F_5OCH_2CH_2NH_2$	[111]
$NH_2CH_2CH_2OH/NaOH$, 20°C	$C_6F_5OCH_2CH_2NH_2$	[90]
$Bu^tOLi(K)$	$C_6F_5OooBu^t$	[84]([259])
PhO^-	C_6F_5OPh	[66]
ArO^-	$C_6(OAr)_6$	[112,113]
2- and 4-$NH_2C_6H_4ONa$	$C_6F_5OC_6H_4NH_2$ (2-, 4-)	[114]
3-$Et_2NC_6H_4ONa$	$C_6F_5OC_6H_4NEt_2$-(3-)	[115]
C_6F_5OK	$(C_6F_5)_2O$	[66,104,130]
$O_2^{\bullet -}$	$(C_6F_5O)_2$	[116]
NaSH	C_6F_5SH	[117]
RS^-	C_6F_5SR	[118]
RS^-	$C_6(SR)_6$	[112,119]
$[Fe(CO)_2C_5H_5]^-$	$C_6F_5Fe(CO)_2C_5H_5$	[120]
$[Re(CO)_5]^-$	$C_6F_5Re(CO)_5$	[121]

Table 2
Nucleophilic substitution reactions with C_6F_5X and $C_6F_{6-x}(CF_3)_x$ compounds

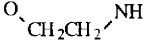
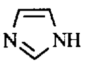
Substituent X	Nucleophile (Ref.)	Orientation of product (%)		
		o	*m*	*p*
H	$LiAlH_4$ [122]	7	1	92
	C_6F_5Li [123] (C_6F_4 also involved)	(✓)		✓
	NH_3 [82]; ArNHLi, ArN(Li)Me;  $O(CH_2CH_2)_2NH$ [124];  [125]	–	–	✓
	Me_2NH [126]	5	–	95
	N_2H_4 [82]; NH_2OH [92,127]; $NaNO_2$ [101]	–	–	✓
	$(EtO)_3P$ [128]; $(EtO)_2PO^-$ [102]	–	–	✓
	HO^- [66]; ArO^- [88,115]; $PhC(Me){=}NO^-$ [129]	–	–	✓
	NaOMe/MeOH [126]; (NaOMe/liq. NH_3 [106])	3	–	97
	C_6F_5ONa [130]	17	–	83

Table 2 (*continued*)

Substituent X	Nucleophile (Ref.)	Orientation of product (%)		
		o	*m*	*p*
	HS^-, PhS^- [117]; $(PhS)_2Pb$ [131]; 4-HC_6F_5SK; 2-$NH_2C_6H_4SK$ [132]	–	–	✓
	$[Fe(CO)_2C_5H_5]^-$ [120,133]	–	–	✓
Me	MeLi [451c]; *n*BuLi [134]; MeO^-, NH_3, N_2H_4 [135]; N_2H_4 [145]; $(PhS)_2Pb$ [131]; KOH [66]; $Ph_3As{=}CH_2$ [136]	–	–	✓
CH_2F; CHF_2	*n*BuLi [134]	–	–	✓
CF_3	$LiAlH_4$, MeLi, NH_3, N_2H_4, EtO^-, HS^-, PhS^- [137]; $CF_3SiMe_3/TASF$ [138]; $PhSO_2CH_2Li$ [71b]; $(CF)_3\bar{C}F$ [139]; $(CF_3)_2\bar{C}CO_2Et$ [140,141]; $C_2F_5\bar{C}FCF_3$ [142]; $PhC{\equiv}C^-$ [143]; C_6F_5Li [123]; Et_2NCOLi [73]; $(C_6F_5COCH_2)^-$ [144]; $R_3\overset{+}{N}{-}\bar{C}HCO_2Bu^t$ [100b]; $(Me_3Si)_2NH/CsF$ [305]; N_2H_4 [145]; $HN(CH_2CH_2OH)_2$ [93]; Bu^tNH_2, Bu^tOLi, Bu^tSLi [84]; $ArCH_2\underline{N}HOH$ [146]; NH_2OH [92], $Ar\bar{N}COAr'$ [147]; $R_3\overset{+}{N}{-}\bar{N}H$ [100a]; $(EtO)_2\bar{P}O^-$, $(EtO)_2PS^-$ [102]; $(EtO)_3P$ [128]; HO^- [148]; oestradiol at 3-OH [149]; Et_2NO^- [150]; $(CF_3)_2NO^-$ [151]; $PhC(Me){=}NO^-$ [129]; 1,3-$C_6F_4(OLi)_2$, 1,4-$C_6F_4(ONa)_2$ [152]; $Na_2S_2O_3$ or $Na_2S \cdot 6H_2O$ [153b]; $(PhS)_2Pb$ [131]; $(NH_2)_2CS$ [383]; $AlCl_3$ [154]; $Et_3GeCl/(Et_2N)_3P$ [155]	–	–	✓
	$MeNH_2/C_6H_6$ [156]	<1	–	98
	$MeNH_2/MeNO_2$ [156]	<1	–	98
	Me_2NH/C_6H_6 [156]	<1	–	98
	$Me_2NH/MeNO_2$ [156]	<1	–	98
	$[Fe(CO)_2C_5H_5]^-$ [120]	–	–	✓
C_2F_5	$LiAlH_4$, MeLi, NH_3, N_2H_4, MeO^- [157]	–	–	✓
2-Cl_3C_4S	2-$LiCl_3C_4S$ (thiophene derivative) [71a]	–	–	✓
$C_3F_7{}^n$	KOH [158]	–	–	✓
Bu^n	Bu^nLi [67,71a]	–	–	✓
$C_4F_9{}^n$	HS^- [158]; $Ph_3As{=}CH_2$ [136]	–	–	✓
$C_4F_9{}^i$	$Ph_3As{=}CH_2$ [136]	–	–	✓
Bu^t	Bu^tLi [71a]	–	–	✓
$C_8F_{17}{}^n$	HS^- [158]	–	–	✓
Substrate: $(C_6F_5)_2CH_2$	4-$NH_2C_6H_4ONa$, $PhCH_2MgCl$ [159]	–	–	✓
Substrate: $(C_6F_5)_3CH$	NH_3 [160]; MeO^- [161]	–	–	✓
Substrate: $C_6F_5CHPh_2$	NH_3 [160]	–	–	✓
Substrate: $(C_6F_5)_2CHPh$	NH_3 [160]	–	–	✓
CH_2CN	$C_6F_5\bar{C}HCN$ [162]	–	–	✓
CH_2OH	NH_3 [160]; $C_6F_5CH_2O^-$ [67]	–	–	✓
	$LiAlH_4$ [163]	✓	–	–
CH(OH)Ph	NH_3 [160]	–	–	✓
	$LiAlH_4$ [163]	✓	–	–
Substrate: $(C_6F_5)_2CHOH$	$LiAlH_4$ [163]	✓	–	–
$CH(OEt)_2$	$LiAlH_4$, Me_2NH, KOH [164a]	–	–	✓
$(CF_3)_2CFCO$	$(CF_3)_2\bar{C}F$ [164b]	–	–	✓
$CH_2{=}CH$	$MeNH_2$, PhNHLi, Me_2NH, NaOMe [165]; NH_2OH [92,127]	–	–	✓
$CF_2{=}CF$	$LiAlH_4$, MeO^- [166]	–	–	✓
$MeCH{=}CH$	$MeCH{=}CHLi$ [72]	–	–	✓
$CH{\equiv}C$	Et_2NH, N_2H_4, KOH, MeO^-, $CF_3(CF_2)_5CH_2O^-$, $H(CF_2)_8CH_2O^-$, $H(CF_2)_{10}CH_2O^-$ [167]	–	–	✓
$Me_3SiC{\equiv}C$	EtMgBr, PhMgBr [168]; PhMgBr, 4-MeC_6H_4MgBr [169]; 4-$H(CH_2)_nO{-}C_6H_4MgBr$ [170]; ArO^- [169,171]	–	–	✓
$Et_3SiC{\equiv}C$	$Et_3SiC{\equiv}CLi$ [172]	–	–	✓
Substrate: $(C_6F_5C{\equiv}C)_2$	$EtNH_2$, $PhCH(Me)NH_2$, $PhNH_2$, Et_2NH, $C_5H_{10}NH$, MeO^- [173], ArO^- [173,174]	–	–	✓
$PhC{\equiv}C$	$PhC{\equiv}C^-$ [143]	–	–	✓

Table 2 (*continued*)

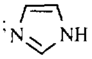
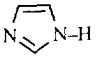
Substituent X	Nucleophile (Ref.)	Orientation of product (%)		
		o	*m*	*p*
C_6F_5	EtMgBr [69]; C_6F_5Li [123]; Me_2NH, N_2H_4, KOH [175]; 4-$NH_2C_6H_4O^-$ [159]; CF_3^- [138]; NH_2OH [92,127]; $(EtO)_3P$ [184]; ArO^- [176a]; $PhC\equiv C^-$ [143,176b]; N_2H_4 [99]; $(PhS)_2Pb$ [131]; $[Fe(CO)_2C_5H_5]^-$ [265]	–	–	✓
4-$CF_3C_6F_4$	$C_6F_5O^-$ [177a]	–	–	✓
Ph	KOH, MeO^- [177b]; PhLi [66,78]; NH_3, N_2H_4, HS^- [78], 1,3-$C_6H_4(OH)NEt_2$ [115]; N_2H_4 [99]	–	–	✓
o-, *m*-, *p*-MeC_6H_4	*o*-, *m*-, *p*-MeC_6H_4Li [79]	–	–	✓
m-, *p*-XC_6H_4	MeO^- [178]	–	–	✓
$CH{=}CHCO_2H$	Et_2NH, HO^-, MeO^- [179]	–	–	✓
CN	$(CF_3)_2\bar{C}H$ [180]; $(CF_3)_2\bar{C}F$ [181]; $CF_3CF{=}\bar{C}CF_3$, $CF_3CF{=}C(CF_3)C(CF_3){=}\bar{C}CF_3$ [182]; $(CF_3)_2\bar{C}CO_2Et$ [141], NH_3, $PhNH_2$, 1,2-$C_6H_4(NH_2)_2$, N_3^-, HO^-, MeO^-, $MeCO_2^-$, $PhCO_2^-$, LiCl, LiBr, NaI [183]; N_2H_4 [145]; $R_3\overset{+}{N}{-}\bar{N}H$ [100a]; $(Me_3Si)_2NH$/CsF [305]; $ArCH_2NHOH$ [146]; $NaNO_2$ [101], NH_2OH [92], $(EtO)_2PO^-$, $(EtO)_2PS^-$ [102]; $(EtO)_3P$ [184]; $PhC(Me){=}NO^-$ [129]; MeO^- (NaCN/MeOH) [185a]; $Na_2S_2O_3$ or $Na_2S\cdot 6H_2O$ [153b]; $Et_3GeCl/(Et_2N)_3P$ [155], $Mn(CO)_5^-$, $Re(CO)_5^-$ [185b]	–	–	✓
	 [125]; $C_6F_5O^-$ [186]; 1,4-$C_6F_4(ONa)_2$, 1,3-$C_6F_4(OLi)_2$ [152]	(✓)	–	✓
	$MeNH_2/C_6H_6$ ($MeNO_2$) [156]	6(<1)	–	94(98)
	Me_2NH/C_6H_6 ($MeNO_2$) [156]	<1(<1)	–	98(98)
PhN=CH	PhMgBr, PhNHMgBr [187]	✓	–	–
$C_6F_5N{=}CH$	PhNHMgBr [187]	✓	–	–
CHO	MeO^-, HS^-, PhS^- [188];  [125]; N_3^- [189]	–	–	✓
	Me_2NH [188]	60	–	40
	PhNHMgBr [187]	✓		–
MeC=O	*o*-, *m*-, *p*-$XC_6H_4NH_2$ [190]; $PhNH_2$ [195]	✓	–	✓
	$MeNH_2/C_6H_6$ ($MeNO_2$) [156]	36(<1)	–	64(98)
	Me_2NH/C_6H_6($MeNO_2$) [156]	18(<1)	–	82(98)
	N_3^- [189]; $C_6F_5CH_2O^-$ [191a]; $Na_2S_2O_3$ or $Na_2S\cdot 6H_2O$ [153b]	–	–	✓
$CF_3C{=}O$	PhLi [193]; $PhNH_2$ [195]	–	–	✓
$C_6F_5C{=}O$	N_2H_4, $PhNHNH_2$ [191b]	–	–	✓
	PhMgBr [192]; PhLi [193]; PhNHMgBr [194]	✓	–	–
	$PhNH_2$ [195]	✓	–	✓
PhC=O	PhNHMgBr [194]; PhMgBr [192]; PhLi [193]; $PhNH_2$ [195]	✓	–	–
	MeO^- [196]; N_2H_4 [191b]; NH_3 [160]	–	–	✓
PhCH=CHC=O	N_3^-/DMF, Et_2NH/DMF, $C_5H_{10}NH$, PhOK/DMF, MeO^-/MeOH [197]	–	–	✓
	Et_2NH/C_6H_6, PhONa/THF [197]	✓	–	–
COOH	NH_2 [198]; N_2H_4 [201]; HO^- [200]; MeO^-, MeS^- [199]; HS^- [202]; Na/liq. NH_3 [203]; $+e$ [204]; $Mn(CO)_5^-$, $[Fe(CO)_2C_5H_5]^-$ [210]	–	–	✓
	$MeNH_2$, Me_2NH [199]	✓	–	✓
	$LiAlH_4$ [163]; RMgX [205,206]; PhLi [193]; ArN(R)MgBr [207]	✓	–	–
	$MeNH_2/C_6H_6$ ($MeNO_2$) [156]	45(<1)	–	55(98)
	Me_2NH/C_6H_6 ($MeNO_2$) [156]	47(6)	–	53(94)
CO_2Me	MeO^- [367], NH_2OH [92], N_3^- [189]; $Et_3GeCl/(Et_2N)_3P$ [155]; $(CF_3)_2\bar{C}F$ [139]; $Na_3S_2O_3$ or $Na_2S\cdot 6H_2O$ [153b]	–	–	✓
	$PhC(Me){=}NO^-$ [129]	✓	–	✓
	PhMgBr [205,208]	✓	–	–
CO_2Et	EtO^- [209]; $NaNO_2$ 101; $Mn(CO)_5^-$, $[Fe(CO)_2C_5H_5]^-$ [210]; $MeCO\bar{C}HCO_2Et$ [211,212]	–	–	✓
	 [125]	✓	–	✓
	EtO^- in 1.0 M EtOH in Et_2O (and in 0.5 M EtOH in Et_2O) [156]	4(97)	–	96(3)
	$MeNH_2/C_6H_6$ ($MeNO_2$) [156]	35(5)	–	65(95)
	Me_2NH/C_6H_5 ($MeNO_2$) [156]	14(<1)	–	86(98)

Table 3
Nucleophilic substitution reactions with C_6F_5X and $C_6F_{6-x}(CF_3)_x$ compounds

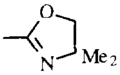
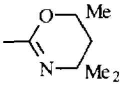
Substituent X	Nucleophile (Ref.)	Orientation of product (%)		
		o	*m*	*p*
$\mathrm{CO_2Pr^i}$	PhMgBr, RMgX [208,213,205]; PhLi [193]; $\mathrm{Et_2NMgBr}$ [214]	✓	–	–
$\mathrm{CONH_2}$	$\mathrm{NH_2}$ [198,215]	–	–	✓
$\mathrm{CONEt_2}$	$\mathrm{NH_2}$ [198]	–	–	✓
 and 	EtMgBr, $\mathrm{Bu^nLi}$, PhN(Me)MgBr [216]	✓	–	–
$\mathrm{NH_2}$	$\mathrm{NH_3}$ [66,82]	–	✓	–
	$\mathrm{NH_3}$ [83,217]	–	87	13
	$\mathrm{MeNH_2}$ [217]	–	88	12
	$\mathrm{Me_2NH}$ [217]	–	90	10
	NaOMe [217]	5	79	16
MeNH	$\mathrm{MeNH_2}$ [66,82]	–	–	✓
	$\mathrm{NH_3}$ [217]	–	40	60
	$\mathrm{MeNH_2}$ [217]	–	60	40
	$\mathrm{Me_2NH}$ [217]	–	52	48
	NaOMe [217]	5	43	52
$\mathrm{Me_2N}$	$\mathrm{NH_3}$ [217]	0	7	93
	$\mathrm{MeNH_2}$ [217]	0	6	94
	$\mathrm{Me_2NH}$ [66,217]	3	5	92
	NaOMe [217]	1	2	97
	EtONa [66]	–	–	✓
$\mathrm{Pr^i_2N}$	$\mathrm{Pr^i_2NLi}$ [259]	–	–	✓
PhNH	$\mathrm{Ph\bar{N}H}$ [85]	–	–	✓
PhNMe	$\mathrm{PhN(Li)SiMe_3}$ [97]	–	–	✓
$\mathrm{Ph_2N}$	$\mathrm{Ph_2\bar{N}}$ [85,96]	–	–	✓
NHCOMe	$\mathrm{HS^-}$ [132]	–	–	✓
$\mathrm{NH_2NH}$	$\mathrm{N_2H_4}$/dioxan,	–	50	50
	$\mathrm{(N_2H_4/THF)}$ [99]		0	100
	$\mathrm{MeS^-}$ [218]	–	–	✓
N(Me)CHO	$\mathrm{Me\bar{N}CHO}$ [219]	–	–	✓
NO	$\mathrm{MeO^-}$, $\mathrm{Me_2NH}$ [220]	–	–	✓
	$\mathrm{MeNH_2}$ [220]	40	–	60
$\mathrm{NO_2}$	$\mathrm{(CF_3)_2\bar{C}H}$ [180]; $\mathrm{(CF_3)_2\bar{C}F}$ [139];	–	–	✓
	$\mathrm{CF_3CF_2\bar{C}FCF_3}$ [142] (and $\mathrm{NO_2}$ subs. by F)	–	–	✓
	$\mathrm{C_6F_5Li}$ [123]	–	–	✓
	$\mathrm{C_6F_5MgBr}$ [221]	10	–	90
	PhC≡CLi [143]	✓	–	–
	$\mathrm{NH_3}$ ether [222]; (liq. $\mathrm{NH_3}$ [223])	70(33)	–	30(66)
	$\mathrm{NH_3}$ [224]	69	–	31
	$\mathrm{MeNH_2}$ [224]	65	–	35
	$\mathrm{Me_2NH}$ [224]	19	–	81
	$\mathrm{MeNH_2}$/benzene ($\mathrm{MeNO_2}$) [156]	77(15)	–	23(85)
	$\mathrm{Me_2NH}$/benzene ($\mathrm{MeNO_2}$) [156]	45(10)	–	55(90)
	 [125]; $\mathrm{(Me_3Si)_2NNa}$ [87]; $\mathrm{(Me_3Si)_2NH/CsF}$ [305]; 1,2- and 1,4-$\mathrm{C_6H_5(NH_2)OH}$ (ambident) [114]	–	–	✓
	$\mathrm{(EtO)_2PO^-}$ [102]	60	–	40
	$\mathrm{(EtO)_3P}$ [128]	–	–	✓
	KOH [225]	59	–	41
	NaOMe/MeOH [224]; (NaOMe in 4% MeOH/$\mathrm{Et_2O}$ [226] [156])	8(50)	–	92(50)
	4,4′-$\mathrm{HOC_6F_4–C_6F_4OH}$, 1,3-$\mathrm{C_6F_4(OH)_2}$ [227]; $\mathrm{NaNO_2}$ [101]	–	–	✓

Table 3 (*continued*)

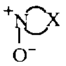
Substituent X	Nucleophile (Ref.)	Orientation of product (%)		
		o	*m*	*p*
	C_6F_5OM (M = Li, Na, K, Cs), $4\bar{O}C_5F_4N$ [228]; $PhC(Me){=}NO^-$ [129]	✓	–	✓
	$4\text{-}HSC_5F_4N$ [228]	✓	–	✓
	C_6F_5SH/DMF, (C_6F_5SK/Et_2O) [229]	0(68)	–	94(32)
	$Na_2S_2O_3$ or $Na_2S \cdot 6H_2O$ [153b], MeS^- [230]	–	–	✓
	$Et_3GeCl/(Et_2N)_3P$ [155]	–	–	✓
				
$X = -(CH_2)_4-$, $-(CH_2)_5-$, $-(CH_2)_2O(CH_2)_2$	NH_3, RNH_2, R_2NH in C_6H_6 (in H_2O, EtOH) [95]	✓	–	(✓)
$X = -(CH_2)_5-$	$MeO^-/MeOH$ [95]	–	–	✓
Substrate:				
$C_6F_5N{=}NC_6F_5$	$LiAlH_4$, MeO^- [231]; NH_3, HO^-, EtO^-, PhS^- [232]	–	–	✓
N_2^+	HO^- [233]	–	–	✓
Ph_2P	MeO^-, $MeNH_2$ [234]	–	–	✓
$Ph_2P{=}O$	$MeNH_2$ [234]	82	–	18
$Ph_2P{=}S$	$MeNH_2$ [234]	46	–	54
HO	KOH [104,235,236a]	–	✓	–
MeO	$NaNH_2$ [66];	–	–	✓
	MeO^- [235]	16	32	52
	$(EtO)_2PO^-$ [102]	24	32	44
Bu^tO	Bu^tO^- [259]	–	–	✓
$HOCH_2CH_2O$	$HOCH_2CH_2ONa$ [91]	–	–	✓
Substrate:				
$[C_6F_5OCH_2]_2$	$HOCH_2CH_2ONa$ [111]	–	–	✓
PhO	PhO^- [66]	–	–	✓
C_6F_5O	$C_6F_5O^-$ [66]	–	–	✓
$4\text{-}NH_2C_6H_4O$	$4\text{-}NH_2C_6H_4O^-$ [159]	–	–	✓
$4\text{-}NH_2C_6F_4O$	NH_3 [227]	–	–	✓
ArO	ArO^- [114]	–	–	✓
S^-	$C_6F_5S^-$ [117]	complex		
MeS	EtO^-, PhS^- [237]; NH_3, MeO^- [132];	–	–	✓
RS	RS^- [118]	–	–	✓
$HOCH_2CH_2S$	$HOCH_2CH_2S^-$ [91,111]	–	–	✓
$HSCH_2CH_2S$	$HSCH_2CH_2S^-$ [236b]	–	–	✓
ArS	PhS^- [237]	–	–	✓
PhS	PhS^- [132]	–	–	✓
C_6F_5S	$LiAlH_4$ [153a]; NH_3, HO^-, MeO^- [153b]; MeS^- [230]; $C_6F_5S^-$ [117]	–	–	✓
C_6F_5SO	ArNHMgBr [238]	✓	–	–
	MeO^- [239]	–	–	✓
SO_2Me	MeO^-, NH_3 [132]	–	–	✓
	$MeNH_2/C_6H_6(MeNO_2)$ [156]	58(5)	–	42(95)
	$Me_2NH/C_6H_6(MeNO_2)$ [156]	21(5)	–	79(95)
	EtO^- in 1.0 M EtOH in Et_2O (and in 0.5 M EtOH in Et_2O) [156]	2(87)	–	98(13)
SO_2R	PhNHMgBr [238]	✓	–	–
$C_6F_5SO_2$	PhNHMgBr, PhN(Me)MgBr [238]	✓	–	–
	MeO^- [240]	–	–	✓
SO_2NH_2	NH_2^- [132]	–	–	✓
SO_2F	$(Me_3Si)_2NH/CsF$ [305]; $Na_2S_2O_3$ or $Na_2S \cdot 6H_2O$ [153b]	–	–	✓
Cl	$LiAlH_4$ [241]	25	5	70
	$PhC{\equiv}CLi$ [176b]	–	–	✓
	$Ph_3P{=}CHR$ [242]	–	–	✓

Table 3 (*continued*)

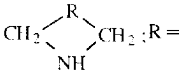
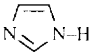
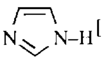
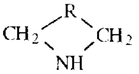
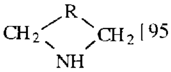
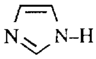
Substituent X	Nucleophile (Ref.)	Orientation of product (%)		
		o	*m*	*p*
	$Ph_3As{=}CH_2$ [136]	–	–	✓
	NH_3 [241]	25	5	70
	Me_2NH [126]	10	3	87
	Pr^i_2NLi [259]			
	 ;$R=(CH_2)_{2-4}$ [95]; $R=CH_2OCH_2$ [93]; $NH_2CH_2CH_2OH$, $NH(CH_2CH_2OH)_2$ [93];  [125]	–	–	✓
	N_2H_4 [241]	25	5	70
	MeO^- [126] ([241])	17(25)	3(5)	80(70)
	CF_3CH_2ONa [108]	20	4	76
	Bu^tOk [259]	–	–	✓
	C_6F_5ONa [130] ([245])	6	0	94(100)
	$2\text{-}NH_2C_6H_4O^-$ [88]	–	–	✓
	$3\text{-}Et_2NC_6H_4O^-$ [115]	–	–	✓
	KOH [246] ([247])	7(11)	26(0)	67(65)
	$(PhS)_2Pb$ [131]; MeS^- [230]	–	–	✓
Br	C_6F_5Li [123] (C_6F_4 also involved)	(✓)	–	✓
	$PhC{\equiv}CLi$ [248]	complex		
	NH_3 [66]; $C_6F_5\bar{N}$, $4H\text{-}C_6F_4\bar{N}H$ [86],  [125],  [95]	–	–	✓
	Me_2NH [126]	5	1	94
	N_2H_4 [126] ([145])	3	0	97(100)
	KOH [126] ([66])	15(✓)	1(0)	84(✓)
	KOH in liq. NH_3 [106]	✓	✓	✓
	MeO^- [126] (MeO^- [66]; EtO^- [209])	12	1	87(100)
	C_6F_5ONa [130]	3	0	97
I	$PhC{\equiv}CLi$ [248]	complex		
	NH_3 [66]; Me_2NH [126];  [95];  [125];			
	N_2H_4 [177b,126]	–	–	✓
	KOH [126] ([66])	7(✓)	0	93(✓)
	MeO^- [126] ([66])	5	0	95(100)
Me_3Si	$LiAlH_4$, $C_5H_{10}NLi$, $C_5H_{10}NH$ [251,252]	–	–	✓
Et_3Ge	$LiAlH_4$, Bu^nLi: $C_5H_{10}NH$, Pr^nS^- [251,253]	–	–	✓
Substrate: $(C_6F_5)_4Ge$	$C_5H_{10}NH$ [253]	–	–	✓
Substrate: $(C_6F_5)_2Hg$	N_2H_4, KOH, MeO^- [254]	–	–	✓
$1,2\text{-}C_6F_4(CF_3)_2$	NH_3, N_2H_4, HS^- [255a]; C_6F_5Li [123]	Position 4		
	$(NH_2)_2CS$ [383]	Thianthren derivative		
$1,3\text{-}C_6F_4(CF_3)_2$	MeLi, N_2H_4, MeO^-, HS^- [255b]	Position 4		
$1,4\text{-}C_6F_4(CF_3)_2$	MeLi, NH_3, N_2H_4, MeO^-, HS^- [255a]	Position 2		
	PhLi, MeO^- [255a]	2,5-di		
$1,3,5\text{-}C_6F_3(CF_3)_3$	NH_3, HO^-, MeO^- [256]	Position 2		
	MeLi, NH_3, MeO^- [256]	2,4-di		
	$LiAlH_4$ [257]	Positions 2; 2,4-di, 2,4,6-tri and some side chain mono-CF_2H analogues		

Table 4
Nucleophilic substitution reactions with polycyclic fluoroaromatic compounds

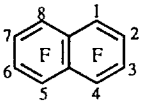
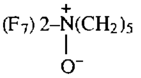
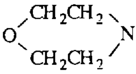
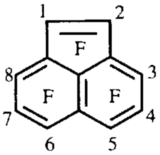
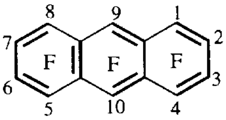
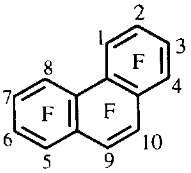
	Nucleophile (Ref.)	Orientation
Octafluoronaphthalene		
	$LiAlH_4$, MeLi, N_2H_4, KOH, NaOMe [258]; Pr^i_2NLi, Bu^tO^- [259], HS^- [260]; KOH/liq. NH_3 [106]	
	 R NH :R=$(CH_2)_4$, $(CH_2)_5$, $(CH_2)_2O(CH_2)_2$, $(CH_2)_6$ [261]	2-
	MeLi [262]	8.4(1-), 91.6(2-)
	Et_2NH [262]	0(1-), 100(2-)
	EtNHLi [262]	4.8(1-), 95.2(2-)
	MeONa [262]	3.7(1-), 96.3(2-)
	RONa [263]	$C_{10}(OR)_8$
	$[Fe(CO)_2C_5H_5]^-$ [265]	2-
(F_7)2-H	MeO^- [264]	6-
(F_7)2-OMe	$C_5H_{10}NH$ [261]	6-
	MeO^- [264]	6- and 7-
(F_7)2-OBu^t	Bu^tO^- [259]	67(6-), 33(7-)
(F_7)2-Li	Bu^nLi [266]	80(6-), 20(7-)
(F_7)2-$N(CH_2)_4$	C_4H_8NH, $C_5H_{10}NH$ [261]	6-
(F_7)2-$N(CH_2)_5$	$C_5H_{10}NH$, C_4H_8NH, MeO^- [261]	6-
(F_7)2-NPr^i_2	Pr^i_2NLi [259]	67(6-), 33(7-)
 $(F_7)\ 2\text{–}\overset{+}{N}(CH_2)_5$ with O^- on N	 $O(CH_2CH_2)_2NH/C_6H_6$ [261]	50(1-), 50(3-)
	$XSC_5H_{10}NH$ (no solvent) [261]	1,3-di
	$C_5H_{10}NH/MeOH$ [261]	6-
	MeO^- [261]	6-; 1,6-di
(F_4) 5,6,7,8 H_4	$LiAlH_4$, N_2H_4 [267]	2-
	MeO^- [267]	2(1-), 98(2-)
Octafluoroacenaphthylene		
	$LiAlH_4$, NH_3, N_2H_4, MeO^- [268]	3-
(F_7) 3-OMe	MeO^- [268]	8-
(F_6) 3,8-$(OMe)_2$	MeO^- [268]	5-
(F_5) 3,5,8-$(OMe)_3$	MeO^- [268]	6-
Decafluoroanthracene		
	MeO^-; Me_2NH [50]	2-
Decafluorophenanthrene		
	MeO^-, Me_2NH [269]	3,6-di

Table 4 (*continued*)

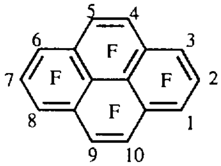
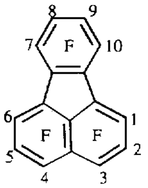
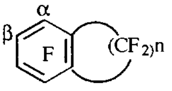
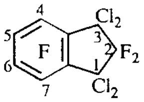
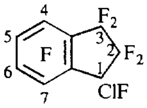
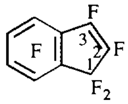
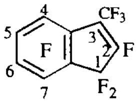
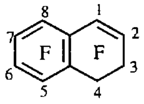
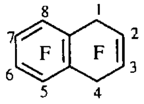
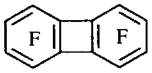
	Nucleophile (Ref.)	Orientation
Decafluoropyrene		
	MeO^- [270]	1-OMe
(F_6)1-OMe	MeO^- [270]	3-; 6-; 8-
$(F_8)(OMe)_2$ isomers	MeO^- [270]	1,3,6- $(OMe)_3$ product
(F_8)-1,3,6$(OMe)_3$	MeO^- [270]	8-
Decafluorofluoranthene		
	$LiAlH_4$, N_2H_4, MeO^- [21]	1-
(F_9) 1-H	$LiAlH_4$ [21]	6-
(F_8) 1,6-$(H)_2$	$LiAlH_4$ [21]	3-
(F_9) 1-OMe	MeO^- [21]	6-
(F_8) 1,6-$(OMe)_2$	MeO^- [21]	3-
(F_7) 1,3,6-$(OMe)_3$	MeO^- [21]	4-
 n=2,3,4	$n=2$: MeONa [271] $n=2$: NH_3 [271] $n=3$: $LiAlH_4$, NH_3, N_2H_4, KOH, MeONa, KSH [272] $n=4$: NH_3, N_2H_4, KOH, MeONa [272]	2.1 parts β-, 1 part α- 1.3 parts β-, 1 part α- β- β-
	$AlCl_3$ [273]	5-
	LiCl [274]	5-, 6-, 5,6-di
	MeLi [275] HO^- (ring opening) [276] MeO^- [276,277]	12.5(2-), 87.5(3-) *o*-*H*-Hexafluorocinnamic acid 3-F
	NH_3 [278]	2-F
	$C_5H_{10}NH$, MeONa [279]	6-, 7-
	C_6F_5Li, NH_3, $C_5H_{10}NH$, N_2H_4, MeONa [279]	6-
	MeO^- [280,282]	20(1-), 80(2-)

Table 5
Nucleophilic substitution reactions with polyfluoroheteroaromatic compounds

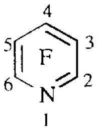
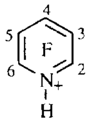
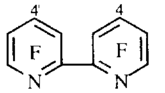
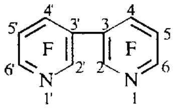
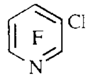
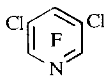
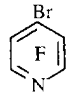
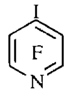
Substrate	Nucleophile (Ref.)	Orientations (%)
	$LiAlH_4$, $MeCH{=}CHLi$, NH_3, Me_2NH, N_2H_4, HO^-, MeO^- [283]; $PhLi$, NH_3, N_2H_4, MeO^- [284]; HO^-/H_2O [285]; $MeLi$ [286,287]; Bu^nLi [287,288]; $(CF_3)_2\bar{C}CO_2Et$ [140,141]; CN^- [286], CF_3^- [138], C_6F_5MgBr [289]; 4-$Br(I)MgC_5F_4N$ [289,290]; 4-LiC_5F_4N [291]; enamine [292]; $R_3\overset{+}{N}-\bar{C}HCO_2Bu^t$ [100b]; $R_3\overset{+}{N}-\bar{C}HCOR$ [293]; $PhSO_2CH_2Li$ [71b]	4-
	$C_2F_5^-$ [139,294–296]; $CF_3\bar{C}FCl$ [181,297,298]; $(CF_3)_2\bar{C}F$ [139,181,299,300], $C_2F_5\bar{C}FCF_3$ [142]; $(CF_3)_3\bar{C}$ [301]; $CF_3CF{=}\bar{C}CF_3$ [302]; c-$C_4F_7^-$, c-$C_5F_9^-$, c-$C_6F_{11}^-$ [303]	4- and poly-
	NH_2OH, NH_2OMe, $MeNHOH$ [92,127]; $ArCH_2NHOH$ [146]; $Ar\bar{N}COAr'$ [147]; N_3^- [304]; $(Me_3Si)_2\bar{N}H/CsF$ [305]; $R_3\overset{+}{N}-\bar{N}H$ [100a]; $PhN{=}S{=}N^-$, Cs phthalimide [306]	4-
	 [307]	4- and poly-
	Pr^i_2NLi [259]	2-, 4- and 2,4-di
	$(EtO)_2PO^-$ [102]; $(EtO)_3P$ [128,184]	4-
	HO^-/Bu^tOH [285]	10(2), 90(4-)
	C_6F_5OH/KF + 18-crown-6 [308–310]	2-, 4-, 2,4-di, 2,6-di, 2,4,6-tri
	oestradiol at 3-OH [149]	4-
	$(CF_3)_2NO^-$ [151]; Et_2NO^- [150]; NH_2OSiMe_3/CsF [127]; $PhC(Me){=}NO^-$ [129]; $NaNO_2$ [312]	4-
	$R^1R^2C{=}NO^-Na^+/C_6H_6$ [313]	50(2-), 50(4-)
	HS^-, 4-$\bar{S}C_5F_4N$, PhS^-, $PhSO_2^-$, SO_3^{2-} [314]; CF_3S^- [315]	4-
	NaI [290]	4-
	$Et_3GeCl/(Et_2N)_3P$ [155]; $[Mn(CO)_5]^-$, $[Re(CO)_5]^-$ [185b]; $[Fe(CO)_2C_5H_5]^-$ [316]	4-
	Cl^-, Br^- [317]	4-
	MeO^- [318]	4-, 4,4'-di
	$MeLi$, NH_3 [319]	6-
	RO^- [319]	4-, 6-, 4,4'-di, 4,6'-di
	NH_3, N_2H_4 [285]; NaI [320]	4-
	HO^-/H_2O [285]	90(4-), 10(6-)
	HO^-/Bu^tOH [285]	10(2-), 55(4-), 35(6-)
	$R_3\overset{+}{N}-\bar{C}HCO_2Bu^t$ [100b]	4-
	$R_3\overset{+}{N}-\bar{N}H$ [100a]	4-
	NH_3, N_2H_4, MeO^- [285]	4-
	HO^-/H_2O [285]	10(2-), 90(4-)
	HO^-/Bu^tOH [285]	70(2-), 30(4-)
	$R_3\overset{+}{N}-\bar{C}HCO_2Bu^t$ [100b]	4-
	$R_3\overset{+}{N}-\bar{N}H$ [100a]	4-
	NH_3, HO^-, MeO^- [289]	2-
	NH_3, HO^-, MeO^- [290]	2-

Table 5 (*continued*)

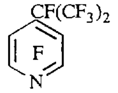
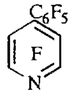
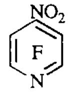
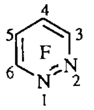
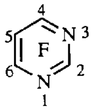
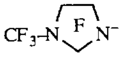
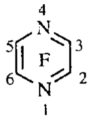
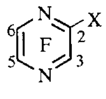
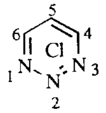
Substrate	Nucleophile (Ref.)	Orientations (%)
	N_3^- [321]	2-
	NH_3, KOH, MeO^- [322]	2-
	NH_3 [323]	25(2-), 48(3-), 27(4-)
	MeO^- [323]	23(2-), 7(3-), 70(4-)
	CsF [47]	4-
	MeO^- [324]	4-, 4,5-di
	NH_3, Et_2NH [324]; M(CO) [325]	4-
	PhS^-, K phthalimide [324]	4,5-di
	C_6F_5Li [326]	3,4,5,6-tetra
	$C_2F_5^-$ [294]	4-, 4,5-di, 3,4,5-tri
	$(CF_3)_2\bar{C}F$ [327,328]	4-, 4,5-di, 3,5-di, 3,4,6-tri
	$C_2F_5\bar{C}FCF_3$ [142]	4-, 4,5-di, 3,5-di
	$(CF_3)_3\bar{C}F$ [301]	4-, 3,5-di, 3,6-di
	$CF_3CF{=}\bar{C}CF_3$ [302]	4-, complex
	$c\text{-}C_6F_{11}^-$ [303]	4-, 3,5-di
	 [307]	4-, 3,5-di, 4,5-di
	CF_3S^- [330]	4-, 4,5-bis, 3,4,5-tris
	$[Fe(CO)_2C_2H_5]^-$ [316]	4-
	H_2O/H_2SO_4; $MeOH/H_2SO_4$ [331];	3-
	Cl^- [331]	3,4,5,6-tetra
	$LiAlH_4$ [332]	2-, 4-
	$PhSO_2CH_2Li$ [71b]	4-
	CF_3^- [333], C_6F_5MgBr [334], NH_3, $MeNH_2$, $PhNH_2$, Me_2NH, H_2O, MeO^- [335]	4-; 4,6-di
	$C_2F_5\bar{C}FCF_3$ [142]; $CF_3CF{=}\bar{C}CF_3$ [302];	4-; 4,6-di
	 [307]	2-, 4-, 2,4-di, 4,6-di
	NH_3 [336]	4-
	N_3^- [337]	4-, 4,6-di
	CF_3S^- [330]	4- + polysubn.
	NaI [332,338]; HCl [339]	4-, 4,6-
	MeLi, Bu^nLi, NH_3, N_2H_4, KOH, MeO^-, $MeOH\text{-}H_2SO_4$, EtO^-, Bu^tOH [340]	2-; polysubn.
	(X = H, Cl, Br) Me_2NH [341]	5-
	(X = OMe) Me_2NH; (X = NMe_2) MeO^- [341];	3-
	(X = Cl) $AlCl_3$ [342]	6-
	(X = NMe_2) Me_2NH [341]	12(3-), 80(5-), 8(6-)
	$(CF_3)_2\bar{C}F$ [343]	perfluoro-4,6-di, and 4,5,6-tri; and complex

Table 5 (*continued*)

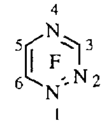
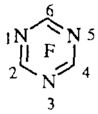
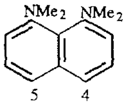
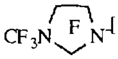
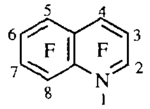
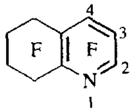
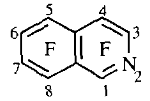
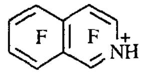
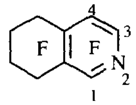
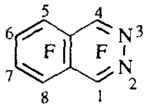
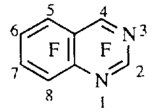
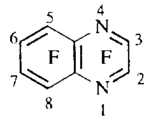
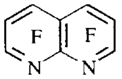
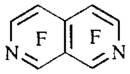
Substrate	Nucleophile (Ref.)	Orientations (%)
NB:tri*chloro* 	MeOH [344]	3,5-di, 5,6-di
	4-$ClC_6H_4NH_2$, Et_2NH [344]	3,5-di
	$(CF_3)_2\bar{C}F$ [345,346]	5-, 3,5-di, 3,5,6-tri
	$Me_2NC_6H_5$ [347]	Mono 4-$C_6H_4NMe_2$
	2-$MeOC_6H_4NMe_2$ [347]	Mono 2-$MeOC_6H_4N(Me)C_3N_3F_2$
	 [347]	4,5-di of diamine
	$CF_3\bar{C}FCl$ [297]	2-
	 [307]	2,4,6-tri
	F^- [348]	Anionic complex
	$[Fe(CO)_2C_5H_5]^-$ [316]	2-
	NH_3, N_2H_4, MeO^- [349]; HO^- [350]	2-, 4-
	NH_3 [351]	43(2-), 57(4-)
	EtO^- [351]	76(2-), 24(4-)
	4-$NO_2C_6H_4O^-$ [351]	16(2-), 84(4-)
	HS^-, PhS^- [351]	>95(4-)
	MeS^-, Pr^iS^-, Bu^tS^- [351]	5(2-), 95(4-)
	$(CF_3)_2\bar{C}F$ [352]	2-, 4-, 2,4-di, 2,4,6-tri
	$C_2F_5\bar{C}FCF_3$ [142]	2,4-di
	H_2O, MeOH [353]; Cl^-, Br^- [317]	2-, 2,4-di
	HI [317]	2,4-di
	NH_3 [354]	50(2-), 50(4-)
	MeO^- [354]	75(2-), 25(4-)
	$LiAlH_4$, NH_3, N_2H_4, MeO^- [349]; HO^- [350]	1-
	$C_2F_5\bar{C}FCF_3$ [142]	complex {1,4,(?)-tri}
	EtO^- [351]	94(1-), 6(6-)
	4-$NO_2C_6H_4O^-$ [351]	100(1-)
	HS^- [351]	100(6-)
	MeS^-, Pr^iS^-, Bu^tS^- [351]	(16-24)(1-), (71-79)(6-), 5(1,6-di)
	4-$NO_2C_6H_4S^-$ [351]	100(6-)
	Cl^-, Br^- [317]	1-
	(X = NH_2, OMe), MeO^- [349]	6-
	MeO^- [354]	3-, 1,3-di
	Et_2NH [354]	3-
 Hexafluorophthalazene	NH_3, H_2O-H_2SO_4, MeO^- [355]	1-
	MeO^- [355]	1,4,5,6,7,8-hexa

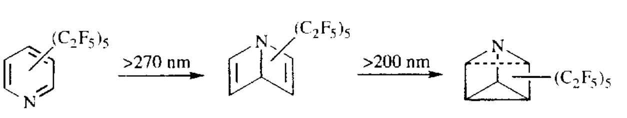
Table 5 (*continued*)

Substrate	Nucleophile (Ref.)	Orientations (%)
 Hexafluoroquinazoline	NH_3 [356] $H_2OH_2SO_4$ [356] MeO^- [356]	4- 2,4-di 2,4,7-tri
 Hexafluoroquinoxaline	MeO^- [357,358] N_2H_4, HO^- or H_2O-H_2SO_4 [358]	2-; 2,3-di; 2,3,6-tri 2,3-di
	[359] Not studied	
	[359] Not studied	

formed, indicating fluoride ion attack at both the 4- and 5-positions (Scheme 8) [299,300].

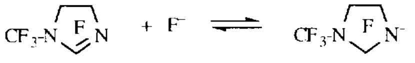
The use of $MeO^-/MeOH$ is routinely used to test for possible nucleophilic substitution of fluorine in polyfluoroaromatic and -heteroaromatic compounds and identifies sites for kinetically controlled reactions because of the irreversibility of the reaction. Tetrafluoropyridazine forms only the 4,5-dimethoxy isomer [324] whereas the variability in the orientations of dipolyfluoroalkylations of tetrafluoropyridazine and other systems is a manifestation of the interplay between kinetic and thermodynamic control of the reaction products (Scheme 9) [301].

Hexafluorobenzene and pentafluoropyridine undergo replacement of all their fluorines by the C_2F_5 group on reaction with $CF_2{=}CF_2/CsF$ in diglyme or DMF [363,295], respectively. Irradiation of these compounds gave Dewar-benzene and -pyridine isomers, and the corresponding prismanes (e.g. Eq. (23)) for the nitrogen heterocycles.



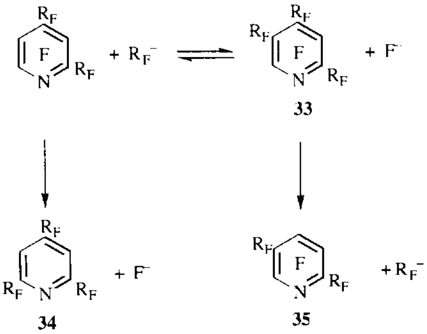
(23)

An extension of the idea for generating other anionic nucleophiles by fluoride ion additions to unsaturated precursors has been realised for nitrogen (Eq. (24)) [307] and more recently for sulphur (Eq. (25)) [315].



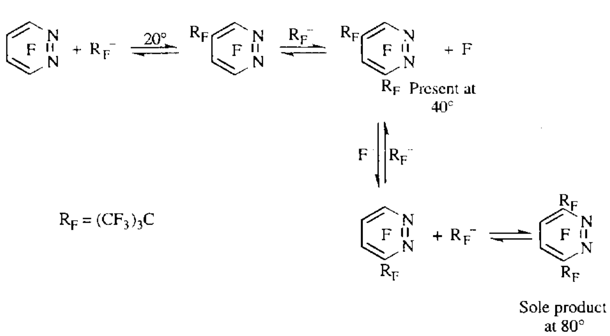
(24)

$$CF_2{=}S+F\rightleftharpoons CF_3S^- \quad (25)$$



$R_F = (CF_3)_2CF$

Scheme 8.

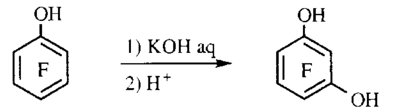


$R_F = (CF_3)_3C$

Scheme 9.

3.1.3. Orientation reactions

The variation in the proportions of ortho, meta and para substitution of fluorine by nucleophiles in C_6F_5X compounds is very uneven (see Tables 2 and 3) and can be profoundly influenced by the nature of the solvent [156,226]; precise isomer ratios have been measured only in a limited number of cases. Meta substitution is the least common site of attack and requires vigorous conditions. Only C_6F_5OH (effectively $C_6F_5O^-$) with KOH gave exclusively meta orientation (Eq. (26)) [104,235,236a].



(26)

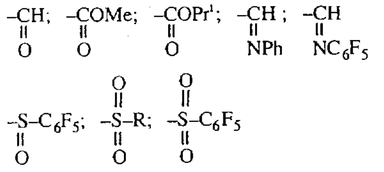
Pentafluoroaniline, $C_6F_5NH_2$, gave more than 87% meta substitution with some nitrogen nucleophiles (the balance being the para isomer) and 79% meta with MeONa/MeOH (16% para, 5% ortho) [83,217]; $C_6F_5NHCH_3$ [217], $C_6F_5NHNH_2$ [99] and $C_6F_5OCH_3$ [102,235] gave between 32 and 60% meta substitution, with para substitution being exclusively or mainly the other product. Meta orientation in these nucleophilic substitutions of fluorine is the result of less deactivation at this site compared with the ortho and para positions—in the same way that electrophilic nitration of nitrobenzene gives mainly *meta*-dinitrobenzene.

The major substitution product from the vast number of C_6F_5X compounds which have been reacted with nucleophiles is the para isomer. However, there are some notable exceptions where ortho substitution is exclusive or predominant and results from specific interaction between the substituent and incoming nucleophile; the synthesis of 1,2-disubstituted C_6F_4XY compounds has been reviewed [364]. Exclusive ortho substitution has been found with substituents X containing carbon or sulphur multiple bonds to oxygen or nitrogen, in reactions with metal-containing reagents, as shown in Table 6.

An example illustrating a reaction of this type [207] is shown in Scheme 10.

Table 6
Substituents in pentafluorophenyl derivatives and reagents which allow exclusive ortho substitution

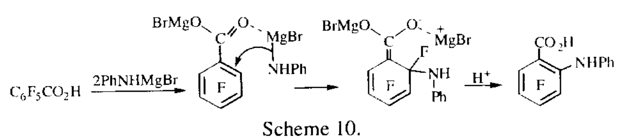
Substituents:



$-\underset{\displaystyle O}{\underset{\|}{C}}H$; $-\underset{\displaystyle O}{\underset{\|}{C}}OMe$; $-\underset{\displaystyle O}{\underset{\|}{C}}OPr^i$; $-\underset{\displaystyle NPh}{\underset{\|}{C}}H$; $-\underset{\displaystyle NC_6F_5}{\underset{\|}{C}}H$

$-\underset{\displaystyle O}{\underset{\|}{S}}-C_6F_5$; $-\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle O}{\underset{\|}{S}}}}-R$; $-\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle O}{\underset{\|}{S}}}}-C_6F_5$

Reagents: MeMgI, EtMgBr, Pr^nMgBr, Bu^nMgBr, $PhCH_2MgCl$, Pr^iMgCl, PhMgBr, PhLi, Et_2NMgBr, PhNHMgBr, PhN(Me)MgBr, ArN(R)MgBr



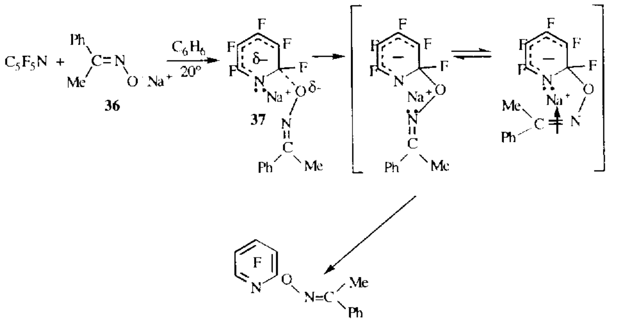
Scheme 10.

The exclusive replacement of ortho fluorine by hydrogen in the reaction of $C_6F_5CO_2H$ and $C_6F_5CH(R)OH$ compounds with $LiAlH_4$ [163] must involve closely knit interactions between substituent and nucleophile.

The polarity of the solvent has a significant effect on the strength of the interactions between the substituent X in C_6F_5X and the incoming nucleophile: a relatively strong bond in non-polar solvents results in significant proportions of ortho substitution, but the opposite effect occurs in polar solvents. Observations such as these have been found in the reactions of $C_6F_5CO_2H$, $C_6F_5CO_2Et$ and $C_6F_5NO_2$ with $MeNH_2$ and Me_2NH in benzene and nitromethane [156]. With nucleophiles such as MeONa, [226], C_6F_5OK and 4-KOC_5F_4N [228], quite dramatic swings in the ortho:para ratio for monosubstitution in $C_6F_5NO_2$ take place on changing from a polar to a non-polar solvent even though there are no obvious hydrogen-bonding effects, as are present in the amines [224]. Thus, with C_6F_5OK in acetonitrile, the ortho:para ratio is 2:98, whereas it is 89:11 in dioxane. Very significant proportions of ortho substitution by $MeNH_2$ occur with C_6F_5NO [220], C_6F_5-*N*-oxides [95], $C_6F_5P(O)Ph_2$ [234] and $C_6F_5P(S)Ph_2$ [234]—evidence, again, of interactions between the nucleophile and substituent.

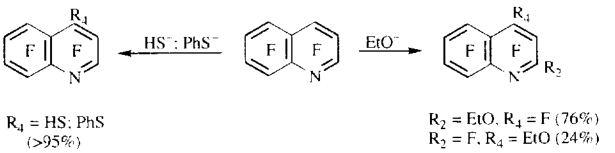
Nucleophilic substitution of fluorine in pentafluoropyridine, the first heterocyclic compound to be prepared, gave exclusively the 4-derivatives [283,284]—with the exception of KOH/Bu^tOH [285] which formed both the 4- and 2-hydroxy compounds in the ratio of 90:10; participation of Bu^tO^- in the reaction accounted for the ultimate presence of the 2-isomer, which was absent when the reaction was conducted in aqueous solution. Only one example has been discovered in which a significant proportion of the 2-derivative accompanies the 4-isomer: with the anti ketooximate salt $Ph(Me){=}NO^-\ Na^+$ (**36**), in benzene, the ratio of these isomers was 50:50 [313]. The presence of a complex involving the nitrogen of the heterocycle and the incoming salt (**37**) was proposed as an intermediate leading to the high proportion of 2-substitution (Scheme 11).

Heptafluoroquinoline underwent nucleophilic displacement of fluorine by $MeO^-/MeOH$ to give a mixture of the 2- and 4-ethers in the ratio of 77:23, and mixtures of 2- and 4-isomers on treatment with NH_3 and N_2H_4 [349]. The prod-

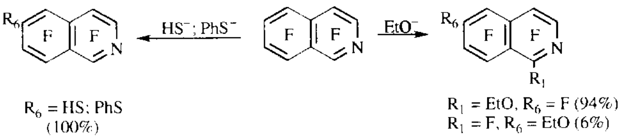


Scheme 11.

ucts isolated from the reaction of heptafluoroisoquinoline with the same nucleophiles and with $LiAlH_4$ [349] were the 1-substituted products, while disubstituted products arose from the further displacement of the 6-fluorine. A more recent study of the reactions of these two heterocycles with oxygen and sulphur nucleophiles has demonstrated that the orientation of fluorine displacement depends remarkably on the nucleophile [351]. The quinoline sways from predominantly 2-substitution with EtO^- to exclusive 4-substitution with HS^- and PhS^-, while the isoquinoline gives a high proportion of 1-derivative with sodium ethoxide and exclusive 6-substitution with sodium hydrosulphide and sodium benzenethiolate. These results are summarised in Eqs. (27) and (28).

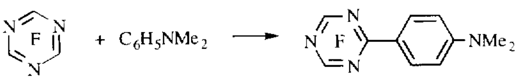


(27)



(28)

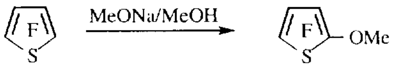
Orientation reactions of an entirely different type have arisen recently with the very reactive 1,3,5-triazine, cyanuric fluoride (**38**), and tertiary aromatic amines, which behave as carbon nucleophiles (Eq. (29)) [347]. Surprisingly, ortho and para substitution occurred with $C_6H_5NEt_2$.



(29)

38

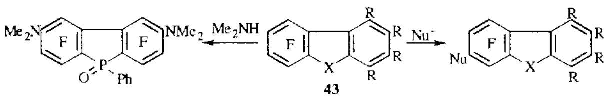
Nucleophilic substitution reactions in polyfluorinated systems containing five-membered rings with six π electrons have been investigated. There are only two fully fluorinated single ring heterocycles in this category: tetrafluorofuran [11,12] and tetrafluorothiophene (**39**) [13]. The former compound did not undergo any noticeable reaction with NaOMe/MeOH at room temperature and polymerisation took place at 60°C. Substitution of the 2-fluorine occurred with the thiophene (Eq. (30)).



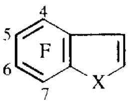
(30)

39

Fused bicyclic five-membered ring systems containing fluorine only in the benzenoid moiety are quite stable and have been studied in detail. The indole derivative (**40b**) underwent attack at the 4- and 6-positions with NaOMe, as did (**40a**) and (**40b**) with secondary amines [366].



Scheme 12.



(**40**) a. X = NH or b. N-Me
(**41**) X = O
(**42**) X = S

Sodium methoxide reacted with the furan derivative (**41**) to give a mixture of the 4-, 6- and 7-derivatives in the ratio 27:57:16 respectively [367], and with 4,5,6,7-tetrafluorobenzo[*b*]-thiophen (**42**), mainly at the 6-position [368,369].

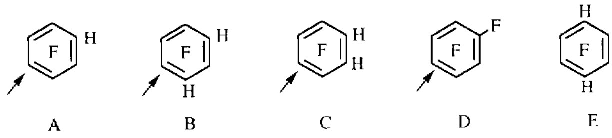
Dibenzofuran derivatives (**43**) with X = O, R = H [370] and X = O, R = F [240] underwent attack at the 3-position, as did the derivatives (**43**) with X = PhP, R = F [371] and X = S, SO_2; R = F [372]. However, for (**43**) with X = P(O)Ph, R = F, nucleophilic attack was at positions 4- and 4′- (Scheme 12) [371].

It is clear from Tables 2–5 that a vast amount of data has been gathered regarding the orientation reactions of C_6F_5X, derivatives, perfluoropolycycloarenes and perfluoroheteroaromatic compounds. Following some early investigations of the kinetics of nucleophilic replacement of fluorine in polyfluoroaromatic systems [281,596], a more intensive study was carried out to provide a rationalisation of these orientations. The following section gives a brief account of this work. A comprehensive review of kinetics work in fluorine chemistry has been published [365].

3.1.4. Kinetics of nucleophilic substitution reactions

The rate of displacement of a fluorine atom from a particular site in a C_6F_5X compound is determined by the group X and the four remaining fluorine atoms. Qualitative work with sodium methoxide in methanol established the site of reaction (arrow) in C_6F_5H [10,233] and the isomeric ortho and meta tetrafluorobenzenes $C_6F_4H_2$ as shown in Scheme 13 [373].

The quantitative determination of the individual rate constants for the reactions, along with the related reaction with C_6F_6 (corrected for the statistical factor), were then measured [374,375]. The ratio of the rate constants k_A/k_B gives a measure of the effect of an ortho fluorine atom relative to the



Scheme 13.

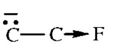
Influence of fluorine	ortho	meta	para
Based on polyfluorobenzenes	57	106	0.43 (relative to H)
	(133	246	1) (relative to the para position)
Based on polyfluoropyridines	(239	91	1) (relative to the para position)

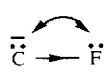
Scheme 14.

point of attack, in comparison with hydrogen at the same position. Thus, for attack at the 4-position in A, $k_A/k_B = k_F/k_H$ (ortho), $k_A/k_C = k_F/k_H$ (meta) and $k_D/k_A = k_F/k_H$ (para). A similar study with highly halogenated pyridines with sodium methoxide in methanol [375] and with ammonia in water–dioxane [376] was also carried out. The overall results of these investigations are shown in Scheme 14.

The ortho/meta order differs for the two systems, but both series show large activation for ortho and meta-fluorine compared to a fluorine para to hydrogen, which is slightly deactivating [377].

The origins of these activating and deactivating effects of fluorine have been explained on the basis of the well-established data that, in situation (**44**), fluorine is strongly carbanion-stabilising whereas, in situation (**45**), the net effect of electron withdrawal and electron pair repulsion is that fluorine is slightly destabilising, with respect to hydrogen at the same position.


44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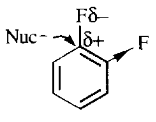


46

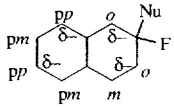
The activating effect of ortho fluorine is not easy to explain but has been attributed to ion dipole interactions (**46**), an initial state effect, making the carbon under attack more electron deficient [377,378].

The orientations of substitution in the polyfluorobenzenes A, B and C are governed by the necessity to have the maximum number of activating fluorines (ortho and meta) and minimum number of para fluorines. Similarly, pentafluorobenzene derivatives C_6F_5X will therefore always undergo predominantly para substitution based on the effects of the fluorine alone. Powerful electron-donating groups will increase the proportion of meta substitution, provided steric effects do not prevent conjugation of the π-electrons on the substituent with the aromatic ring; (thus, $X = O^-$ gave exclusive meta substitution [235]). Special interaction between the incoming nucleophile and the substituent X can be the only reason for enhanced ortho substitution.

Activating effects of ring nitrogen [379], chlorine [380] and the CF_3 group [379], compared to hydrogen at sites ortho, meta and para to the site of nucleophilic substitution of fluorine, have been determined (Scheme 15). Substitution of the fluorine at position 4 in pentafluoropyridine is therefore a consequence of the combined activating effect of the five fluorines and the 1-nitrogen. The use of heterocycles with readily replaced fluorine substituents in the dyestuffs field has been reviewed recently [21].

Influence of substituent	ortho	meta	para
Ring nitrogen	6.2×10^4	8.5×10^2	2.3×10^5 (relative to H)
	[72	1	226 (relative to the meta position)]
Cl	86	24	6.9 (relative to H)
CF_3	2.4×10^3	–	4.5×10^3 (relative to H)

Scheme 15.



o,m = *ortho-, meta-*
p*m*,p*p* = 'pseudo-meta'.
'pseudo-para'

$$\frac{\text{k pseudo} - \textit{para}\ \text{F}}{\text{k pseudo} - \textit{para}\ \text{H}} = 0.81;\quad \frac{\text{k pseudo}\ \textit{meta}\ \text{F}}{\text{k pseudo}\ \textit{meta}\ \text{H}} = 30.3;\quad \frac{\text{k}\ \textit{ortho}\ \text{F}}{\text{k}\ \textit{ortho}\ \text{H}} = \text{ca. } 25$$

Scheme 16.

The method of determining the influence of fluorine substituents, relative to hydrogen, on the rate of attack at sites in monocyclic rings has been extended to polyfluoronaphthalene systems where there are remote sites of substitution [378]. Scheme 16 shows a Wheland-type structure for nucleophilic attack at position 2 and serves to introduce additional terminology.

The observed orientation of nucleophilic substitution in perfluoro-naphthalene, -anthracene and -biphenylene (Table 3), follows again from the requirement to maximise the number of activating fluorines and minimise deactivating para and pseudo-para fluorines in the Wheland intermediates [378], though other considerations need to be taken into account with other polycyclic systems.

Application of this approach to heptafluoro-quinoline and -isoquinoline, taking into account only those sites which delocalise charge onto nitrogen, does not discriminate between the most favoured 2- and 4-sites in the quinoline, but comes out clearly in favour of attack at the 6-position in the isoquinoline—the site favoured by sulphur nucleophiles, whereas 1-derivatives are formed with oxygen nucleophiles. Considerations of the "hardness" of the nucleophile have been proposed to rationalise these orientations [351].

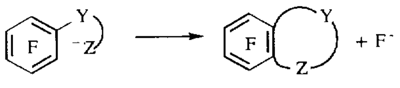
3.2. Synthesis of polyfluoro fused-ring carbocycles and heterocycles from fluorinated precursors

3.2.1. Via nucleophilic substitution of fluorine

This section is devoted to reactions of the type shown in Scheme 17, where Y, Z = C, N, O, S.

3.2.1.1. Carbocycles

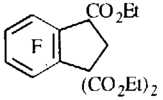
The formation of a limited number of five- and six-membered fused-ring systems has been described (Table 7).



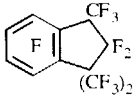
Scheme 17.

Table 7
Carbocycles and heterocycles formed via nucleophilic substitution of fluorine. Some sites of nucleophilic substitution (→)

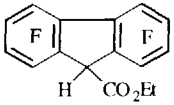
Carbocycles



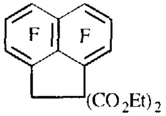
[381,382]



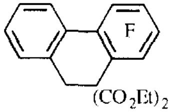
[384]



[385]

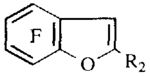


[381]

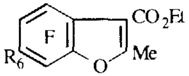


[386]

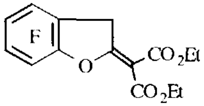
Heterocycles



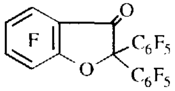
R_2 = H [387]; Me [388]; CH_2Ph [389]; Ph [387]; C_6F_5 [390]



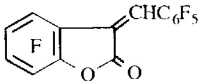
R_6 = F [81], H [391]



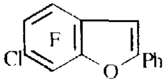
[388]



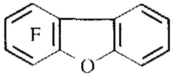
[392]



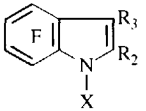
[393]



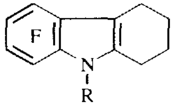
[394]



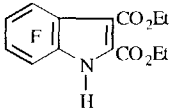
[370]



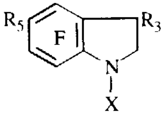
X, R_2, R_3 = H [395]; X, R_3 = H, R_2 = CH_2OH [396]; X = NH_2, R_2, R_3 = H [397]; X = $CHMe_2$, R_2, R_3 = H [398]; X = Ph, R_2 = Me, R_3 = H [399]; X = Ph, R_2 = Ph, R_3 = H [400]



R = Me, Et, $(CH_2)_4F$ [401]



[402]



X = H, R_3 = H, R_5 = F [395,403]; X = H, R_3 = Me, R_5 = F [404]; X = H, R_3 = OH, R_5 = F [405]; X = NH_2, R_3 = OH, R_5 = F [397]; X = OH, R_3 = OH, R_5 = F [405]; X, R_3, R_5 = H [406]

Table 7 (*continued*)

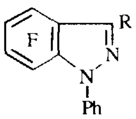
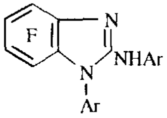
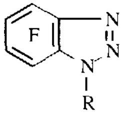
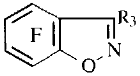
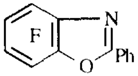
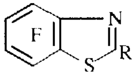
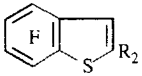
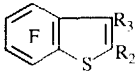
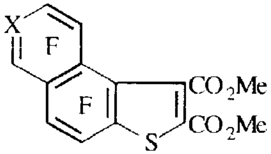
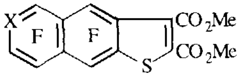
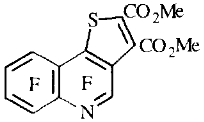
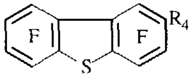
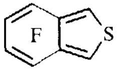
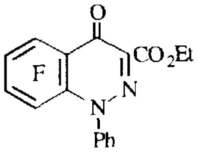
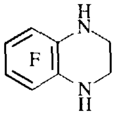
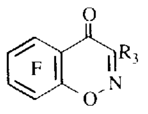
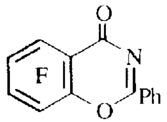
 [407]	 [408]	 $R = C_6F_5NH$, OH [409]
 $R_3 = CH_2Ar$ [410]; C_6F_5CO [411]	 [147]	
 [412]		
 $R_2 = Me$ [399]; CO_2H [369]	 R_2, $R_3 = CF_3$ [413]; R_2, $R_3 = CO_2Et$ [361,413]; $R_2 = Ph$, $R_3 = CO_2Et$ [413]	 X = CF [260]; N [414]
 X = CF [260]; N [414]	 [414]	 $R_4 = F$ [415]; MeO [372]
 [416]		
 [417]	 [91]	

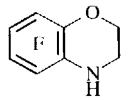
Table 7 (*continued*)



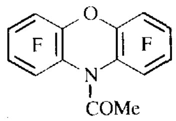
R_3 = Ph [418]; C_6F_5 [411]; CO_2Et [419,420]



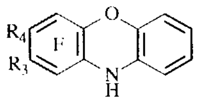
[418]



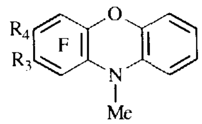
[90,91]



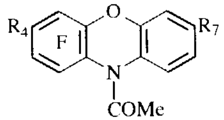
[421]



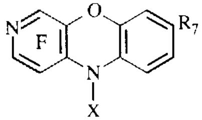
R_3, R_4 = F [422,423]; R_3 = Cl, R_4 = F; R_3 = F, R_4 = Cl [423]; R_3 = F; R_4 = CF_3, NO_2 [425]



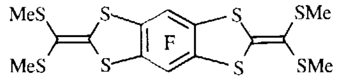
R_3, R_4 = F; R_3 = Cl, R_4 = F; R_3 = F, R_4 = Cl [423]



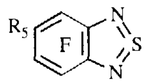
R_4 = F, R_7 = H [421,423]; R_4 = H, R_7 = H [88]; R_4 = Cl, R_7 = H [88,423]; R_4 = CF_3, NO_2; R_7 = H [424,425]; R_4 = F, H, Ph, Cl; R_7 = NEt_2 [115]



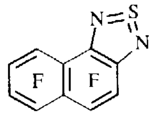
X = H, COMe [425]



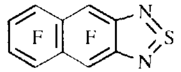
[426]



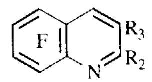
R_5 = F [306]; H, Me, Br, CF_3 [427]



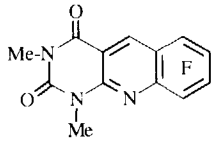
[428]



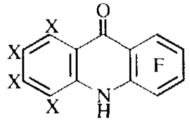
[428]



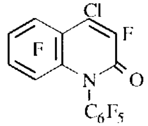
[429]



[430]

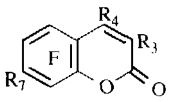


X = H, F [431]

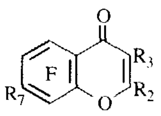


[432]

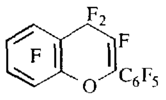
Table 7 (*continued*)



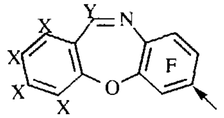
R_3, $R_4 = H$, $R_7 = F$ [433]; $R_3 = C_6F_5$, $R_4 = H$, $R_7 = F$ [393]; $R_3 = PhCONH$, $R_4 = H$, $R_7 = F$ [434]; R_3, $R_4 = H$, $R_7 = Et_2N$, HO, MeO, F [179]



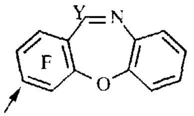
R_2, $R_3 = H$, $R_7 = F$ [435]; $R_2 = Me$, Ph, C_6F_5, $R_3 = CO_2Et$, $R_7 = F$ [436,437]; $R_2 = C_6F_5$, $R_3 = H$, $R_7 = F$ [438]; $R_2 = C_6F_5$, $R_3 = F$, $R_7 = F$ [438]; $R_2 = C_6F_5CH_2$, $R_3 = CO_2Et$, $R_7 = F$ [439]; $\overset{\frown}{R_2\,R_3} = -(CF{=}CF)_2-$, $R_7 = F$ [440]



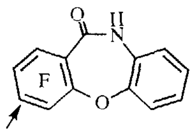
[530]



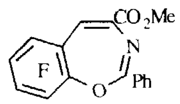
X = F, H; Y = H [441]; X = H; Y = H [442] + Nu (arrow); X = H, Y = Cl [443]; + Nu:–Cl



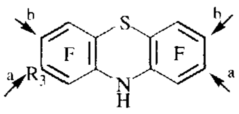
Y = H [441,444]; Y = H, + Nu (arrow) [442]; Y = Cl, + Nu (arrow) [443];



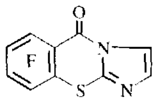
[443]; + Nu [445]



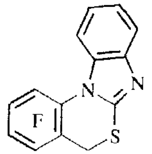
[434]



$R_3 = F$ [446]; [239], + Nu: ~ 1:1 two di-subsns. $R_3 = H$ [422]



[447]



[447]

Table 7 (*continued*)

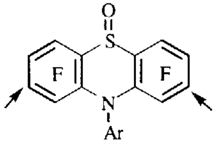
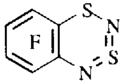
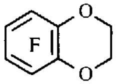
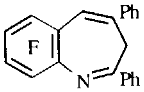
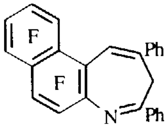
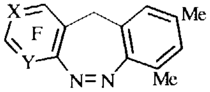
 [238,239]; + Nu: di-subsn.		
 [448]		
 [91]		
 [449]	 [449]	 X, Y = CF; X = N, Y = CF;X = C–CF$_3$, Y = CF; X, Y = N[450] ([451a ,452])

Table 8

Tetrafluorobenzo fused ring compounds synthesised from  derivatives. Some sites of nucleophilic substitution

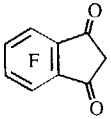
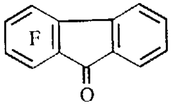
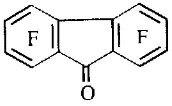
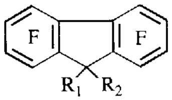
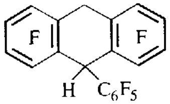
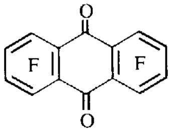
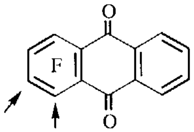
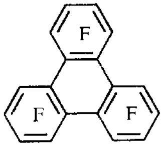
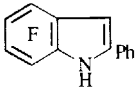
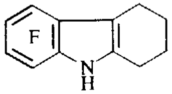
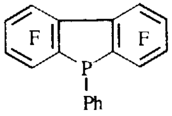
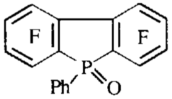
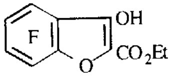
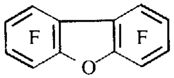
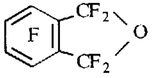
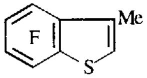
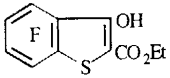
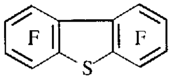
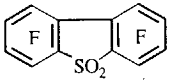
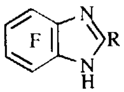
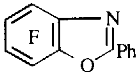
 [454,455]	 [329,456,457]	 [458–461]	 $R_1=F$; $R_2=F$, C_6F_5 [458]; $R_1=H$, $R_2=C_6F_5$ [462]; $R_1=H$; $R_2=CO_2Et$ [460]; R_1, $R_2=H$; $R_1=H$, $R_2=OH$ [460]
 [463]	 [464]	 [465]; + Nu (monosubsn. with solvent effects) [466–468]	 [469,566]
 [470]	 [470,471]	 [371]	 [371]
 [362]	 [240]	 [472]	 [473]
 [361]	 [329,474–476]	 [329,240]	

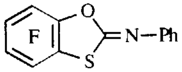
Table 8 (*continued*)



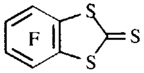
R = CF_3, NH_2 [222]; C_6F_5NH [408]; Me [477]



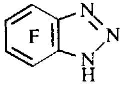
[225]



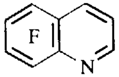
[225]



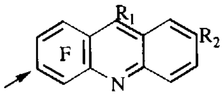
[478]



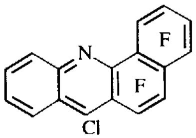
[409]



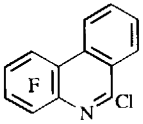
[479]



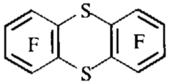
R_1, R_2 = H [187]; R_1 = Me, R_2 = H [195,480];
+Nu; R_1 = Me, R_2 = Me, Me_2N, MeO, Br [190];
R_1 = 2-$MeOC_6H_4$, R_2 = H [481];
R_1 = H, R_2 = H, alkyl, MeO, Hal [482];
R_1 = Cl, R_2 = H [483–487];
+Nu: –Cl; –F; –Cl, –F; R_1 = Cl, R_2 = Bu^n [488];
+Nu: –Cl; R_1 = Ph_3P=N, R_2 = H [488]; +Nu



[489]

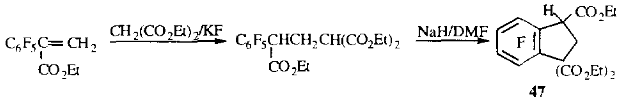


[457]; +Nu: –Cl



[476,490]

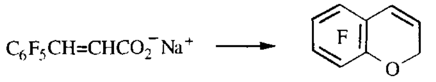
Eq. (31) gives an example for an indane derivative (**47**) [381,382].



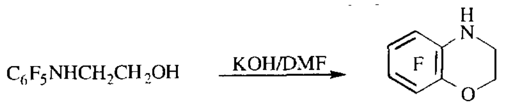
(31)

3.2.1.2. Heterocycles

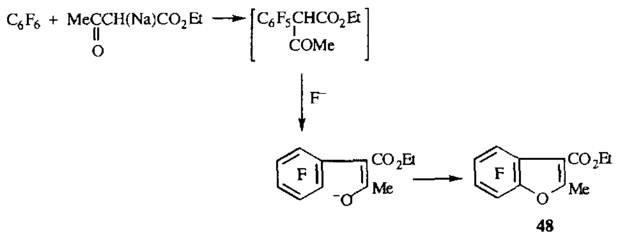
A notable exclusion from the series of nucleophiles capable of forming a C_6F_5–C bond with C_6F_6 (Table 1) is the sodio derivative of ethyl acetoacetate. When this experiment was carried out, the initial reaction was rapidly followed by ring cyclisation of the type under discussion, to give the benzo[*b*]furan derivative (**48**) (Scheme 18) [81]. Since this discovery, a large number of fused five- and six-membered ring systems with various heteroatoms in various numbers and sequence in the ring have been synthesised, together with a limited number of seven-membered derivatives (Table 7). By far the most common cyclisation process is to exploit a heteroatom as the nucleophilic species in a substrate containing a carbon or a deactivating heteroatom already bonded to the aromatic ring, as shown in Eq. (32) [433] and Eq. (33) [91] respectively.



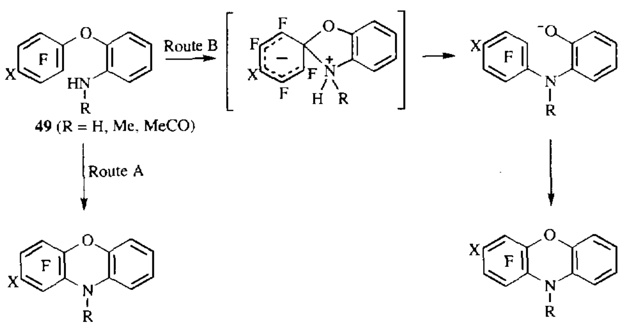
(32)



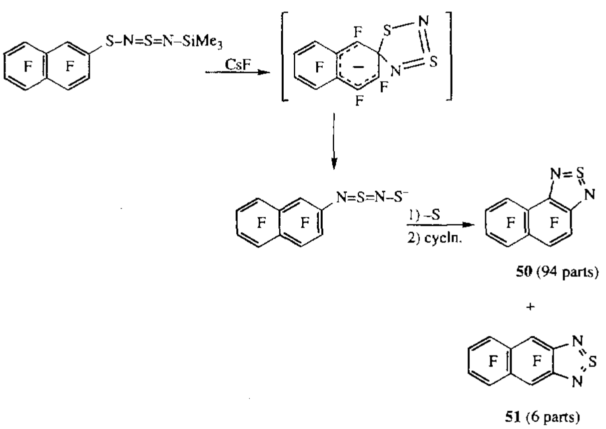
(33)



Scheme 18.



Scheme 19.



Scheme 20.

The synthesis of the phenoxazine ring system from aryl ethers using a nitrogen nucleophile in the ring-forming reaction has been shown to proceed by two possible processes by using 4-substituted polyfluoroaryl derivatives of (**49**) (Scheme 19):

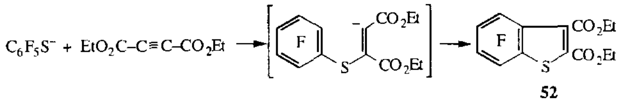
(a) direct displacement of ortho fluorine by nitrogen in the normal way (Route A); and

(b) displacement of fluorine by oxygen, following the initial attack on the C–ether bond by the nitrogen and ring-opening of the spiro-Meisenheimer intermediate (Route B) (Smiles rearrangement).

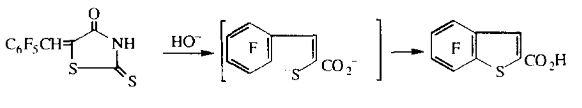
The relative incidence of these processes have been thoroughly discussed in a recent review [453].

The formation of the fused five-membered ring polyheterocycles (**50**) and (**51**) was rationalised by invoking an unusual Smiles-type rearrangement (Scheme 20) [428].

Ring closure via a carbanionic species is rare, but has been proposed in the formation of some seven-membered rings [449–451a,452]. More explicitly, the direct formation of the benzo[*c*]thiophene derivative (**52**) by this methodology (Eq. (34)) [361] complements the more usual mode of cyclisation via the sulphur atom (Eq. (35)) [369].



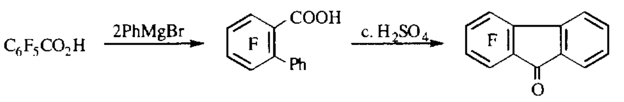
(34)



(35)

3.2.2. From 1,2-C_6F_4XY derivatives

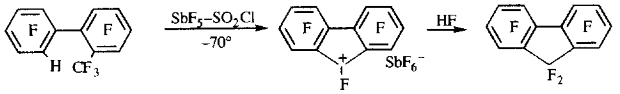
The syntheses of compounds of the type 1,2-C_6F_4XY have been reviewed [364] and many have been used to prepare carbocyclic and heterocyclic compounds; Table 8 surveys the broad range of materials which have been made available from these derivatives in a variety of chemical transformations. Nucleophilic substitution reactions with C_6F_5X compounds giving ortho derivatives have been a rich source of carbocycles and heterocycles, as illustrated in Eq. (36) [456] and Eq. (37) [187].



(36)

(37)

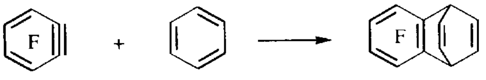
Other electrophilic substitution reactions have led to the formation of novel perfluorocarbons, e.g. Eq. (38) [458].



(38)

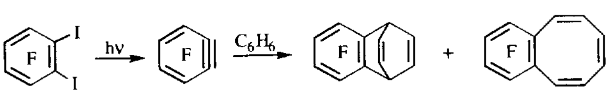
3.2.3. *From tetrafluorobenzyne C_6F_4*

The decomposition of $C_6F_5MgCl(Br)$ or C_6F_5Li in benzene resulted in the formation of the Diels–Alder addition product between the dienophile, tetrafluorobenzyne C_6F_4 and the hydrocarbon behaving as a diene (Eq. (39)) [491–493].



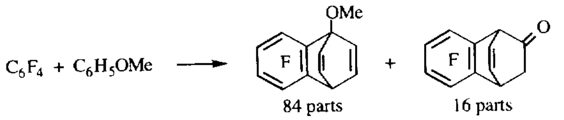
(39)

In a photochemical reaction generating C_6F_4 from o-$C_6F_4I_2$, the products suggested that both $(2+4)\pi$ and $(2+2)\pi$ reactions occurred [494a] (Eq. (40)).



(40)

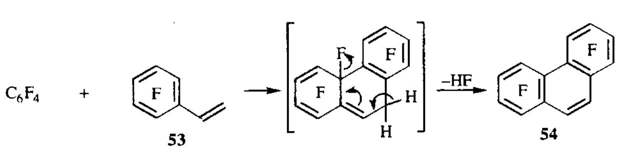
A priori, the number of adducts possible from the addition of C_6F_4 to both a benzene derivative C_6H_5X and a disubstituted derivative $C_6H_4X_2$ of any orientation is two. Eq. (41) shows the reaction with anisole; two products were formed, the carbonyl derivative resulting from hydrolysis of the methyl vinyl ether derivative [493].



(41)

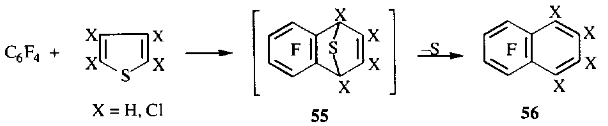
Other C_6H_5X derivatives studied include X = Me [491,493], Et, i-Pr and Bu^t [493], NMe_2 [494b] and HO [495]. Two adducts are formed with 1,2- and 1,3-dimethylenebenzene, but only the non-substituted bridged derivative with the 1,4-isomer [491,493]. Tetrafluorobenzyne gave (2+4) cycloaddition products with the following compounds: mesitylene [493]; 1,2- and 1,4-$C_6H_4(OMe)_2$ (some hydrolysed derivatives) [496]; the three adducts expected from 6-methoxytetralin [497]; only the non-substituted bridge-head product from durene [491,493]; the dibenzobarrelene derivative from naphthalene [493]; and the triptycene derivative from anthracene [493].

The external double bond formed half of the 4π diene unit in styrene in its reaction with C_6F_4. The initial product isomerised to the 9,10-dihydrophenanthrene compound [498,491,499] which was then dehydrogenated to 1,2,3,4-tetrafluorophenanthrene, but with 2,3,4,5,6-pentafluorostyrene (**53**) the adduct aromatised in situ by loss of HF to give the octafluorophenanthrene derivative (**54**) (Eq. (42)) [499].



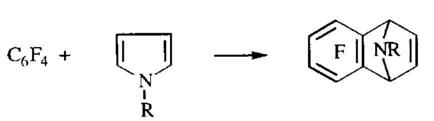
(42)

More conventional dienes for reaction with C_6F_4 include cyclopentadiene [491,500], 7,7-dimethylfulvene [501], 1,3-cyclohexadiene [500], furan [502,503] and its derivatives [503]. The adducts (**55**) with thiophene and tetrachlorothiophene immediately lost sulphur, with the formation of the corresponding naphthalene derivatives (**56**) (Eq. (43)) [491].



(43)

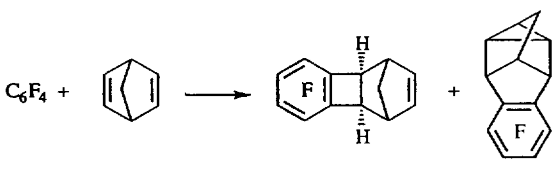
The first ever stable Diels–Alder adducts with pyrrole derivatives were formed with tetrafluorobenzyne (Eq. (44)).



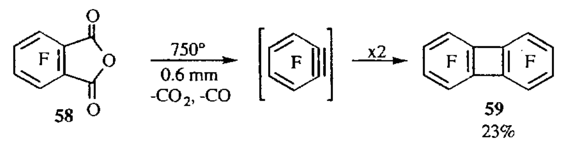
(44)

R = Me [491]; CH_2Ph [504]; $SiMe_3$ [505].

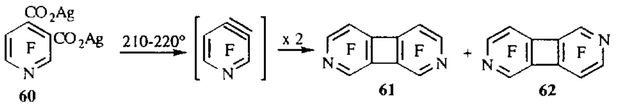
A number of $(2+2)\pi$ adducts have been formed between C_6F_4 and alkenes; these included hex-3-ene [506]; tertiary cyclic vinylamines [507] and norbornene [508], and norbornadiene, which also formed a $(2+2+2)\pi$ adduct (Eq. (45)) [508].



(45)

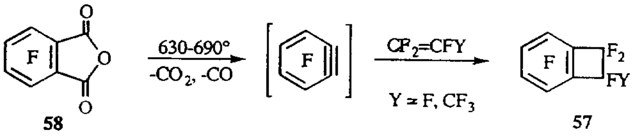


Scheme 21.



Scheme 22.

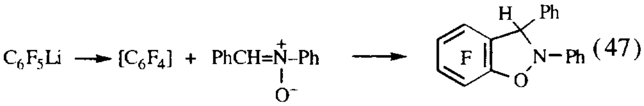
A convenient method for the preparation of polyfluorobenzocyclobutenes (**57**) has been developed involving the thermolytic generation of C_6F_4 from the anhydride (**58**) in the presence of fluoroalkenes (Eq. (46)) [509–511].



(46)

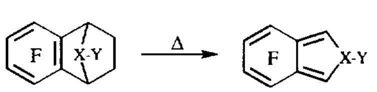
When the thermolysis of (**58**) alone was carried out at 750°C/0.6 mmHg under flow conditions, octafluorobiphenylene (**59**) was formed (Scheme 21) [281]. Other routes to (**59**) have been described [282,512a]. Pyrolysis of the disilver salt (**60**) resulted in the formation of small amounts of the isomeric diazabiphenylenes (**61**) and (**62**) (Scheme 22) [512b].

Recently, C_6F_4 has been reacted with a nitrone, a 1,3-dipolarophile (Eq. (47)) [513].



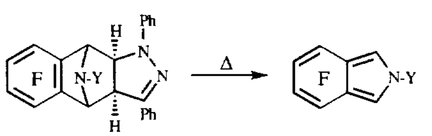
(47)

Retro-Diels–Alder reactions have proved to be fruitful routes to 4,5,6,7-tetrafluoroisoindole derivatives [504, 514,505] and 4,5,6,7-tetrafluorobenzo[*c*]furan [514]. In all the reactions, two carbon atoms are eliminated from the molecules as a C=C entity (Eqs. (48) and (49)).



(48)

X-Y = N-H [504]; N-Me [514]; N-CH_2Ph [504]; O [514].



(49)

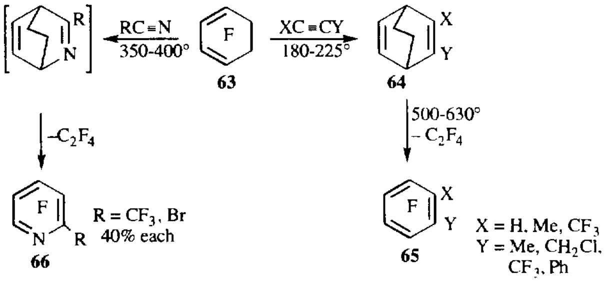
Y = H, Me [505].

3.2.4. Via Diels–Alder/pyrolysis reactions

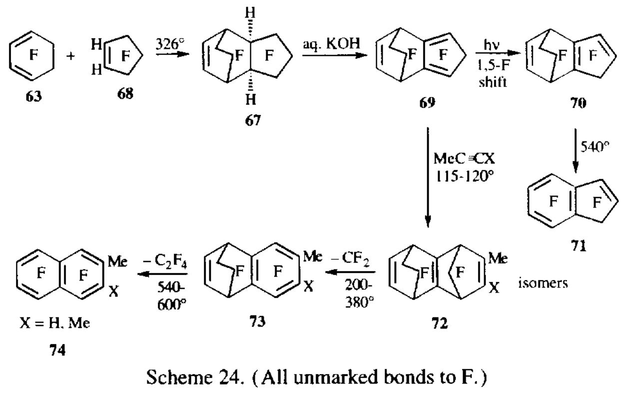
Octafluorocyclohexa-1,3-diene (**63**) formed Diels–Alder adducts (**64**) with acetylenic compounds XC≡CY, which on pyrolysis gave *o*-C_6F_5XY compounds (**65**) in high yields (Scheme 23) [515]. The related reaction of nitriles RC≡N with (**63**) resulted in the formation of rare 2-R pyridine derivatives (**66**) (Scheme 23) [516].

The Diels–Alder adduct (**67**) from (**63**) and 1*H*,2*H*-hexafluorocyclopentene (**68**) on dehydrofluorination produced the 1,3-diene (**69**) [517] which in turn was photoisomerised to compound (**70**) via a 1,5-suprafacial fluorine shift. Pyrolysis of (**70**) gave perfluoroindene (**71**) (Scheme 24) [518]. The diene (**69**) formed the adducts (**72**) on heating with the acetylenes MeC≡CX which, in turn, on pyrolysis lost difluorocarbene to give (**73**). Complete aromatisations to the 2,3-disubstituted hexafluoronaphthalenes (**74**) took place on pyrolysis at higher temperatures (Scheme 24) [519].

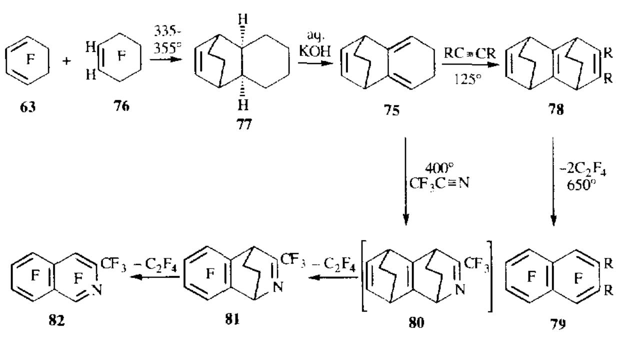
Another 1,3-diene (**75**) was the starting point for the synthesis of polyfluoro-naphthalene and -isoquinoline derivatives. The reaction of (**63**) with 1*H*,2*H*-octafluorocyclohexene (**76**) gave (**77**), which was dehydrofluorinated to (**75**) [517]. Reaction of (**75**) with the acetylenes RC≡CR and pyrolysis of the adducts (**78**) gave 2,3-disubstituted naphthalenes (**79**) once again (Scheme 25) [520]. In the high-temperature reaction of (**75**) with trifluoroacetonitrile, the adduct (**80**) spontaneously decomposed, first to (**81**) (17%), from which tetrafluoroethylene was also eliminated to give the 3-trifluoromethyl isoquinoline derivative (**82**) (38%) (Scheme 25) [521].



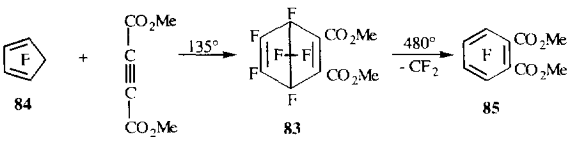
Scheme 23. (All unmarked bonds to F.)



Scheme 24. (All unmarked bonds to F.)



Scheme 25. (All unmarked bonds to F.)



Scheme 26.

The Diels–Alder adduct (**83**) from hexafluorocyclopentadiene (**84**) and 1,2-dimethyl acetylenedicarboxylate has been converted into dimethyl tetrafluorophthalate (**85**) (Scheme 26) [522].

3.3. *Electrophilic substitution of hydrogen in polyfluoroaromatic compounds*

The presence of hydrogen on the nucleus of a polyfluoroaromatic compound presents the opportunity to introduce functional groups via classical electrophilic substitution reactions. These reactions will be considered in the following sections, as well as the use of new electrophilic agents generated in the presence of exceptionally powerful Lewis acid catalysts such as SbF_5 which, simultaneously, is potentially an oxidising agent. For this reason, polyfluorinated aromatic compounds are particularly stable substrates for use compared with their hydrocarbon analogues. Reviews have been published which also include accounts of the formation of Se, Te and Hg derivatives [523,524].

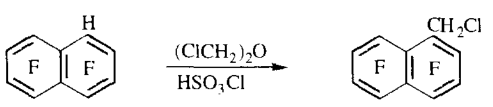
3.3.1. *Formation of C–C bonds*

3.3.1.1. *Alkylation reactions*

The use of $AlCl_3$ in the Friedel–Crafts methylation of C_6F_5H with MeCl gave only 8% of the toluene derivative [525] and with CCl_4, 18% $C_6F_5CCl_3$ [526a], but CH_2Cl_2 and $CHCl_3$ gave high yields of the bis- and tris-pentafluorophenyl methanes respectively [525] (Eq. (50)).

$$C_6F_5H + CHCl_3 \xrightarrow{AlCl_3} (C_6F_5)_3CH\ (92\%) \qquad (50)$$

Chloromethylation reactions have been carried out using bis(chloromethylether)/HSO_3Cl with 1-*H*- and 2-*H*-heptafluoronaphthalenes [526b,527] (e.g. Eq. (51)).



(51)

Antimony pentafluoride promoted both alkylation and chlorine substitution by fluorine in the formation of the ethylbenzene derivative shown in Eq. (52) [528].

$$C_6F_5H + CFCl_2CF_2Cl \xrightarrow{SbF_5} C_6F_5CF_2CF_2Cl\ (50-55\%) \qquad (52)$$

Treatment of C_6F_5H with SbF_5/hexafluoropropene gave the thermodynamically more stable 1-phenylpropene derivative (**86**) along with the products of further reaction (Scheme 27) [529,530].

Perfluoro(diphenylmethane) (**87**) is readily prepared via side-chain ionisation of octafluorotoluene and reaction with C_6F_5H (Scheme 28) [531,532].

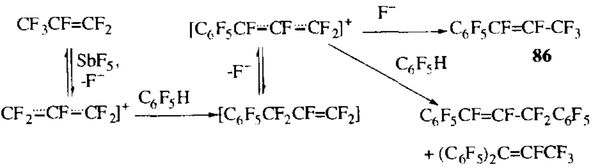
3.3.1.2. *Acylation reactions*

No practically useful acylation reactions have been developed for conventional processes using hydrocarbon-containing acyl halides or acid anhydrides with $AlCl_3$. However, perfluoro-acyl or -aryl chlorides, or the anhydrides, in conjunction with SbF_5, readily give ketones (Eq. (53)) [533].

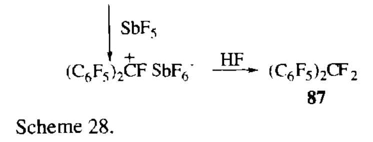
$$C_6F_5H + R_FCOCl\ [\text{or } (R_FCO)_2O] \xrightarrow{SbF_5} C_6F_5\text{-}\underset{\underset{O}{\|}}{C}\text{-}R_F \qquad (53)$$

3.3.2. *Formation of C–N bonds and C–P bonds*

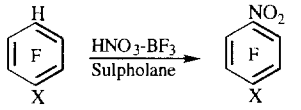
Early attempts to nitrate pentafluorobenzene with the conventional reagent HNO_3/H_2SO_4 were unsuccessful—for reasons which are now well understood as a result of Russian work in this area (see Section 3.4). An effective reagent for carrying out this reaction and related reactions with some 4-substituted tetrafluorobenzene derivatives and the *o*- and *m*-$C_6F_4H_2$ compounds (but not the *p*-$C_6F_4H_2$ isomer) was a mixture of fuming nitric acid and BF_3 in sulpholane (Eq. (54)) [534].



Scheme 27.



Scheme 28.



X = Me, MeO, Br, F (54)

The formation of some carbon–phosphorus compounds has been described (Eq. (55)) [535]

$$4-XC_6F_4H \xrightarrow[AlCl_3]{PCl_3} 4-XC_6F_4PCl_2 \quad (55)$$

where X = H, F, CF_3.

3.3.3. *Formation of C–S bonds*

3.3.3.1. *Sulphonation and related reactions*

Fuming sulphuric acid [451b] or liquid SO_3 [536] readily convert pentafluorobenzene to the sulphonic acid (Eq. (56)).

$$C_6F_5H+(H_2SO_4)SO_3 \xrightarrow{25°C} C_6F_5SO_3H \quad (56)$$

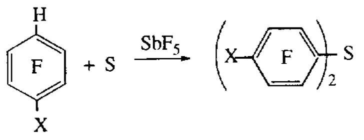
The sulphonation and chlorosulphonation of 1-*H*- and 2-*H*-heptafluoronaphthalene have been described [526b, 527]. Pentafluorobenzenesulphonyl fluoride and pentafluorobenzenesulphinyl fluoride undergo reaction with C_6F_5H in the presence of SbF_5 to form the corresponding sulphone (**88**) and sulphoxide (**89**) respectively [537] (Eqs. (57) and (58)).

$$C_6F_5SO_2F+C_6F_5H \xrightarrow{SbF_5} \underset{\mathbf{88}}{(C_6F_5)_2SO_2} \quad (57)$$

$$C_6F_5SOF+C_6F_5H \xrightarrow{SbF_5} \underset{\mathbf{89}}{(C_6F_5)_2SO} \quad (58)$$

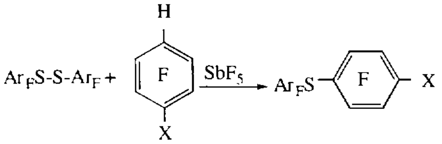
3.3.3.2. *Unconventional sulphur electrophiles*

Antimony pentafluoride is not only an exceptionally strong Lewis acid, but also a strong oxidising agent, a property which has been exploited to generate novel sulphur electrophiles. Partially fluorinated aromatic compounds have been reacted with elementary sulphur to form bis-(polyfluoroaryl)sulphides in high yield [538] (Eq. (59)) and the fact that pentafluorophenylsulphenyl chloride and SCl_2 reacted similarly with C_6F_5H/SbF_5 [538] suggested that $C_6F_5S^+$ was a reactive intermediate.



X = H, F, MeS, Br (59)

This and related electrophiles were also formed by oxidative cleavage of the S–S bond in disulphides which has led to a general method for the preparation of unsymmetrical polyfluoro(diaryl sulphides) (Eq. (60)) [539].



(60)

Perfluorodialkyl disulphides have been used in a related reaction (Eq. (61)) [540].

$$C_6F_5H+(CF_3)_3CSSC(CF_3)_3 \xrightarrow{SbF_5} C_6F_5SC(CF_3)_3 \quad (61)$$

A spectacular transformation from nucleophilic to electrophilic sulphur takes place in the reaction of lead thiocyanate with pentafluorobenzene in SbF_5 (Eq. (62)) [541].

$$C_6F_5H+Pb(SCN)_2 \xrightarrow{SbF_5} C_6F_5SCN \quad (62)$$

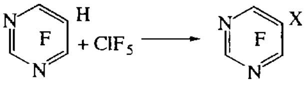
3.3.4. *Formation of C–halogen bonds*

Pentafluorobenzene is readily brominated and iodinated in sulphuric acid (Eq. (63)) [451b].

$$C_6F_5H+X_2 \xrightarrow{H_2SO_4} C_6F_5X \quad X=Br, I \quad (63)$$

Chloropentafluorobenzene was formed with Cl_2/SbF_5 during studies of intermediate cationic species [542]. All three products (C_6F_5X, X = Cl, Br, I) are important in that they form Grignard reagents (Section 3.7.1.1).

Replacement of hydrogen by fluorine in 2,4,6-trifluoropyrimidine (**90**) was originally carried out using AgF_2 [336]. Chlorine pentafluoride also effected the same transformation, in competition with chlorination (Eq. (64)) [544].



90

X = F (15%)
X = Cl (9%) (64)

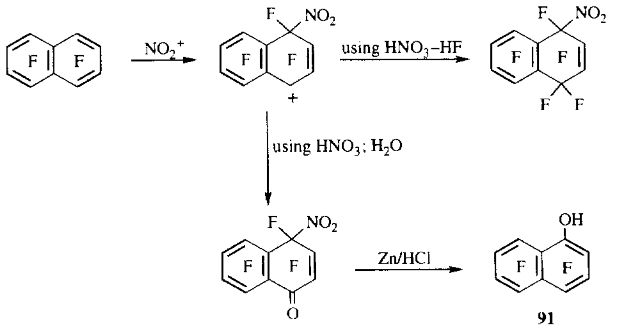
3.4. *Reactions of electrophiles at C–F bonds (ipso attack) in polyfluoroaromatic compounds*

Russian workers discovered that electrophiles *do* react at a C–F bond in the electron-poor rings of polyfluoroaromatic compounds and give addition products rather than substitution of fluorine, since F^+ cannot be eliminated [545,546]. Nitration, halogenation and methylation reactions have been investigated, as well as the use of some unusual electrophiles—polyfluoroarenium ions and radical cations. Simple transformations of some of the products have enabled derivatives to be obtained which are inaccessible by nucleophilic substitution of fluorine, so that there is some complementarity in the chemistry. A review of this work has been published [547].

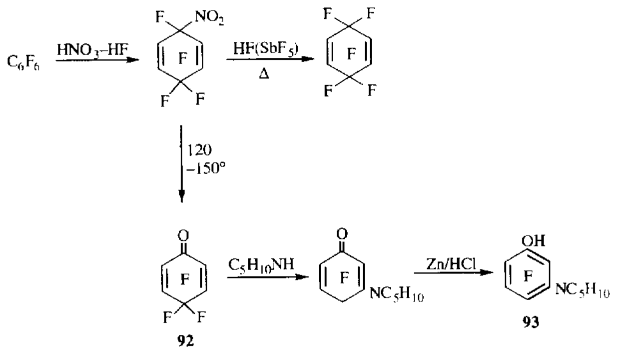
3.4.1. Reactions with nitrating agents

The products obtained in these reactions depend on the nature of the nitrating agent. In general there are two types: (i) nitro-cyclohexadienones using nitric acid, and (ii) nitro-fluoro-cyclohexadienes with HNO_3–HF (equivalent to $NO_2^+ F^-$). Scheme 29 illustrates the use of these reagents with octafluoronaphthalene, which also highlights a general principle with polyfluoropolycyclic aromatic compounds, that the site of attack is that found for "normal" electrophilic attack with hydrogen-containing analogues—the α-position in this case. Decafluoroanthracene formed the corresponding 9,10-derivatives [548]. Scheme 29 also shows the route to heptafluoro-1-naphthol (**91**) [549], complementary to the 2-OH compound formed by nucleophilic substitution of fluorine in $C_{10}F_8$ by HO^- [258].

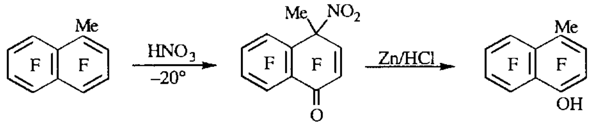
The nitrofluorination reaction of hexafluorobenzene is shown in Scheme 30 [550], as well as two general reactions of the $>C(NO_2)F$ group: thermal conversion to $>C{=}O$ [550,545], and the formation of the $>CF_2$ group [546,550]. The fluorine at position 3 in the dienone (**92**) is replaceable by nucleophiles and reduction of the product results in aromatisation to a rare meta derivative (**93**) [551]. Only one regio-product is formed in the nitrofluorination of C_6F_5Me (Eq. (65)) [552].



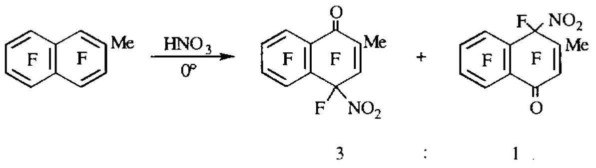
Scheme 29.



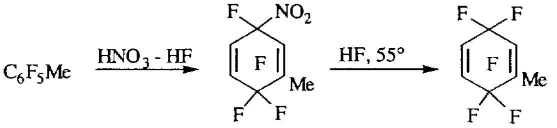
Scheme 30.



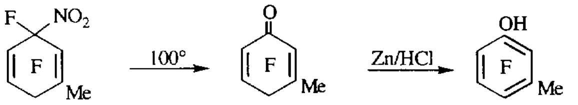
Scheme 31.

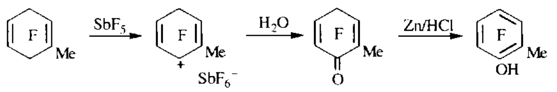


Scheme 32.

 (65)

Further examples of the synthetic use of the dienes shown in Eq. (65) are given in Eq. (66) [552] and Eq. (67) [553,547].

 (66)

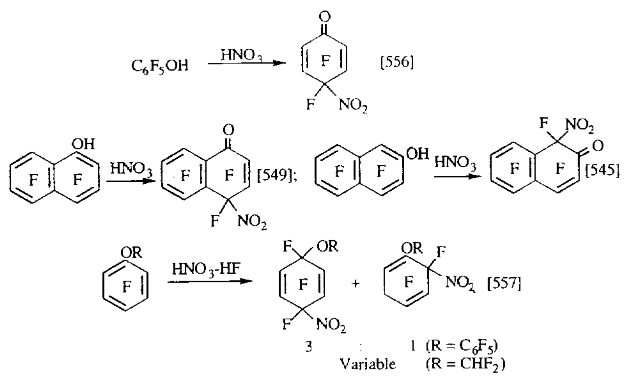
 (67)

Attack at position 1 in 1-methylheptafluoronaphthalene occurred with nitric acid (Scheme 31), which also shows a rearomatisation reaction of the dienone; nitrofluorination with NO_2BF_4 in sulpholane took place at three α-positions: 1-, 5- and 8- [554].

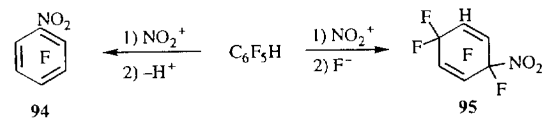
2-Methylheptafluoronaphthalene gave products with nitric acid which resulted from attack at both α-positions in the substituted ring, the preferred site again being meta to the methyl group (Scheme 32) [552]. Parallel nitration studies have been carried out with $C_6F_5Cl(Br)$ [550] and with 1- and 2-Cl(Br) heptafluoronaphthalenes [555].

Electron-donating substituents such as HO, OAlk and OAr are more powerful than fluorine in stabilising a carbocationic centre. Phenolic compounds reacted with nitric acid to produce cyclohexadienones [556]. However, in the nitrofluorination of the aryl ether, the site of attack para to the ether group is preferred, the only case where this orientation is found for a substituent other than fluorine (Scheme 33) [557].

Probably the most spectacular reactions with nitrating agents are those in which there is hydrogen on the ring, yet addition products arise, in avoidance of conventional electrophilic substitution of the hydrogen! With pentafluorobenzene, formation of both the nitrobenzene (**94**) and the nitrofluori-



Scheme 33.

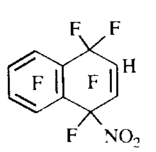


Scheme 34.

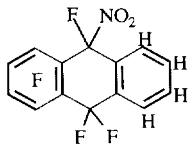
nation adduct (**95**) can occur, depending on the nature of the nitrating agent (Scheme 34). The traditional reagent (HNO_3–H_2SO_4) gave a low yield of (**94**) (about 20%) as the only product isolated; HNO_3–HF produced 70% (**94**) and 30% (**95**); only (**94**) (about 100%) was obtained with HNO_3-HF-SbF_5 or NO_2BF_4 in sulpholane (non-nucleophilic ions) [549,550,558]; see also [534].

Nitrofluorinations of 1-*H*- and 2-*H*-heptafluoronaphthalenes are of particular interest. Even though the 1-*H* isomer has the most reactive site for electrophilic attack (position 1), with HNO_3–HF no nitro compound (**96**) was formed. However, position 1 was attacked to give the remarkably stable nitrofluorination adduct (**97**) (50%) accompanied by the 5- and 8-nitrofluorination adducts (**98**) and (**99**) respectively (50%) (Scheme 35). Nitration at position 1 was more successful with NO_2BF_4 in sulpholane (70%) (**96**), with (**98**) and (**99**) (30%) accounting for the remainder [559].

2-*H*-Heptafluoronaphthalene was not nitrated with HNO_3/HF; nitrofluorination was initiated by attack at position 4 to give (**100**) [527]. In a similar way, NO_2^+/F^- added to the more reactive 9,10-position in 1,2,3,4,9,10-hexafluoroanthracene to give (**101**) [548].

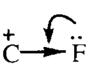


100

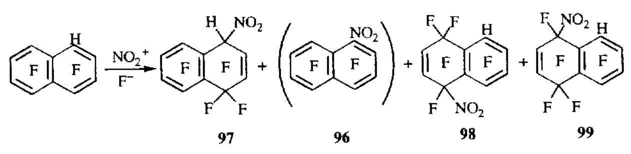


101

The general picture to emerge from all these studies with nitrating agents is as follows: (i) in polyfluoropolycyclic aromatic systems, attack by the electrophile occurs at those sites which are the most active in the hydrogen-based analogues, even if fluorine is present at that site; (ii) additions occur to give 1,4-products; (iii) the positive charge which develops at position 4 to the site of attack is stabilised by 4-substituents in the order O > F > Me > H; fluorine is activating compared with hydrogen because



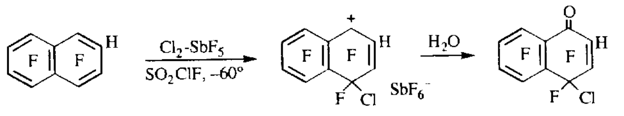
is overall cation-stabilising; and (iv) fluorine meta to the site of attack is to be avoided, unless oxygen would be meta, because it destabilises positive charge at the para (4-) position in the transition state on account of the unfavourable interaction $\overset{+}{C}$–C→F. These electronic effects exerted by fluorine are the opposite of those which operate when nucleophilic aromatic substitution is being considered (see Section 3.1.4).



Scheme 35.

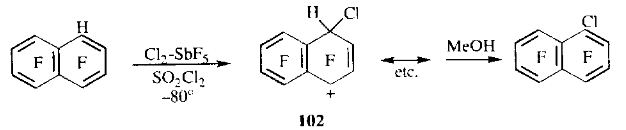
3.4.2. *Reactions with halogenating agents*

Electrophilic chlorinations of polyfluoroaromatic compounds have been carried out using the system Cl_2–SbF_5 in SO_2 or SO_2ClF [560–562], and gave arenium ions with regioselectivity similar to that described for nitration. Quenching the ion is frequently carried out using water so that chlorohexadienones are formed (e.g. Eq. (68)) [542].



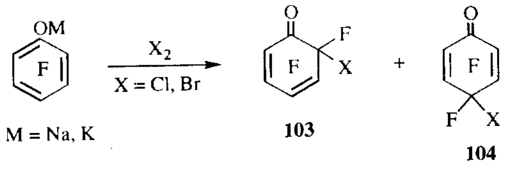
(68)

Chlorination of 1-*H*-heptafluoronaphthalene at a low temperature gave a relatively stable arenium ion (**102**) by attack at position 1, a rare case of the real intermediate in the electrophilic substitution of hydrogen (Eq. (69)) [542].



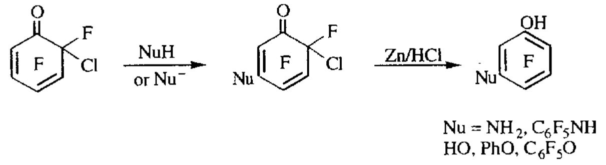
(69)

The simple chlorination or bromination of salts of pentafluorophenol gave mixtures of 2,4- (**103**) and 2,5-cyclohexadienones (**104**) (Eq. (70)) [563].



(70)

Compound (**103**) (X = Cl) has been widely used to synthesise meta-substituted phenols (Scheme 36) [551].

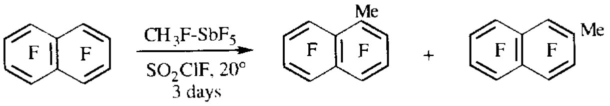


Scheme 36.

3.4.3. Reactions with carbon electrophiles

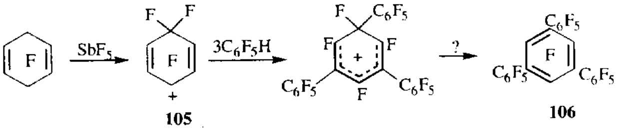
Some fascinating reactions have been described involving carbon electrophiles and polyfluoroaromatic compounds which formally require loss of F^+ to account for the products. Consequently, the mechanisms of these processes are obscure.

The simplest of these reactions involved octafluoronaphthalene and the Friedel–Crafts reagent $CH_3F–SbF_5$ (Eq. (71)) [564].



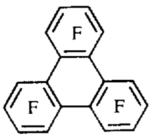
(71)

Treatment of the unusual electrophile, heptafluorobenzenium ion (**105**) with three equivalents of C_6F_5H gave perfluoro-1,3,5-triphenylbenzene (**106**) in high yield (about 70%) (Eq. (72)) [565]. The problem in this case rests in the aromatisation of the arenium ion which arose from the heptafluorobenzenium ion.



(72)

Other compounds obtained with arenium ions include perfluorotriphenylene (**107**) (from $C_6F_7{}^+$ + 2*H*,2′*H*-octafluorobiphenyl) [566] and compound (**108**) prepared from (**109**) and C_6F_5H [566].



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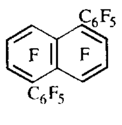

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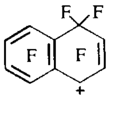

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Polyfluoronaphthalenes form high concentrations of stable radical cations in SbF_5 (see Section 3.11). Treatment with C_6F_5H or *o*-$C_6F_4H_2$ proceeds to the products shown in Scheme 37 [567,568].

An intriguing electrophilic cyclisation reaction to form polyfluorochloroindanes has been discovered (Scheme 38) [569]. The mechanism proposed for the reaction involves ipso attack at the ortho C–F bond of the C_6F_5 ring.

3.5. Reactions of radicals at C–F bonds

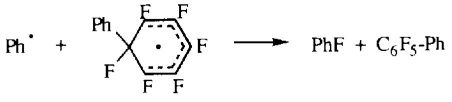
The substitution of hydrogen in aromatic compounds by radicals is a well-established process, but with perfluoroaromatic systems, a substitution reaction raises the question of how the fluorine atom is eliminated. A review has highlighted some of the peculiarities of these reactions [585].

The decomposition of hydrogen-containing aryl peroxides in hexafluorobenzene gave good yields of the fluorine-substituted product (Eq. (73)) [570].

$$C_6F_6 + (RC_6H_4CO_2)_2 \xrightarrow[\text{or sealed tube at 85 – 95°C 36h – 14d}]{\text{Reflux}} RC_6H_4–C_6F_5 \qquad (73)$$

R = H, *m*-Me, -Cl, -Br; *p*-NO_2

Generation of the phenyl radical by reaction of aniline and pentyl nitrite in C_6F_6, however, resulted in a low (10%) yield of C_6F_5–Ph, as well as giving some fluorobenzene, indicating that some of the radicals were consumed in the defluorination of the σ-complex (**110**) (Eq. (74)) [571].



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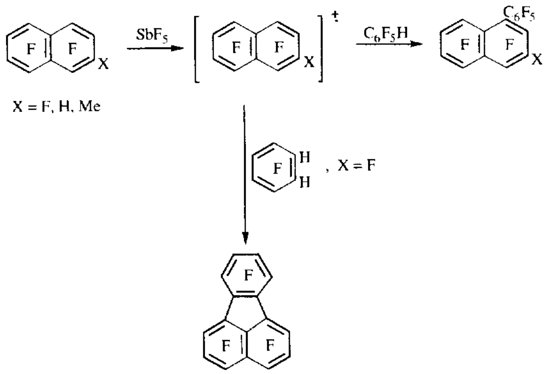
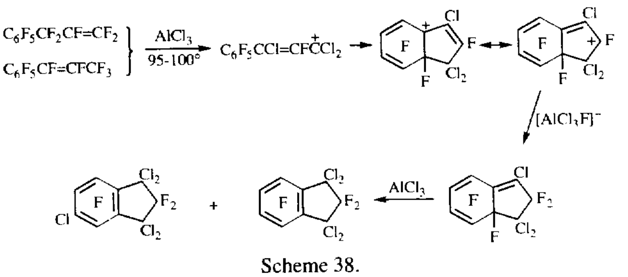
(74)

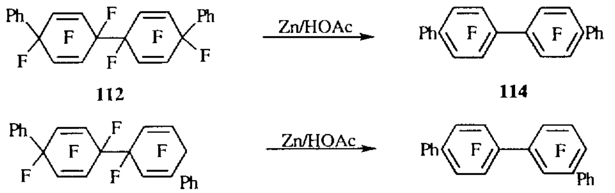
Decomposition of phenylazotriphenylmethane as the source of Ph˙ in C_6F_6 gave very little C_6F_5Ph (>0.1%), but the addition of benzoic acid led to an increased yield (8%) [572]. This acid (BzOH) is now regarded as being an essential component in the production of the biaryl via the ther-



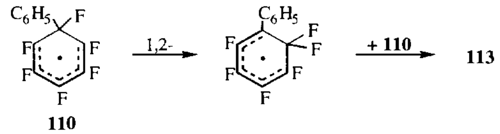
Scheme 37.



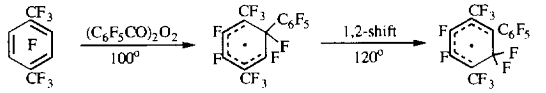
Scheme 38.



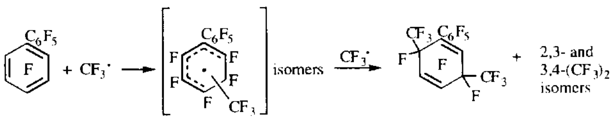
Scheme 39.



Scheme 40.

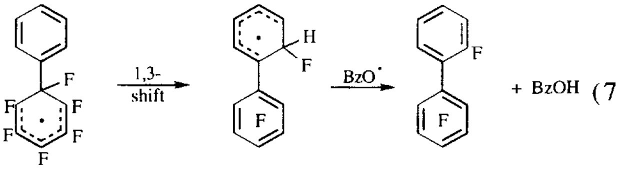


Scheme 41(a)



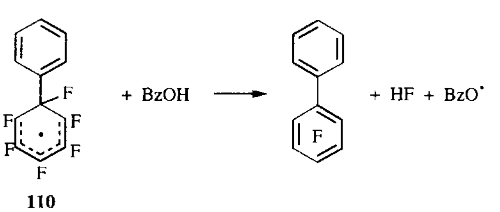
Scheme 41. (b).

molysis of benzoyl peroxide in C_6F_6 [573] and is formed along with another minor component identified in the product, 2,2′,3,4,5,6-hexafluorobiphenyl (**111**), following a rearrangement of the initial σ-complex (**110**) (Eq. (75)) [574].



(75)

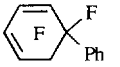
The acid induces aromatisation of (**110**) via an addition–elimination reaction (Eq. (76)).



(76)

Under milder reaction conditions, the dimer of (**110**), i.e. compound (**112**), and an isomer (**113**) have been identified in the product by dehalogenation to the corresponding quaterphenyls (**114**) and (**115**), respectively, whose structures were determined by ^{19}F NMR (Scheme 39) [575].

A 1,2-shift of fluorine in the σ-complex (**110**) was proposed to account for the formation of (**113**) (Scheme 40). However, a later analysis of the volatile products from the reaction by gas chromatography–mass spectroscopy revealed the presence of another component corresponding to (**116**) or (**117**),



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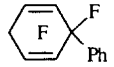

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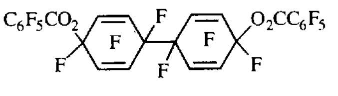
either of which could react with (**110**) and be trapped to give a material which would yield (**115**) on dehalogenation [576], so that the true mode of formation of (**115**) remains uncertain. Nevertheless, a 1,2-shift of fluorine has been detected by ESR spectroscopy following the addition of $C_6F_5^{\bullet}$, from $(C_6F_5CO_2)O_2$, to p-$C_6F_4(CF_3)_2$ (Scheme 41a) [844].

Pentafluorobenzoyl peroxide has been synthesised [577,578] and reacted with hexafluorobenzene. At 80°C, the major product was the dimer of the $C_6F_5CO_2^{\bullet}$ adduct to the C_6F_6 (**118**) [579], and at 200°C, the dimer of the 3-C_6F_5–$C_6F_6^{\bullet}$ species (**119**) [580,581]. Minor products included C_6F_5–C_6F_5 [579,582] and $C_6F_5CO_2C_6F_5$ [579].



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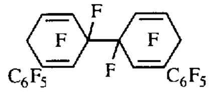

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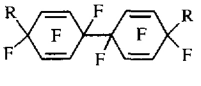
Table 9
Products from reaction of $R^{\bullet-}$ radical with C_6F_6

Radical R	Source	**120**	**121**	**122**	Other	Ref.
$Me^{\bullet}$	$(MeCO_2)_2$	✓	–	–	C_6F_5Me (15%)	[584]
$Me^{\bullet}$	$(Bu^tO)_2$	✓	✓	✓		[585]
$Me^{\bullet}$	MeMgI/AgCl or CuI	–	–	–	C_6F_5Me (18-27%) $C_6F_5CH(Me)OEt$ (5-8%)	[586]
$CF_3^{\bullet}$	$(CF_3CO_2)_2$	✓	–	–		[585]
$C_2F_5^{\bullet}$	$(C_2F_5CO_2)_2$	✓	–	–		[584]
cyclo-$C_6H_{11}^{\bullet}$	cyclo-$C_6H_{12}/(Bu^tO)_2$	✓	✓	✓	some C_6F_5–C_6H_{11}	[587]
cyclo-$C_6H_{11}^{\bullet}$	cyclo-C_6H_{12}, $Ph_2CO/h\nu$				C_6F_5–C_6H_{11}	[588]
$HOCH_2^{\bullet}$	CH_3OH, $Ph_2CO/h\nu$				$C_6F_5CH_2OH$ + 1,2-(H–CH_2OH) adduct	[589]

Generation of $C_6F_5^{\bullet}$ from $C_6F_5NHNH_2/Ag_2O$ [98] similarly gave (**119**) along with the 3,4′- and 4,4-isomers [583].

Alkyl radicals with a variety of polarities and steric requirements reacted with C_6F_6 to give products (**120**), (**121**) and (**122**), the results of which are presented in Table 9.



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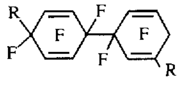

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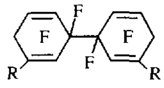


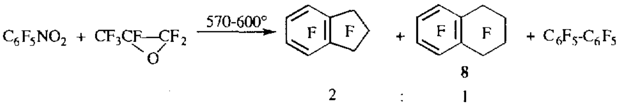
122

The reactions of radicals with C_6F_5X substrates, pentafluoropyridine and octafluoronaphthalene have the possibility of attack at different sites. The results of some of these studies are shown in Table 10 and factors affecting the orientations of the products have been discussed [585]. Cyclohexadiene adducts with decafluorobiphenyl and CF_3 are formed in accordance with Scheme 41b [593].

Di-*t*-butylperoxide as a source of $Me^{\bullet}$ radicals, on reaction with $C_{10}F_8$ gave a high yield of 2-methylheptafluoronaphthalene (72% at 140°C), along with dimers of the $Me^{\bullet}$ adduct (Scheme 42) [598].

Treatment of pentafluorophenol with $(C_6F_5CO_2)_2$ resulted in reactions governed by the formation of $C_6F_5CO_2^{\bullet}$ rather than $C_6F_5^{\bullet}$ (Scheme 43) [602].

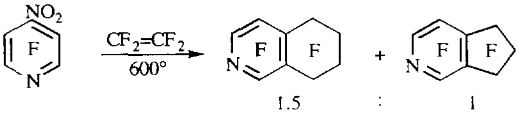
An important C–C bond forming reaction involving radicals took place during the co-pyrolysis of pentafluoronitrobenzene with hexafluoropropene oxide, usually considered as a source of difluorocarbene, CF_2 (Eq. (77)) [603,604].



(77)

The formation of perfluorotetralin also occurred in the reaction of pentafluoronitrobenzene or pentafluorophenylsulphonyl fluoride with tetrafluoroethylene at 720°C [604], the mechanism proposed for the process being shown in Scheme 44. The mechanism for the formation of the indane is given in Section 3.6.2.2

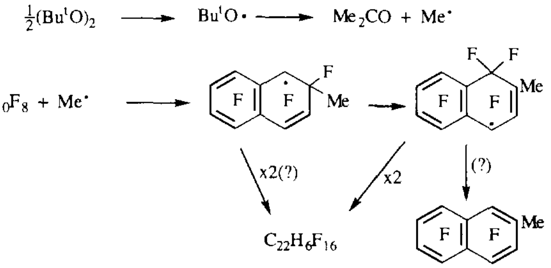
An analogous reaction took place with 4-nitrotetrafluoropyridine (Eq. (78)) [605].



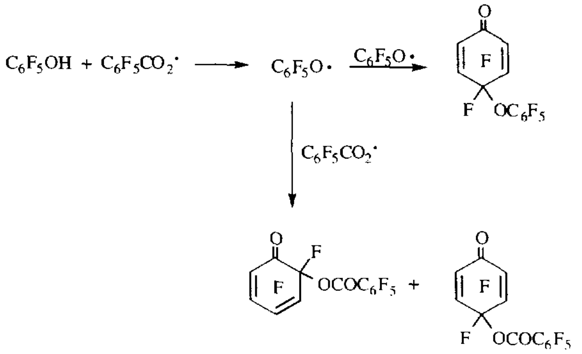
(78)

Overall substitution of fluorine by a silicon unit resulted from the photolysis of C_6F_6 with trichlorosilane in a process which has been suggested to involve an internal displacement of chlorine by fluorine (Scheme 45) [606].

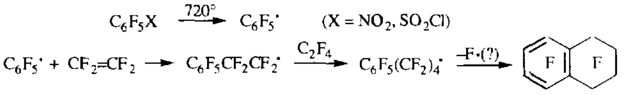
Nitrogen radical intermediates have been invoked in the formation of octafluorophenazine (**123**) (6%) as one of the products formed during the electrochemical oxidation of pentafluoroaniline at a platinum anode (Scheme 46) [607,608].



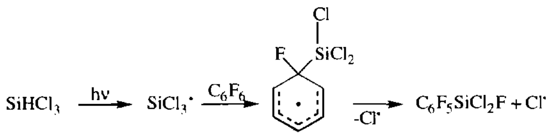
Scheme 42.



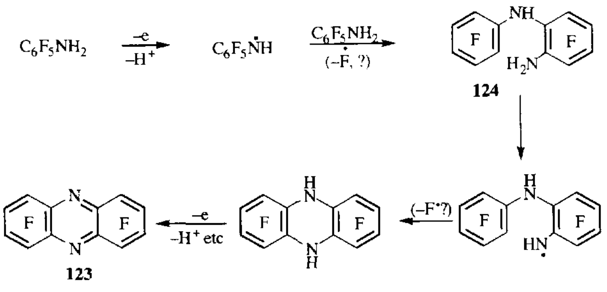
Scheme 43.



Scheme 44.

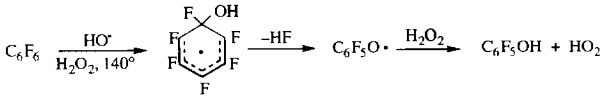


Scheme 45.

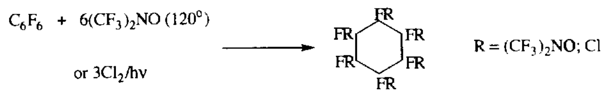


Scheme 46.

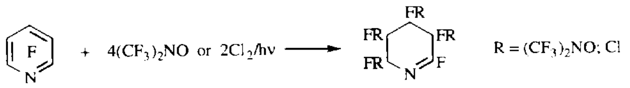
Oxidation of $C_6F_5NH_2$ with lead tetraacetate also gave (**123**) (28%) together with decafluoroazobenzene (48%) [232]. The proposed intermediate (**124**) in Scheme 46, as substrate in an analogous electrochemical reaction, gave an improved yield of the heterocycle (**123**) (40%); significantly, (**124**) failed to undergo nucleophilic cyclisation using strong bases as catalysts [608]. The electrochemical oxidation of 2-aminopolyfluorobenzophenones (**125**) to give acridone derivatives (**126**) via N–C bond formation extended the breadth of the electrocyclisation process (Eq. (79)) [609].



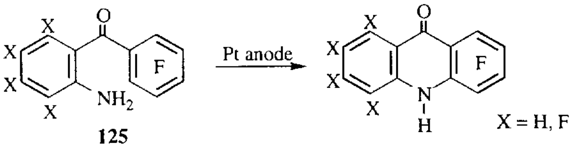
Scheme 47.



Scheme 48.



Scheme 49.



125 **126** (79)

Treatment of hexafluorobenzene with hydrogen peroxide (90%) resulted in the formation of a C–O bond to give pentafluorophenol, as shown in Scheme 47 [610]. A wide range of products was formed in the corresponding reaction with octafluoronaphthalene [611].

The unsaturation in C_6F_6 was removed completely on heating with bistrifluoromethyl nitroxide [612], or on ultraviolet irradiation with chlorine [1] (Scheme 48). In the analogous reactions with pentafluoropyridine, unsaturation to nitrogen was retained [613] (Scheme 49).

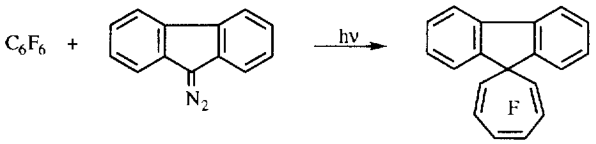
3.6. Reactions of carbenes and nitrenes at C–F bonds

Carbenes as "reactive species" are usually generated and reacted under mild conditions. Russian workers, however, have discovered that their generation under conditions of very high temperature and their interaction with polyfluoro-aromatic and -heteroaromatic compounds have opened up important new areas of synthetic chemistry [604]. Reactions involving nitrenes are much less common.

3.6.1. Reactions under mild conditions

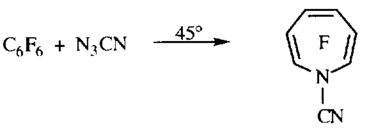
The generation of carbenes from diazomethane [614] and its derivatives in the presence of C_6F_6 under both thermal [615] and photochemical conditions [616,617] resulted in the formation of ring-expanded materials among the products (e.g. Eqs. (80) and (81)).

(80)



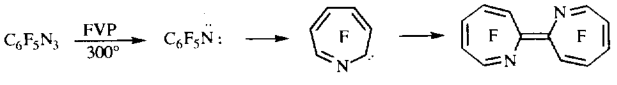
(81)

A perfluoroazepine derivative has been produced by an intermolecular reaction between C_6F_6 and a nitrene (Eq. (82)) [618]



(82)

whereas in a related intramolecular ring expansion reaction the initial process involved pentafluorophenylnitrene (Eq. (83)) [619].

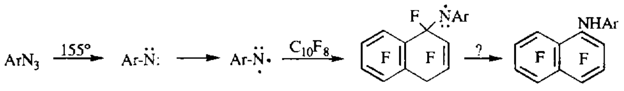


(83)

The decomposition of *p*-tolyl and *p*-anisyl azides in octafluoronaphthalene under nitrogen gave small amounts of the corresponding *N*-aryl-1-heptafluoronaphthylamine derivatives (**127**), the process being interpreted in terms of a reaction involving triplet nitrenes (Scheme 50) [620].

3.6.2. High temperature reactions

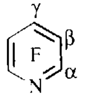
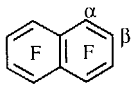
American workers first described the formation of octafluorotoluene in low yield from the co-pyrolysis of C_6F_6 with $CF_2{=}CF_2$ at 850°C [105], a reaction now recognised as involving difluorocarbene as the reactive intermediate. Subsequently, three areas of chemistry have been developed which involve the reactions of carbenes under vigorous conditions with highly fluorinated substrates. These reactions involve: (i) the formation of CF_3 derivatives; (ii) a cyclisation reaction giving polyfluoro saturated five-membered fused rings; and (iii) the synthesis of styrenes. Sources of difluorocarbene, CF_2, used extensively in these studies include tetrafluoroethylene, poly(tetrafluoroethylene), $CHClF_2$ and fluoroform at 500–850°C [604].



127

Scheme 50.

Table 10
Orientation of products from reactions of radicals with polyfluoro-aromatic and -heteroaromatic compounds

Substrate	Radical (Source)	Product			Other	Ref.
		o-; (α-)	m-; (β-)	p-; (γ-)		
$C_6F_5CF_3$	$Me^\bullet$ (MeMgI–Et_2O/AgCl; CuI)	37	24	39		[590]
	$EtO\dot{C}HMe$	8	18	74		
	$C_6F_5^\bullet$ [$(C_6F_5CO_2)_2$]	–	(✓)	–	A dimer of adduct radical	[591]
C_6F_5Cl	$Ph^\bullet$ [$(PhCO_2)_2$]	44.1	35.0	20.9		[573]
C_6F_5Br	$Ph^\bullet$ [$PhCO_2)_2$]	43.6	39.0	17.4		[573]
C_6F_5H	$HOCH_2^\bullet$; (cyclo-$C_6H_{11}^\bullet$) {CH_3OH; cyclo-C_6H_{12}, $Ph_2CO/h\nu$}	14(25)	–	86(75)	Some 1,2-adducts	[592]
C_6F_5OMe	$HOCH_2^\bullet$; (cyclo-$C_6H_{11}^\bullet$) {CH_3OH; cyclo-C_6H_{12}, $Ph_2CO/h\nu$}	22(28.5)	44(43)	34(28.5)		[592]
$C_6F_5C_6F_5$	$Me^\bullet$ (MeMgI–Et_2O/AgCl; CuI)	–	–	–		
	$EtO\dot{C}HMe$	2	16	82		[590]
	$CF_3^\bullet$ [$(CF_3CO_2)_2$]	(✓)	(✓)	(✓)	Dienes and dimers of adduct radicals	[593]
	$C_6F_5^\bullet$ [$(C_6F_5CO_2)_2$]	(✓)	(✓)	(✓)	Dimers of adduct radicals	[594]
	$Ph^\bullet$ [$(PhCO_2)_2$]	47.7	22.1	30.3		[573]
	cyclo-$C_6H_{11}^\bullet$ (cyclo-C_6H_{12}, $Ph_2CO/h\nu$)	–	–	✓	4 subn.	[592,595]
	$HOCH_2^\bullet$ (CH_3OH, $Ph_2CO/h\nu$)	–	–	✓	4 subn.	[592,597]
	$Me^\bullet$ (MeMgI–Et_2O/AgCl; CuI)	90	10			[585]
	$EtO\dot{C}HMe$	50	50	–		[586]
	$Me^\bullet$; $Bu^tO^\bullet$ [$(Bu^tO_2)_2$] at 110°C	–	–	–	Cyclic dienones and a 2-Me-2,5-dieneone	[598]
	$Me^\bullet$ [$(Bu^tO_2)_2$] at 140°C	–	✓	–	Dimers of Me adducts	[598]
	$Me^\bullet$ [$(Bu^tO_2)_2$] at 160°C	✓	✓	–	Dimers of Me adducts	[598]
	$HOCH_2^\bullet$ (CH_3OH, $Ph_2CO/h\nu$)	✓	✓			[592]
	$PhCO_2^\bullet$ (a), $Ph^\bullet$ (b) [$(PhCO_2)_2$]	(a) (b)	(a) (b)		Quinones; complex	[599] [601]
	$C_6F_5CO_2^\bullet$, $C_6F_5^\bullet$ [$(C_6F_5CO_2)_2$]				$C_6F_5CO_2^\bullet$ (α- and β-substitution 1.5%); quinones; complex. Dimers of α-$C_6F_5CO_2^\bullet$ adduct	[600]

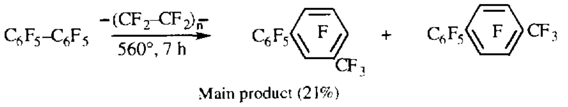
3.6.2.1. Formation of CF_3 derivatives

The optimum conditions for the formation of octafluorotoluene have now been established in a co-pyrolysis reaction (Eq. (84)) [604].

$$C_6F_6 \xrightarrow[720-770°C]{CF_2=CF_2} C_6F_5CF_3\,(65-67\%) \qquad (84)$$

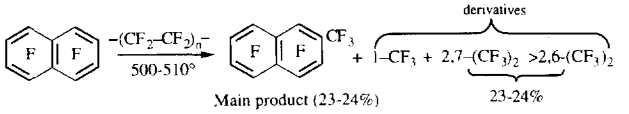
The usual question of orientation arises for the reaction with C_6F_5X derivatives, polyfluoropolycyclic aromatic compounds and unsymmetrical heterocycles. The results of some of these investigations are shown in Eqs. (85)–(88).

$$C_6F_5CF_3 \xrightarrow[770-850°C]{CF_2=CF_2} \underset{m>p\,(40\%)}{C_6F_4(CF_3)_2} + \underset{7-15\%}{1,3,5-C_6F_3(CF_3)_3}\ [604] \qquad (85)$$



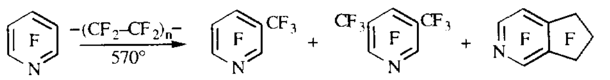
(86)

[604]



(87)

[604,621]



(88)

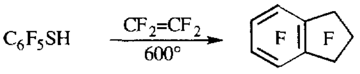
[622]

The available evidence suggests that the mechanism for the trifluoromethylation reaction proceeds by the direct insertion of CF_2 into the C–F bond and that the orientations observed are a reflection of the electrophilic character of the carbene—though thermodynamic factors are dominant with octafluoronaphthalene [604].

Chloropentafluorobenzene C_6F_5Cl reacted with $CF_2{=}CF_2$ at 700°C to give $C_6F_5CF_2Cl$ among the products—the result of $\ddot{C}F_2$ insertion into the C–Cl bond, along with $C_6F_4(CF_3)Cl$ compounds [604]. The product from the corresponding reaction with poly(tetrafluoroethylene) at 550°C contained perfluoroindane, signifying the incursion of another type of process.

3.6.2.2. Formation of perfluoroindane and derivatives

Perfluoroindane (**128**) was the main product in the reaction of F_2 with C_6F_5X derivatives where X = NH_2, OH, OMe, SH, the most effective reaction being shown in (Eq. (89)) [603,623].

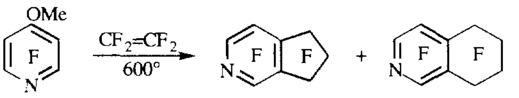


128 67%

(89)

Although it is not clear how the carbene reacts with the C–X bond in C_6F_5X, the heptafluorobenzyl radical is probably deeply involved in the mechanism of the reaction, as shown in Scheme 51.

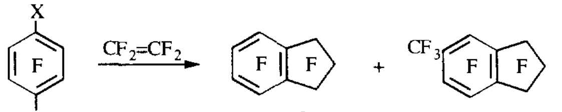
Perfluoro-2-pyrindane (**129**) is the major product from the co-pyrolysis of 4-amino- [625] or 4-methoxytetrafluoropyridine with tetrafluoroethylene (Eq. (90)) [605].



129 24-26% 6-9%

(90)

Surprisingly, perfluoroindane (**128**) was formed along with the expected 5-substituted derivative (**130a**) in reactions of 4-bromotetrafluoroanisole and of 4-heptafluorocresol and -thiocresol with tetrafluoroethylene (Eq. (91)) [604].



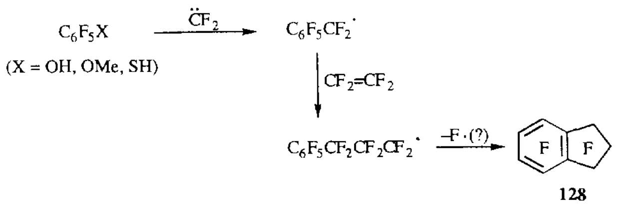
X=OH, SH

128 23-24%

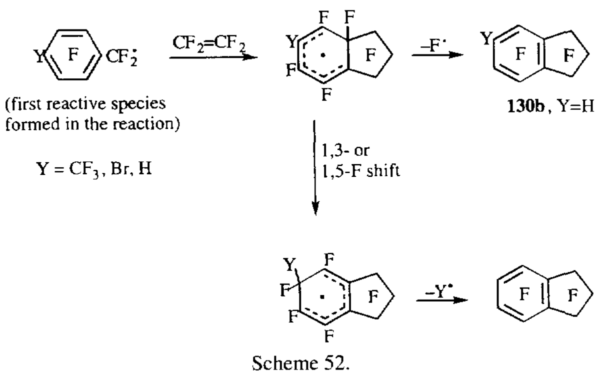
130a 18-22%

(91)

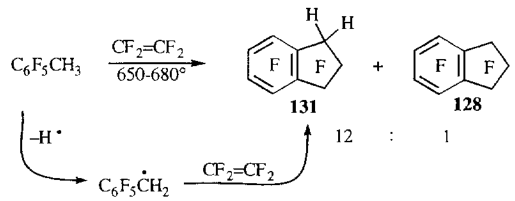
In order to account for the loss of CF_3 and Br in these vapour-phase reactions, a 1,3- or 1,5-sigmatropic shift of fluorine was invoked (Scheme 52) [604]. When Y = H (Scheme 52), using 2,3,5,6-tetrafluorophenol in the co-pyrolysis reaction (OH being eliminated), only 1% perfluoroindane was pro-



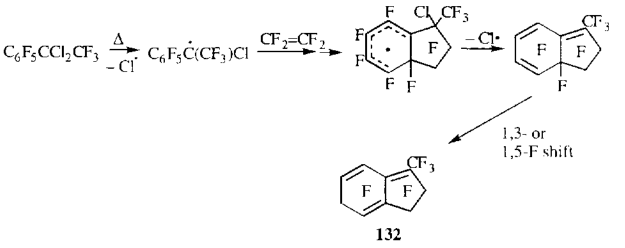
Scheme 51.



Scheme 52.



Scheme 53.

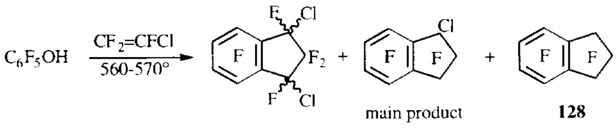


Scheme 54.

duced, the major product (50%) being the expected 5-*H*-indane (**130b**) [272].

1,1-Dihydrooctafluoroindane (**131**) was the major product from the reaction of 2,3,4,5,6-pentafluorotoluene with tetrafluoroethylene, implicating $C_6F_5CH_2^{\bullet}$ rather than $C_6F_5CF_2^{\bullet}$ as the primary intermediate (Scheme 53) [626,627]. The corresponding reaction with 1,4-$C_6F_4(CF_3)(CH_3)$ also gave 1,1-dihydrooctafluoroindane, via a sigmatropic fluorine shift and loss of CF_3 [627].

Polyhaloindane compounds were formed in the co-pyrolysis of pentafluorophenol with chlorotrifluoroethylene, which is a source of F_2 and FCl (Eq. (92)) [628]. The presence of the geminal fluorines at position 2 is in accord with the expected regioselectivity of a radical addition to the alkene.



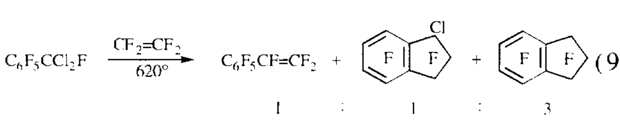
(92)

3.6.2.3. Formation of styrenes and indanes

A dramatic change in the course of the reaction took place when $C_6F_5CF_3$ was replaced by $C_6F_5CCl_3$ in its reaction with sources of $\ddot{C}F_2$: perfluoro-α-chlorostyrene was the major component (40–50%) of a complex product (Eq. (93)) [629,630].

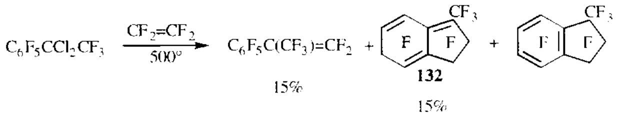
$$C_6F_5CCl_3 \xrightarrow[620°C]{CF_2=CF_2 \text{ or } CHClF_2} C_6F_5CCl=CF_2 \qquad (93)$$

Styrene and indane products were formed using $C_6F_5CCl_2F$ and $\ddot{C}F_2$ (Eq. (94)) [629,604].



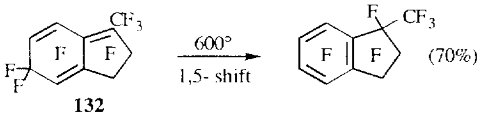
(94)

The absence of chlorine in the major product in Eq. (94), perfluoroindane, presented an interesting problem, the solution to which was illuminated by the isolation of the triene system (**132**) shown in Eq. (95) for a related example [604].



(95)

The mechanism proposed for the formation of (**132**) requires the loss of chlorine and is shown in Scheme 54. In a separate experiment, aromatisation of the triene (**132**) demonstrated unambiguously the sigmatropic shift of fluorine (Eq. (96)) [604].



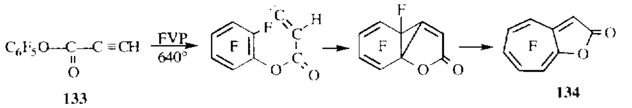
(96)

3.6.2.4. Ring expansion reactions

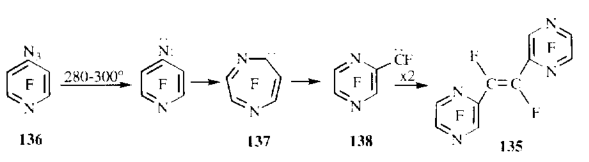
The pyrolysis of pentafluorophenyl propynoate (**133**) resulted in the formation of the seven-membered ring compound (**134**) via an initial acetylene–methylene carbene rearrangement followed by a carbene insertion reaction, as shown in Scheme 55 [631].

The presence of a small amount of the pyrazine derivative (**135**) in the product from the vapour-phase pyrolysis of the 4-azidopyridine (**136**) was rationalised by proposing a nitrene–carbene ring expansion to (**137**) and ring contraction to the isomeric carbene (**138**) which dimerised, Scheme 56 [632].

The identification of tetrafluoropyrazine in the complex product from the low-pressure pyrolysis of 4-*N*,*N*-dichlorotetrafluoropyridine implicated (**137**) in the course of the transformation [633].



Scheme 55.



Scheme 56.

Table 11
Reactions of C_6F_5MgX with electrophiles

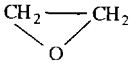
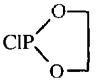
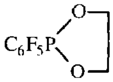
Electrophile	Product	Reference
D_2O	C_6F_5D	[451b]
Me_2SO_4	C_6F_5Me	[451c]
$C_6F_5CHCl_2$	$[(C_6F_5)_2CH]_2$	[635]
	$C_6F_5CH_2CH_2OH$	[638,639]
$(EtO)_3CH$; HCO_2Et; $PhN(Me)CHO$	C_6F_5CHO	[451b,c,636]
MeCHO	$C_6F_5CH(OH)Me$	[451b,634,636]
RCHO ($R = CCl_3$, $CHCl_2$, CH_2Br, CF_2Cl, CF_3)	$C_6F_5CH(OH)R$	[640]
R_FCHO [$R_F = C_3F_7^n$, $C_7F_{15}^n$, $CF_2H(CF_2)_3$]	$C_6F_5CH(OH)R_F$	[158]
PhCHO	$C_6F_5CH(OH)Ph$	[451c]
HCO_2Et; C_6F_5CHO	$(C_6F_5)_2CHOH$	[451c,635]
Me_2CO	$C_6F_5C(OH)Me_2$	[451c]
$(MeCO)_2O$	C_6F_5COMe	[636]
MeCOCl	C_6F_5COMe	[451c]
CF_3CO_2Li	$C_6F_5COCF_3$	[451c]
$ClCO_2Me$	$(C_6F_5)_2O$	[636]
$EtO_2C–CO_2Et$	$C_6F_5CH(OH)CO_2Et$, $C_6F_5COCO_2Et$	[641]
$EtO_2C–CMe_2–CO_2Et$	$C_6F_5CH(OH)–CMe_2–CO_2Et$, $C_6F_5CO–CMe_2–CO_2Et$	[641]
$EtO_2C(CH_2)_{2\text{-}4}CO_2Et$	$C_6F_5CO(CH_2)_{2\text{-}4}CO_2Et$, $C_6F_5CO(CH_2)_{2\text{-}4}COC_6F_5$	[641]
$[CO_2Bu^t]_2$	$C_6F_5COCO_2Bu^t$, $C_6F_5CH(OH)CO_2Bu^t$	[642]
R_FCOF [$R_F = C_2F_5O(CF_2CF_2O)_2CF_2–$, $C_3F_7OCF(CF_3)–$]	$C_6F_5COR_F$	[643]
CO_2	$C_6F_5CO_2H$	[451a,636,644a]
PCl_3	$(C_6F_5)_3P$	[644b]
		[645]
S	C_6F_5SH	[360]
$SOCl_2$	$C_6F_5SOC_6F_5$	[646]
Me_3SiCl	$C_6F_5SiMe_3$	[637]

Table 12
Reactions of polyfluoro aryl and heteroaryl Grignard reagents with electrophiles

Grignard reagent	Electrophile	Product	Reference
$p\text{-}HC_6F_4MgBr$	CO_2	$p\text{-}HC_6F_4CO_2H$	[68]
$p\text{-}C_6F_4(MgBr)_2$	CO_2	$p\text{-}C_6F_4(CO_2H)_2$	[68]
$p\text{-}C_6F_5OC_6F_4MgBr$	CO_2	R_FCO_2H	
	PBr_3	$(R_F)_3P$	[647]
$1\text{-}C_{10}F_7MgBr$	CO_2	$1\text{-}C_{10}F_7CO_2H$	[526b]
$2\text{-}C_{10}F_7MgBr$	$HCONMe_2$	$2\text{-}C_{10}F_7CHO$	[648]
1- and $2\text{-}C_{10}F_7MgCl$	H^+	1- and $2\text{-}C_{10}F_7H$	[636]
$4\text{-}IMgC_5F_4N$	CO_2	4-COOH	
	PhCHO	4-CH(OH)Ph	
	Ph_2CO	$4\text{-}C(OH)Ph_2$	
	C_5F_5N	$4,4'\text{-}NC_5F_4–C_5F_4N$	[290]
$4\text{-}BrMgC_5F_4N$	CO_2	$4\text{-}CO_2H$	
	EtCOMe	4-C(OH)(Me)Et	
	C_5F_5N	$4,4'\text{-}NC_5F_4–C_5F_4N$	[289]
$3\text{-}ClMgC_5F_4N$	CO_2	$3\text{-}CO_2H$	
	Br_2	3-Br	[649]

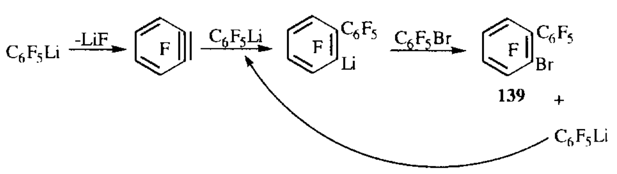
3.7. Reactions of organometallic compounds and carbanion-producing systems

3.7.1. Reactions of Ar_F–metal compounds

3.7.1.1. Grignard reagents and organolithium compounds

Grignard reagents and lithium derivatives are readily formed from C_6F_5I [451b], C_6F_5Br [451b,634] and C_6F_5Cl [7,635–637] and also from hydrogen-containing compounds via metallation [68]. The reactions of these organometallic compounds with electrophilic species have been extensively investigated and their use as nucleophiles for effecting replacement of fluorine in polyfluoroarenes can be seen in Section 3.1. The present section documents their more familiar role in organic chemistry, not least in reactions with carbonyl compounds, in Tables 11–14. Stepwise metallations of *o*-, *p*- [68] and *m*-$C_6F_4H_2$ [657] have been accomplished.

The role of the solvent is important in a number of these reactions, e.g. the carbonation of C_6F_5MgBr is considerably



Scheme 57.

enhanced in THF [644a] compared with Et_2O [451b], as is the reaction with ethylene oxide [638].

The reaction of C_6F_5Li with C_6F_5Br (Table 13) provided an interesting route to 2-bromononofluorobiphenyl (**139**) (Scheme 57) [644b,123]; other C_6F_5X compounds (X = Hal, H) reacted similarly with the lithium reagents. Reviews of polyfluoroaryl derivatives of metals and metalloids prepared from Grignard reagents and lithium compounds have been published [2c,d].

3.7.1.2. Organocopper reagents

The formation of the polyfluoroarene copper species often involves the simple addition of Cu(I)I to the Grignard reagent or lithium derivative in solution. Recently, the considerably more stable organocadmium reagents have been used in the metathesis reaction with copper(I) halides (Eq. (97)) [660,661].

$$C_6F_5Br \xrightarrow[\text{DMF, RT } 25^\circ\text{C}]{\text{Cd}} C_6F_5CdBr \xrightarrow[(Y=\text{Cl, Br})]{\text{CuY}} C_6F_5Cu \qquad (97)$$

The important reactions of Ar_FCu compounds are with halogen-containing substrates where the halogen (Cl, Br and I, and exceptionally, with F in acid fluorides) is substituted (see Table 15). The order of halogen mobility is I ~ Br > Cl > > F and is illustrated in Eq. (98) [655].

$$C_6F_5Li \xrightarrow{\text{CuI}} C_6F_5Cu \xrightarrow{CF_2{=}CFI} C_6F_5CF{=}CF_2 \qquad (98)$$

3.7.1.3. Nickel-mediated reactions

Pentafluoroiodobenzene has been reacted with acid chlorides in monoglyme at 85°C in the presence of specially prepared nickel to give the corresponding ketones (Eq. (99)) [677].

$$C_6F_5I + MeO_2C(CH_2)_3COCl \xrightarrow[85^\circ\text{C diglyme}]{\text{Ni}} C_6F_5CO(CH_2)_3CO_2Me \qquad (99)$$

3.7.2. Reactions of copper(I) compounds with polyfluoroaryl bromides/iodides

In contrast to the halogen mobility in simple nucleophilic substitution processes, where F > > Cl ~ Br ~ I, copper(I) reagents bring about the replacement of these halogens in the reverse order, I ~ Br > Cl > > F. Consequently, some complementarity to synthetic reactions can be accomplished, and clearly reflects differences in mechanism. The reaction of pentafluorobromobenzene with cuprous thiobutoxide in

Table 13
Reactions of C_6F_5Li with electrophiles

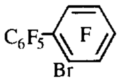
Electrophile	Product	Reference
PhCHO	$C_6F_5CH(OH)Ph$	[502]
HCO_2Et, PhN(Me)CHO	C_6F_5CHO	[502]
$(MeO)_2CO$	$C_6F_5COC_6F_5$	[459]
$(C_6F_5)_2CO$; $C_6F_5CO_2Et$; $(EtO)_2CO$	$(C_6F_5)_3COH$	[650]
$(CO_2Me)_2$	$C_6F_5COCOC_6F_5$	[651]
$C_6Cl_5COCO_2Me$	$C_6F_5COCOC_6Cl_5$	[651]
ArCOAr′	$C_6F_5C(OH)ArAr'$	[652]
$CF_2XCOCFYCl$	$CF_2XC(OH)(C_6F_5)CFYCl$	[653]
X = Y = F; Cl; X = Cl, Y = F		
$CF_2{=}CFCl$	$C_6F_5CF{=}CFCl$	[654]
$CF_2{=}CFI$	$C_6F_5CF{=}CFI$ (trans)	[655]
$CF_2{=}CCl_2$	$C_6F_5CF{=}CCl_2$	[654]
$CFCl{=}CFCl$, $CF_2{=}CHCl$	$C_6F_5C{\equiv}CCl$	[654]
$CF_2{=}CFH$, $CF_2{=}CFBr$	$C_6F_5C{\equiv}CC_6F_5$	[654]
cyclo-C_6F_{10}	cyclo-1-$C_6F_9C_6F_5$	
	cyclo-1,2-$C_6F_8(C_6F_5)_2$	[123]
cyclo-1-C_6F_9Ph	cyclo-1,2-$C_6F_8(Ph)C_6F_5$	[656]
C_6F_5Br		[123,644b]
$B(OMe)_3$; H_2O_2/HO^-	C_6F_5OH	[360]
(i) SO_2; (ii) $SF_4(SOCl_2)$	$C_6F_5SO_2F(Cl)$	[646]
Br_2	C_6F_5Br; o-$C_6F_4Br_2$	[502]
Hg	$(C_6F_5)_2Hg$	[502]

Table 14
Reactions of polyfluoro aryl and heteroaryl lithium reagents with electrophiles

Lithium reagent	Elecrophile	Product	Reference
o-$C_6F_4(H)Li$	CO_2	o-$C_6F_4(H)CO_2H$	[68]
o-$C_6F_4Li_2$	CO_2	o-$C_6F_4(CO_2H)_2$	[68]
m-$C_6F_4(H)Li$	EtHgCl	m-$C_6F_4(H)HgEt$	[657]
p-$C_6F_4(H)Li$	CO_2	p-$C_6F_4(H)CO_2H$	[68]
p-$C_6F_4Li_2$	CO_2	p-$C_6F_4(CO_2H)_2$	[68]
p-$C_6F_4(CO_2Li)Li$	S	p-$C_6F_4(SH)CO_2H$	
	Cl_2	p-$C_6F_4(Cl)CO_2H$	[658]
p-$C_6F_4(X)Li$ X = Me, CF_3, p-HC_6F_4, NH_2, OH, SH	CO_2	p-$C_6F_4(X)CO_2H$	[145]
p-$C_6F_5OC_6F_4Li$	CO_2	R_FCO_2H	
	$SnCl_4$	$(R_F)_4Sn$	[647]
2-$C_{10}F_7Li$	CO_2	2-$C_{10}F_7CO_2H$	
	Br_2	2-$C_{10}F_7Br$	[266]
3-LiC_5F_4N	CO_2	3-CO_2H	[659]
4-LiC_5F_4N	CO_2	4-CO_2H	[659]
3,5-$Li_2C_5F_3N$	CO_2	3-CO_2H, 5-H	
		3,5$(CO_2H)_2$	[659]

Table 15
Reactions of polyfluoro aryl and heteroaryl copper compounds with electrophiles

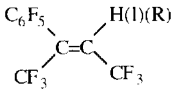
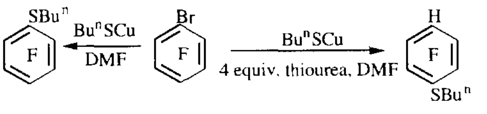
Electrophile	Product	Reference
Reactions with C_6F_5Cu		
MeI	C_6F_5Me	[662]
Bu^nI	$C_6F_5Bu^n$	[663]
CH_2I_2	$(C_6F_5)_2CH_2$	[663]
$CH_2{=}CH{-}CH_2Br$	$C_6F_5CH_2CH{=}CH_2$	[662,663]
$CF_2{=}CFI$	$C_6F_5CF{=}CF_2$	[664]
C_2Br_5H, $CHBr_2CHBr_2$, $CHCl_2CHCl_2$, $CBr_2{=}CBr_2$, $CBr_2{=}CHBr$, $CCl_2{=}CHCl$,	$C_6F_5C{\equiv}CC_6F_5$	[665,666]
$(C_6F_5I + Cu)$, $CF_2{=}CFI$	$C_6F_5CF{=}CF_2$	[664]
$(C_6F_5I + Cu)$, $CFI{=}CFCl$	$C_6F_5CF{=}CFCl$	[667]
(C_6F_5Cu), O_2, DMAC(THF)	$C_6F_5C_6F_5$	[668]
$(C_6F_5Br + Cu)$, p-IC_6H_4R	p-$C_6F_5C_6H_4R$	[669,670]
PhI	C_6F_5Ph	[662,663]
$BrC{\equiv}CSiMe_3$	$C_6F_5C{\equiv}CSiMe_3$	[172]
MeCOCl	C_6F_5COMe	[672,637,671]
$(CH_2COCl)_2$	$(C_6F_5COCH_2)_2$	[671]
$ClCO(CH_2)_nCOCl$ ($n = 0,2,4$)	$C_6F_5CO(CH_2)_nCOC_6F_5$	[673]
R_FCOF [$R_F{=}C_2F_5O(CF_2CF_2)_2CF_2{-}$; $C_3F_7OCF(CF_3){-}$]	$C_6F_5COR_F$	[643]
PhCOCl	C_6F_5COPh	[671,672]
p-$NO_2C_6H_4COCl$	p-$NO_2C_6H_4COC_6F_5$	[662]
$CF_3C{\equiv}CCF_3$: H^+; (I_2); (RI)		[660,674]
CO_2(DMAC)	$C_6F_5CO_2H$	[668]
Reactions with the di-copper species p-$C_6F_4Cu_2$		
$CH_2{=}CH{-}CH_2Br$	p-$C_6F_4(CH_2{-}CH{=}CH_2)_2$	[675,676]
EtCOCl	p-$EtCOC_6F_4COEt$	[676]
Reactions with the pyridine derivative 4-CuC_5F_4N		
$PhCH{=}CH{-}CH_2Cl$, $CF_3CF{=}CFI$(trans), ArI; AlkCOCl; ArCOCl	Replacement of Cl, I → 4-RC_5F_4N	[661]

Table 16
Reactions of polyfluoro aryl and heteroaryl halides with Cu(I)X compounds

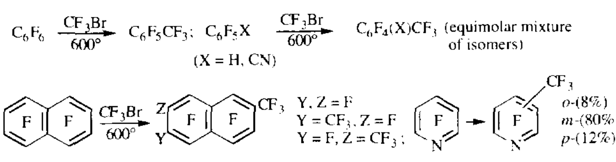
Halide	Reagent	Product	Reference
C_6F_5Br	Cu_2O, Ac_2O, DMF	C_6F_5H	[679]
p-$C_6F_4Br_2$	Cu_2O, Ac_2O, DMF	p-$C_6F_4H_2$	[679]
$C_6F_5Br(I)$	CuCN, DMF	C_6F_5CN	[679, (634)]
o-$C_6F_4Br_2$	CuCN, DMF	o-$C_6F_4(CN)_2$	[679]
p-$C_6F_4Br_2$	CuCN, DMF	p-$C_6F_4(CN)_2$	[679]
$C_6F_5Br(I)$	$PhC{\equiv}CCu$, DMF(C_5H_5N)	$C_6F_5C{\equiv}CPh$	[680,681a, (678)]
$C_6F_5Br(I)$	$C_6F_5Br(I) + Cu$	$C_6F_5C_6F_5$	[79,451b,634]
C_6F_5Br	Bu^nSCu, DMF	$C_6F_5SBu^n$	[678]
C_6F_5Br	Bu^nSCu, DMF/thiourea	p-$HC_6F_4SBu^n$	[678]
C_6F_5Br	C_6F_5SCu, DMF	$C_6F_5SC_6F_5$	[679]
C_6F_5Cl	$KBr/CuSO_4$, 300°C	C_6F_5Br	[681b]
C_6F_5Br	CuCl	C_6F_5Cl	[679]
p-$C_6F_4Br_2$	CuCl	p-$C_6F_4Cl_2$	[679]
1-$C_{10}F_7Br$	1-$C_{10}F_7Br + Cu$	1,1′-$C_{10}F_7$–$C_{10}F_7$	[526b]
2-$C_{10}F_7Cl$	2-$C_{10}F_7Cl + Cu$	2,2′-$C_{10}F_7$–$C_{10}F_7$	[526b]
4-BrC_5F_4N	4-$BrC_5F_4N + Cu$	4,4′-NC_5F_4–C_5F_4N	[289]

DMF provided an interesting case of the influence of the state of the cuprous species on the course of the reaction [678]. In DMF alone, exclusive replacement of bromine occurred, whereas in the presence of 4 equivalents of thiourea, a powerful complexing ligand, hydrodebromination and almost exclusive replacement of the para fluorine took place, Scheme 58.

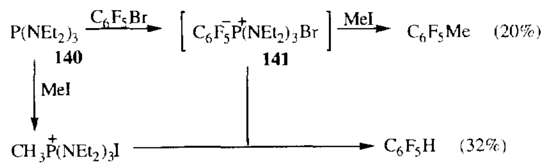
The copper(I) compounds which have been used in these reactions range from inorganic materials (CuCN, CuCl) to organocopper compounds ($PhC{\equiv}CCu$ and Ar_FCu), as shown in Table 16 which also includes Ullmann coupling reactions of aryl bromides/iodides with copper.



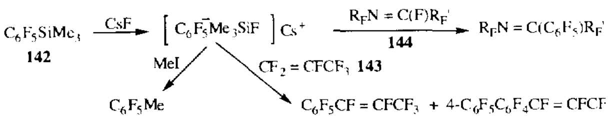
Scheme 58.



Scheme 59.



Scheme 60.



Scheme 61.

Intriguing cross-coupling reactions involving fluorine replacement have been reported between polyfluoro-aromatic and -heteroaromatic compounds and CF_3Br at high temperatures (600–650°C) in flow systems through a copper–chromite material (80% CuO, 17% Cr_2O_3) [682]. Scheme 59 shows some of the results of these investigations.

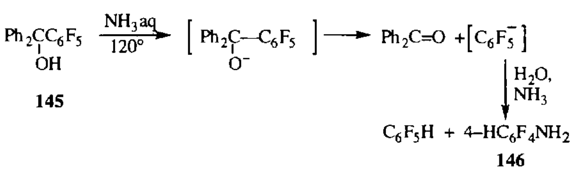
3.7.3. Carbanion-producing systems: pentafluorophenylation reactions

The phosphorus(III) compounds (**140**) promoted some pentafluorophenylation of methyl iodide when added to a mixture of C_6F_5Br and the alkyl halide, though proton abstraction by the reactive intermediate species (**141**) was more significant (Scheme 60) [683].

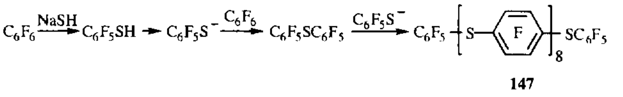
However, the use of the more powerful electrophiles Me_3SiBr and Et_3GeBr gave $C_6F_5SiMe_3$ (**142**) and $C_6F_5GeEt_3$ respectively in good yields [683,684].

Pentafluorophenyltrimethylsilane (**142**) in the presence of caesium fluoride provided a source of $C_6F_5^-$ for reaction with MeI [685], perfluoroalkenes (**143**) [686] and perfluoroazaalkenes (**144**) [687] (Scheme 61); $C_6F_5GeEt_3$ has been used in a related process with $(CF_3)_2C{=}CF(C_2F_5)$ [688]. The trispentafluorophenyl compounds $(C_6F_5)_3E$ where E = P, As, Sb [689] and Bi [690] were useful pentafluorophenylating agents when used in conjunction with CsF.

The pentafluorophenyl anion has been shown to be an excellent leaving group in relatively simple molecules. For example, the triaryl carbinol (**145**) on treatment with aqueous ammonia underwent a haloform-type reaction to give pentafluorobenzene and thence the amino product (**146**) arising by fluorine substitution (Scheme 62) [160]. The influence of fluorine in polyfluoroaryl groups to stabilise negative charge directly (as in $C_6F_5^-$) or in benzylic positions ($C_6F_5\bar{C}^-$) has been reviewed [691].



Scheme 62.

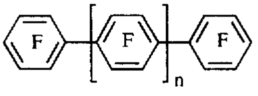


Scheme 63.

3.8. Oligomers and polymers prepared by the nucleophilic substitution of fluorine

The preparation of C_6F_5SH from C_6F_6 and sodium hydrosulphide in ethylene glycol/pyridine was accompanied by the concurrent formation of an amorphous solid when the $HS^-:C_6F_6$ molar ratio was less than 1.5:1 [117]. Desulphurisation of the solid with Raney nickel gave C_6F_5H and p-$C_6F_4H_2$ in the ratio of 1:4, which indicated a perfluoro (p-phenylene sulphide) (**147**) of 10 units—provided there were no terminal thiol groups (Scheme 63).

The attempted preparation of C_6F_5MgCl from C_6F_5Cl and magnesium in hot tetrahydrofuran resulted in the formation of an intractable polymeric material [7]. Pentafluorophenylmagnesium bromide decomposed in THF to give a product from which three compounds (**148**), soluble in ether, were identified [692].



148

n = 0, 1, 2

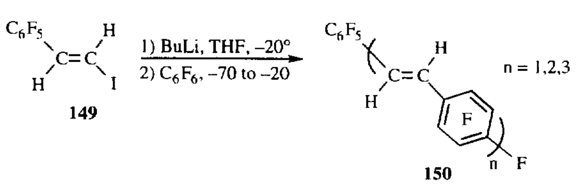
It is possible, therefore, that the polymeric material described above resulted from repeated para substitution by the Grignard reagent on another molecule of Grignard reagent, though the possibility of decomposition to tetrafluorobenzyne (C_6F_4) and further reactions cannot be excluded.

Treatment of (E)-2-(pentafluorophenyl)ethenyl iodide (**149**) with butyllithium in THF and addition to C_6F_6 gave a yellow product, from which three white compounds (**150**), soluble in CH_2Cl_2, were isolated and characterised (Scheme 64) [693]. The insoluble yellow material was assumed to be higher oligomeric material. When the lithium derivative of (**149**) was allowed to self-react in the absence of C_6F_6, a bright yellow material with approximately 12 repeating phenylenevinylene units was formed, presumed to terminate in C_6F_5 and $CH_2{=}CH$.

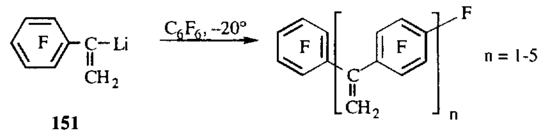
1-Lithio-1-(pentafluorophenyl)ethene (**151**) has been reacted with C_6F_6 to give five products (**152**) (Scheme 65) [694].

The hydrolysis of 2,3,4,5,6-pentafluorobenzyl bromide (**153**) resulted in the formation of polymer (**154**) via the intermediate benzyl alkoxide (**155**) (Scheme 66) [67].

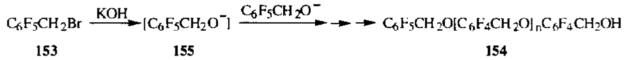
In a similar manner, the self-polymerisation of the alkoxide (**156**) gave viscous liquids of oligomeric ethers (**157**) after short reaction times and intractable solids after extended periods of reaction (Scheme 67) [695].



Scheme 64.



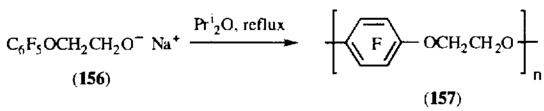
Scheme 65.



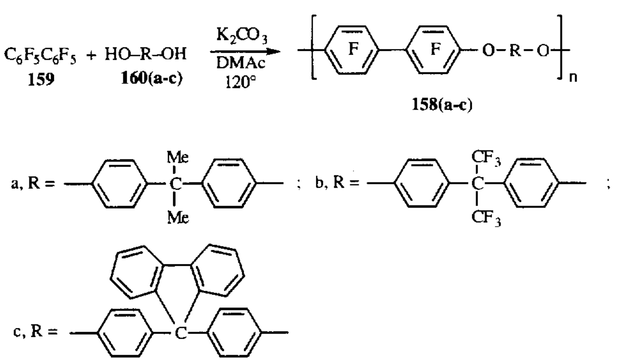
$$C_6F_5CH_2Br \xrightarrow{KOH} [C_6F_5CH_2O^-] \xrightarrow{C_6F_5CH_2O^-} \rightarrow\rightarrow C_6F_5CH_2O[C_6F_4CH_2O]_nC_6F_4CH_2OH$$

153 **155** **154**

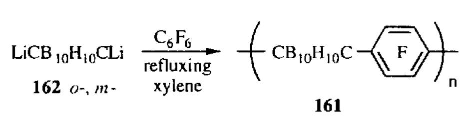
Scheme 66.



Scheme 67.



Scheme 68.

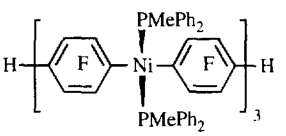


Scheme 69.

Tractable fluorinated ethers (**158**) have been obtained from decafluorobiphenyl (**159**) and bis-phenols (**160a–c**) (Scheme 68) [696].

Poly-m- and -o-carboranyleneperfluorophenylenes (**161**) as ether-soluble and ether-insoluble fractions have been prepared by the reaction of o- or m-dilithiocarborane (**162**) with C_6F_6 in refluxing xylene (Scheme 69) [697].

Some unusual nickel-bridged trimetallic (**163**) [698] and oligomeric species (**164**) [699] have been described.



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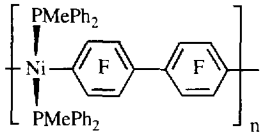


164

3.9. Reactions of polyfluoro aromatic and heteroaromatic radicals

The decompositions of bis(pentafluorobenzoyl)peroxide in benzene gave mainly the expected pentafluorobiphenyl (30–40%), the result of homolytic substitution of hydrogen by C_6F_5, though pentafluorobenzoic acid (25–40%) and small amounts of pentafluorophenyl pentafluorobenzoate (3%) and phenyl pentafluorobenzoate (2–4%) were also identified (Scheme 70) [577,578,582].

Generation of $C_6F_5^{\bullet}$ from $C_6F_5NH_2$ and pentyl nitrite [571] was a more satisfactory process for studying the orientation reactions with benzene derivatives C_6H_5X (X = Me, NO_2, Cl, Br) [571] and X = F [700]. Comparative product studies using $C_6F_5^{\bullet}$ and $Ph^{\bullet}$ in their reaction with a common substrate revealed the expected high electrophilic character of the fluorine-containing radical with nitrobenzene where substitution of the meta-hydrogen predominated (Scheme 71).

Alternative methods for generating polyfluoroaryl radicals involve the action of bleaching powder on hydrazines [98], a method also used with tetrafluoro-4-hydrazinopyridine [284]; the photochemical decomposition of iodopentafluorobenzene has also been used [79], Scheme 72.

Application of the photochemical method to *o*-$C_6F_4I_2$ in benzene gave 1,2,3,4-tetrafluorobiphenylene (**165**) among the products (Scheme 73) [701].

The thermal decomposition of C_6F_5I in carbon tetrachloride resulted in a facile abstraction of chlorine (Scheme 74) [79].

Homolytic abstraction reactions of *p*-$RC_6F_4^{\bullet}$ radicals (R = F, H, Br, MeO) with $CHCl_3$, $CBrCl_3$ and CCl_4 have been studied [702]. The yields of the products reflected the ease of removal of the atom from the carbon: Br,H > Cl (Scheme 75).

The unusual compound $C_6F_5Xe^+AsF_6^-$ (**166**), the most stable xenon compound yet prepared with a C–Xe bond, undergoes reactions which suggest the intermediacy of the radical $C_6F_5^{\bullet}$ [703]. Halides Cl^-, Br^- and I^- gave the corresponding C_6F_5Hal, but with F^-, $C_6F_5C_6F_5$ and C_6F_5H were formed. Decomposition of the salt in the presence of benzene derivatives gave mixtures of *o*-, *m*- and *p*-biphenyl derivatives (Scheme 76) [704].

Decafluorodiphenyl was formed when $C_6F_5N_2^+F^-$ was decomposed by copper bronze [233].

3.10. Substitution reactions: Ar_F–X → Ar_F–Y

3.10.1. Conversions of Ar_F–X → Ar_F–H

3.10.1.1. X = Hal, SR; Y = H

The catalytic hydrogenolysis of C–F bonds in C_6F_6 over Pd at 300°C resulted in a mixture of products, shown in Scheme 77 [705].

$$(C_6F_5CO_2)_2 \xrightarrow{C_6H_6} C_6F_5CO_2^{\bullet} \xrightarrow{-CO_2} C_6F_5^{\bullet} \xrightarrow{C_6H_6} C_6F_5Ph$$

Scheme 70.

$$Ph^{\bullet} + C_6H_5NO_2 \longrightarrow C_6H_4(NO_2)Ph\ [o\text{-}(65.5\%);\ m\text{-}(9.8\%);\ p\text{-}(27.7\%)]$$

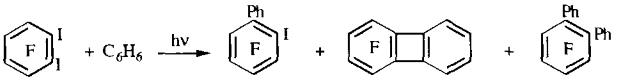
$$C_6F_5^{\bullet} + C_6H_5NO_2 \longrightarrow C_6H_4(NO_2)C_6F_5\ [o\text{-}(20.8);\ m\text{-}(53.4);\ p\text{-}(25.8)]$$

Scheme 71.

$$C_6F_5NHNH_2 \xrightarrow[C_6H_6]{Ca(OCl)_2} C_6F_5Ph\ ;\ C_6F_5I \xrightarrow[PhMe]{h\nu} C_6H_4(Me)C_6F_5$$

o-(37%); *m*-(19%); *p*-(20%)

Scheme 72.



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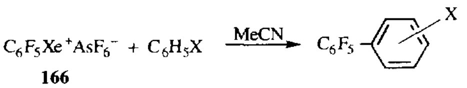
Scheme 73.

$$C_6F_5I + CCl_4 \xrightarrow{290^{\circ}} C_6F_5Cl\ (93\%)$$

Scheme 74.

$$\begin{tikzcd} C_6F_5NH_2 \arrow[r, "C_5H_{11}ONO"] & C_6F_5^{\bullet} \arrow[r, "CHCl_3"] \arrow[dr, "CBrCl_3"] & C_6F_5H\ (18\%) + C_6F_5Cl\ (0.5\%) \\ & & C_6F_5Br\ (43\%) + C_6F_5Cl\ (1.1\%) \end{tikzcd}$$

Scheme 75.



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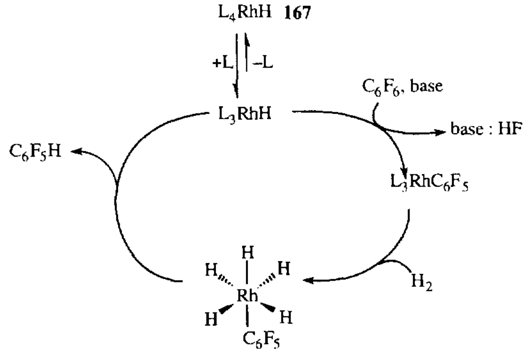
X = Me, CF_3, CN, NO_2, F

Scheme 76.

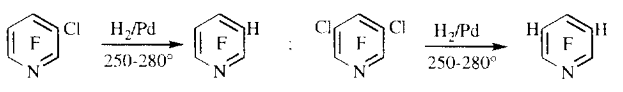
$$C_6F_6 \xrightarrow[Pd,\ 300]{H_2} C_6F_6\ (45\%) + C_6F_5H\ (40\%) + C_6F_4H_2\ (10\%) + C_6F_3H_3\ (4\%) + C_6F_2H_4\ (1\%)$$

Scheme 77.

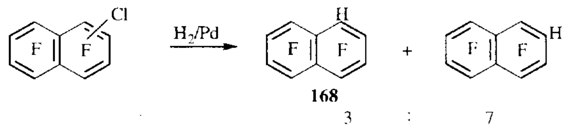


Scheme 78.

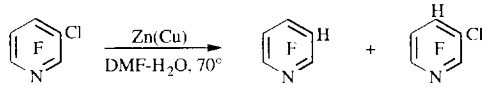
Recently, a soluble trimethylphosphine complex of rhodium, L_4RhH (L = Me_3P) (**167**), has been used to bring about the conversion of C_6F_6 to C_6F_5H at 95–100°C by reaction with hydrogen (85 psi) in the presence of Et_3N; the initial reaction involves nucleophilic displacement of fluorine by the metal (Scheme 78) [706]. Pentafluorobenzene



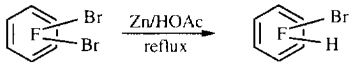
Scheme 79.



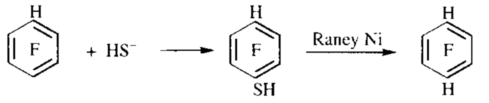
Scheme 80.



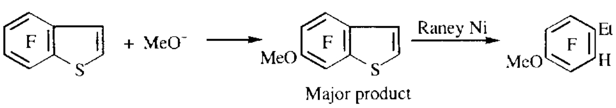
Scheme 81.



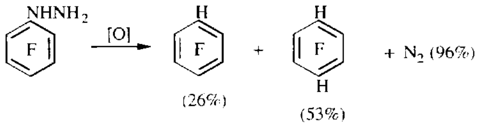
Scheme 82.



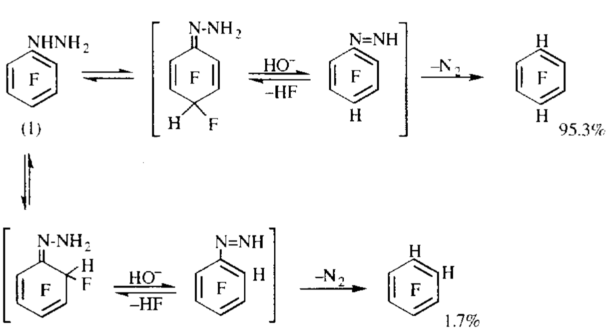
Scheme 83.



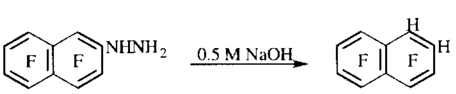
Scheme 84.



Scheme 85.



Scheme 86.



169

Scheme 87.

reacted in a similar manner to give p-$C_6F_4H_2$ as the main product.

The overall replacement of the halogen in C–Cl and C–Br bonds has been much more widely investigated. Straightforward substitutions take place using Pd–H_2 with C_6F_5Hal [707], and with polyfluorochloropyridines (Scheme 79) [659].

Catalytic hydrogenolysis of the mixture of 1- and 2-heptachloronaphthalene isomers enabled the important 1-$HC_{10}F_7$ (**168**) compound to be separated by preparative GLC (Scheme 80) [43].

Dissolving metal reductions of carbon–halogen bonds with Cu/H_2O occurred at 300°C with C_6F_5Cl and with mixtures of isomeric naphthalene derivatives $C_{10}F_7Cl$ [708]. Products arising from both C–Cl and C–F cleavage were obtained from 3-chlorotetrafluoropyridine and a zinc–copper couple in dimethylformamide–water under mild conditions (Scheme 81) [709].

The use of powdered zinc in boiling glacial acetic acid has enabled selective removal of one bromine in *o*- and *m*-$C_6F_4Br_2$ to be achieved (Scheme 82) [710].

Desulphurisation reactions with Raney nickel have played an important role in determining the orientation of fluorine replacement by sulphur nucleophiles, as shown in Scheme 83 [117], and also in reactions carried out on benzo[*b*]-thiophene derivatives (Scheme 84) [368].

3.10.1.2. $X=N_2^+$, $NHNH_2$; Y = H

Pentafluoroaniline, diazotised in 80% HF (to avoid replacement of ring fluorine), lost nitrogen as expected on treatment with H_3PO_2 to give C_6F_5H (51%) [233].

The oxidation of the tetrafluophenylhydrazine product from C_6F_5H and hydrazine with Fehling's solution to the known p-$C_6F_4H_2$ proved chemically that the fluorine para to the hydrogen in the arene had been replaced [82]. Pentafluorophenylhydrazine with Fehling's solution at 80°C gave C_6F_5H, but the major product was p-$C_6F_4H_2$ (Scheme 85) [98].

In view of the absence of C_6F_5OH in the product, the possible intermediacy of $C_6F_5^+$ was considered unlikely. The formation of p-$C_6F_4H_2$ in this reaction can be rationalised on the basis of later work carried out with the hydrazine and aqueous sodium hydroxide; the products were p-$C_6F_4H_2$ (95.3%), its ortho isomer (1.7%) and C_6F_5H (3%), the dihydro derivatives arising via quinonoid tautomerism (Scheme 86) [711].

The reaction of heptafluoro-2-naphthylhydrazine (**169**) with alkali resulted in the replacement of fluorine by hydrogen at position 1 [264] (Scheme 87).

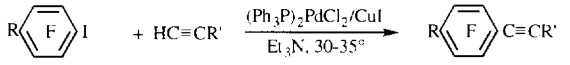
3.10.2. Other reactions

3.10.2.1. $X=N_2^+$, $NHNH_2$; Y = Cl, Br, I, N_3

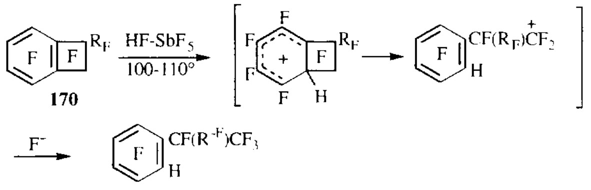
Pentafluorobenzenediazonium fluoride underwent normal Sandmeyer reactions with Cu(I)Cl and Cu(I)Br, and with KI to give the corresponding pentafluorohalogenobenzene [233]; 4-tetrafluoropyridinediazonium fluoride also gave the

$$\mathrm{Ar^FNHNH_2} \xrightarrow{\mathrm{CuY_2,\ HY}} \mathrm{Ar^F\text{-}Y} \qquad (\mathrm{Y = Cl, Br})$$

Scheme 88.



Scheme 89.



Scheme 90.

4-bromo derivatives with Cu(I)Br [289]. Diazotisation of $C_6F_5NH_2$ in trifluoroacetic acid/THF followed by treatment with sodium azide provided a convenient synthesis of $C_6F_5N_3$ [712,98].

As an alternative to the direct diazotisation of $C_6F_5NH_2$, $C_6F_5NHNH_2$ has been converted into C_6F_5Br with Br_2 [98]. Polyfluoro-aromatic or -heteroaromatic derivatives of hydrazine, in general, with copper(II) chloride or bromide, gave the corresponding chloro or bromo derivative respectively (Scheme 88) [648].

3.10.2.2. X = I; Y = R'C≡C

Convenient syntheses of polyfluoroaromatic acetylene derivatives have been reported, involving the coupling of polyfluoroiodobenzene compounds and terminal acetylenes under the influence of bis(triphenzlphosphine)palladium dichloride and copper(I) iodide in diisopropylamine [713a] or triethylamine (Scheme 89) [713b]. Two acetylenic groups have been introduced onto the aromatic ring using p-$C_6F_4Br_2$ and m-$C_6F_4I_2$ [714].

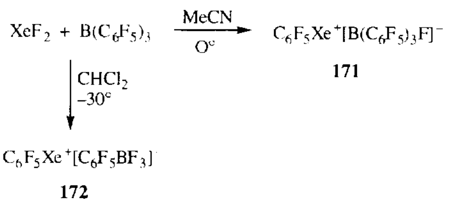
3.10.2.3. Ring-opening reaction

Perfluorobenzocyclobutenes (**170**) undergo a regiospecific ring-opening reaction under highly acidic conditions, according to the mechanism shown in Scheme 90 [715].

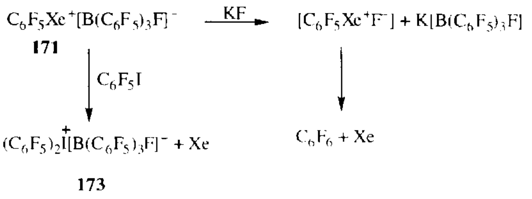
3.10.2.4. X = $(C_6F_5)_2B$; Y = $Xe^+[B(C_6F_5)_3F]^-$. X = $Xe^+[B(C_6F_5)_3F]^-$; Y = F, $C_6F_5I^+[B(C_6F_5)_3F]^-$

The first xenon compounds with a stable Xe–C bond (**171**) and (**172**) were obtained by the reactions shown in Scheme 91 [716,717].

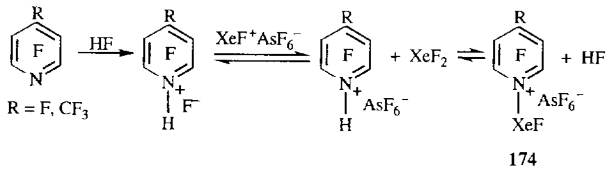
They were characterised by ^{129}Xe and ^{19}F NMR spectroscopy, and by further transformations. With potassium fluoride, hexafluorobenzene and xenon were formed from (**171**) whereas pentafluoroiodobenzene gave the novel bis(pentafluorophenyl)iodine cation (**173**) (Scheme 92) [716].



Scheme 91.



Scheme 92.



Scheme 93.

3.10.2.5. X = $SiMe_3$; Y = BrF_2, BrF_4

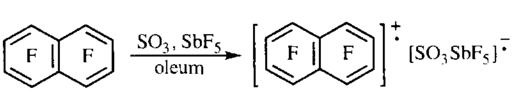
Stable high valency fluorides of bromine, $C_6F_5BrF_2$ and $C_6F_5BrF_4$ have been formed in the reactions of $C_6F_5SiMe_3$ with BrF_3 [718] and BrF_5 [719] respectively.

3.10.2.6. X = H; Y = XeF bonded to N^+

Fluoro(perfluoropyridine) xenon(II) cations (**174**) containing the novel Xe–N bond have been prepared in HF and BrF_5 solutions (stable up to −30°C) and their AsF_6^- salts isolated (Scheme 93) [720].

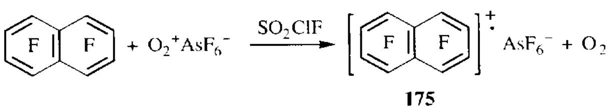
3.11. Radical cations and radical anions

Octafluoronaphthalene forms an intensely green solution when dissolved in oleum, SO_3 or SbF_5, the ESR spectrum of which characterised the presence of a radical cation (Eq. (100)) [721–723].



(100)

The hexafluoroarsenate salt (**175**), prepared by electron oxidation of $C_{10}F_8$ with $O_2{}^+AsF_6^-$, is indefinitely stable at room temperature (Eq. (101)) [724].



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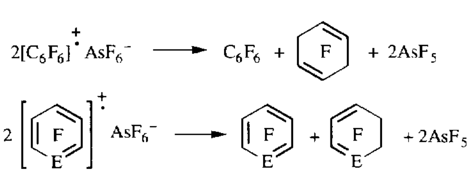
(101)

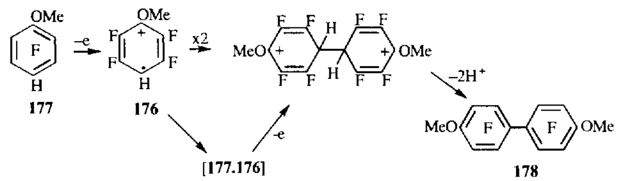
Radical cation salts, $[\mathrm{Ar_FF}]^{\cdot+}\mathrm{AsF_6^-}$, were prepared in a similar manner from C_6F_6 [724,725], $C_6F_5CF_3$ [724] and pentafluoropyridine [726]. The thermal decomposition of the monocyclic cation salts, or their reaction with F^- (CsF), gave the parent perfluorocarbon and a perfluorodiene in equimolar amounts: the 1,4-diene was produced from $C_6F_6^{\cdot+}\mathrm{AsF_6^-}$ [724], whereas 1,3-dienes resulted from $[C_6F_5CF_3]^{\cdot+}\mathrm{AsF_6^-}$ [724] and $[C_5F_5N]^{\cdot+}\mathrm{AsF_6^-}$ [726] (Scheme 94).



E = C-CF$_3$; N

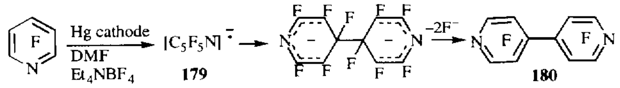
Scheme 94.

Radical cations (**176**) were generated during the anodic oxidation of the tetrafluoroanisole derivative (**177**), possible routes to the product, 4,4′-dimethoxyocta-fluorobiphenyl (**178**), being shown in Scheme 95 [727].



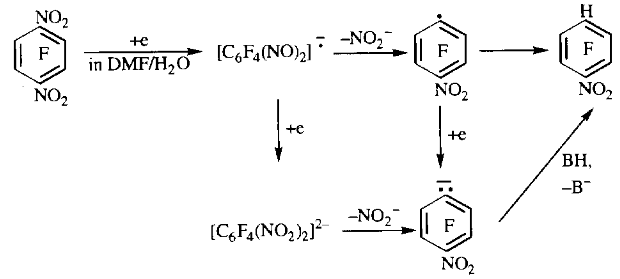
Scheme 95.

Anion radicals (**179**) have been implicated in the electrochemical reductive coupling of pentafluoropyridine to 4,4′-octafluorobipyridyl (**180**) (Scheme 96) [728].



Scheme 96.

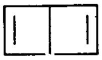
Related reductive coupling reactions of $C_6F_5NO_2$ [729,730] and C_6F_5CN [731] with the formation of the corresponding 4,4′-disubstituted octafluorobiphenyls have been studied by cyclic voltammetry and ESR spectroscopy. The selective substitution of one NO_2 by H has been observed in the electrochemical reduction of *o*-$C_6F_4(NO_2)_2$; possible mechanisms are shown in Scheme 97 [732].



Scheme 97.

3.12. Valence isomers

It is not very long ago since standard textbooks of organic chemistry discussed the historical developments which led to the current formulation of the structure of benzene [733]. Structures considered were (**181**) (Dewar benzene) and Ladenberg's prismane (**182**).



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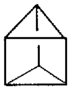

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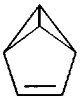
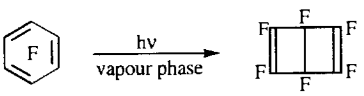


183

Derivatives of (**181**), (**182**) and another isomer (**183**) have now been isolated and characterised with fluorine and/or perfluoroalkyl groups as substituents and with analogues containing one or two nitrogen atoms. The significance of the "fluorine connection" has been discussed [734].

Irradiation of hexafluorobenzene with ultraviolet light in the vapour phase produced the first perfluoro Dewar benzene (**184**) (Eq. (102)) [735–738].



184

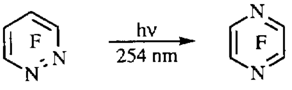
(102)

In related reactions, octafluorotoluene gave both possible para-bonded isomers [735–738] whereas, with C_6F_5X compounds (Me, CH_2F, CHF_2 and CF_3), Russian workers identified only the 2-substituted isomers [739]. Studies with the *o*-, *m*- and *p*-perfluoroxylenes have shown that of the six possible Dewar benzene structures which could have been formed, three have been fully characterised, two tentatively identified, while the 1,4-isomer was absent [740]. The formation of prismane intermediates was invoked during these interconversions.

The irradiation of perfluoro-1,3,5-trimethylbenzene (**185**) in the vapour phase led to the reversible formation of the isomeric perfluoro-1,2,4-trimethylbenzene (**186**) via two para-bonded derivatives and, central to the process, an unstable prismane (**187**) (Scheme 98) [18].

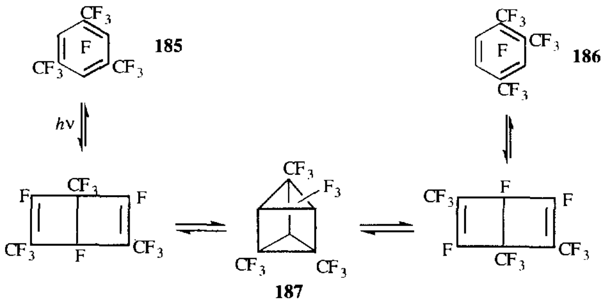
The first stable analogues of structures (**182**) and (**183**), above, as well as (**181**), arose from the irradiation of hexakis(trifluoromethylbenzene) [741].

Tetrafluoropyridazine has been converted photochemically into tetrafluoropyrazine, a formal 1,3-shift of nitrogen having taken place (Eq. (103)) [742].

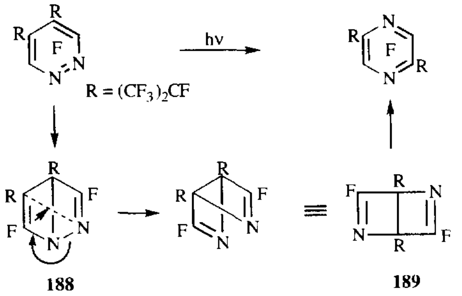


(103)

The use of polyfluoroalkyl substituents in positions 4 and 5, however, enabled a mechanistic pathway to the product, a pyrazine substituted at positions 2 and 5, to be suggested (Scheme 99) [742]. Individual para-bonded species (**188**)



Scheme 98.

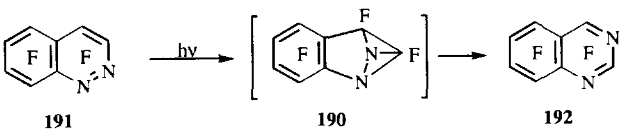


Scheme 99.

and (**189**) have been isolated in this and other cases, and converted into the next component along the reaction pathway by photo or thermal reactions [743].

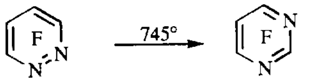
Pyridine compounds containing two different polyfluoroalkyl substituents in the ring, at sites 2, 4 and 6, and at 3 and 5, respectively, on irradiation gave a 1-azabicyclo[2.2.0] hexadiene derivative and azaprismanes, which exhibited high thermal stability [744].

A benzodiazabenzvalene derivative (**190**) has been proposed to account for the photochemical rearrangement of perfluorocinnoline (**191**) to the quinazoline (**192**) (Eq. (104)) [745].



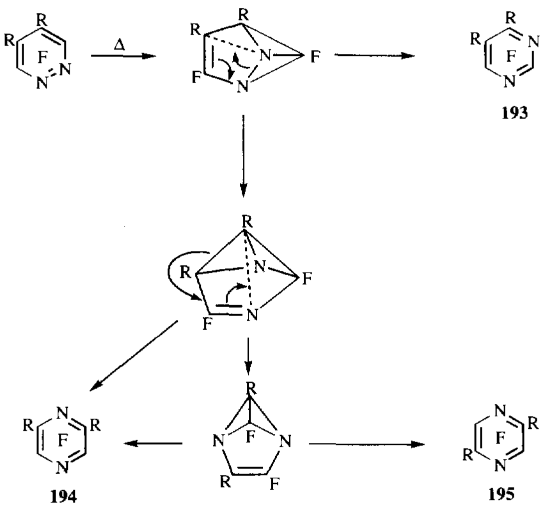
(104)

The pyrolysis of tetrafluoropyridazine gave the isomer tetrafluoropyrimidine as the major product (30%) (Eq. (105)) [746], though at 815°C, tetrafluoropyrazine was among the products.

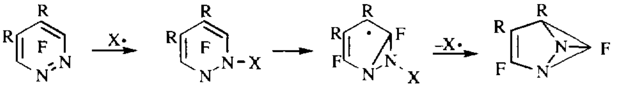


(105)

Once again, the use of 4,5-di(polyfluoroalkyl) derivatives and the orientation of the substituents in the products enabled the reaction pathway to be rationalised on the basis of the formation and rearrangement of three intermediate diazabenzvalenes (Scheme 100) [747]. For R = C_2F_5, the major component (**193**) was accompanied by a small amount of



Scheme 100.



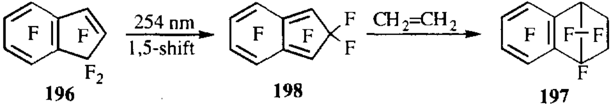
Scheme 101.

the 2,6-substituted pyrazine (**194**), whereas for R = $(CF_3)_2CF$, (**193**) is formed with a smaller amount of the 2,5-substituted pyrazine (**195**). Later studies pointed to a radical-initiated formation of the first diazobenzvalene species (Scheme 101) [748].

3.13. Photochemical reactions

3.13.1. Photoisomerisation

A major proportion of photochemical isomerisation work is covered in Section 3.12, which deals with the formation of valence isomers. A completely different type of isomerisation reaction, however, took place on irradiation of perfluoroindene (**196**) in the presence of ethylene. The final product (**197**) resulted from the cycloaddition of the alkene to perfluoroisoindene (**198**), formed via an unambiguous 1,5-sigmatropic shift of fluorine in the substrate (Eq. (106)) [749].

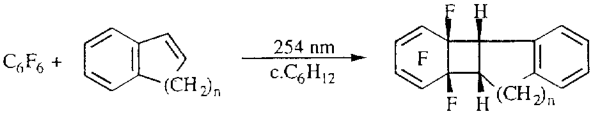


(106)

3.13.2. Photocycloaddition reactions

3.13.2.1. With alkenes

Hexafluorobenzene readily undergoes 1,2-cycloaddition reactions with alkenes upon irradiation, the stereochemistry of ring fusion being a major point of interest. In cyclohexane, reaction with cyclopentene (**199**, $n = 1$) gave predominantly the anti adduct (**200**), the syn adduct (**201**) being unstable at room temperature, the four-membered ring opening to form a cyclooctatriene derivative (**202**) (Scheme 102) [750]. Increasing the ring size of the cycloalkene, however, decreased the proportion of anti adduct in the product, with only 53% being formed with cyclooctene ($n=4$) [751a]. Photoreactions with indene and 1,2-dihydronaphthalene occurred stereospecifically syn to give stable adducts (**203**) (Eq. (107)) ($n=1,2$) [751b].



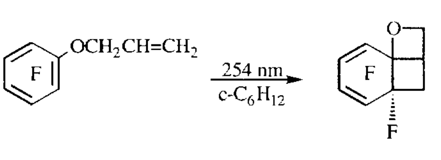
203

(107)

The general outcome of reactions with norbornene [751a], norbornadiene [752] and benzonorbornadiene [753–756] was for exclusive exo attack to take place, giving stable anti[2+2] adducts and products resulting from the ring-opening reactions of unstable syn[2+2] adducts, i.e. eight-membered ring compounds, analogous to that shown in Scheme 102. In the absence of solvent, irradiation of C_6F_6 and *cis*-cyclooctene gave a mixture of 1:1 addition products which arose via both 1,2- and 1,3-addition processes and subsequent isomerisations of the initial adducts [757]. Scheme 103 shows the 1,3-adduct (**204**) which was formed, together with the product of its conversion to (**205**) via the thermally allowed 1,5-hydrogen shift.

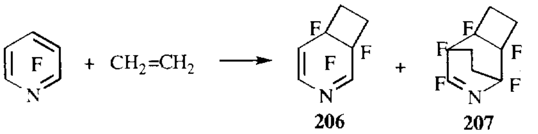
Photoreactions of the ethers C_6F_5OR ($R=Me, Et, Pr^i, Bu^t$) presented both stereochemical and regioselectivity problems in [2+2] cycloaddition reactions with cycloalkenes [758]. Addition to the 3,4-positions in the arene took place, irrespective of the size of the group R, and irrespective of the initial stereochemistry of the adducts (anti with cyclopentene and syn and anti with cycloheptene and cyclooctane); ring closure in the six-membered ring always followed (Scheme 104).

An intramolecular [2+2] cycloaddition reaction involving the 1,2-positions in the ring occurred on irradiation of pentafluorophenyl prop-2-enyl ether [759] (Eq. (108)).



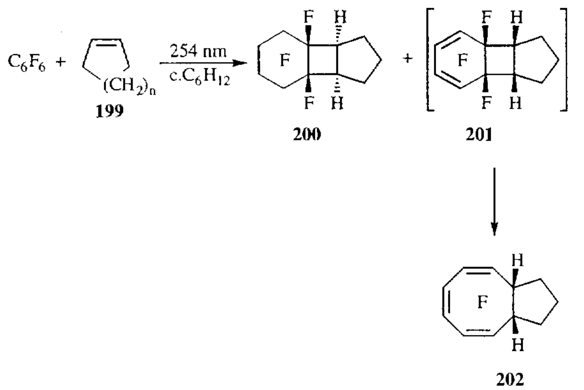
(108)

Pentafluoropyridine has been reacted photochemically with ethylene to give a 1:1 adduct (**206**) via a [2+2] cycloaddition to the 3,4-position in the ring, and a 1:2 adduct (**207**) by a slow thermal [4+2] addition of ethylene to (**206**) (Eq. (109)) [760].

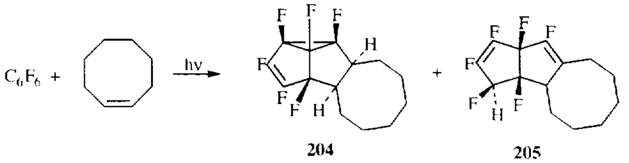


206 **207**

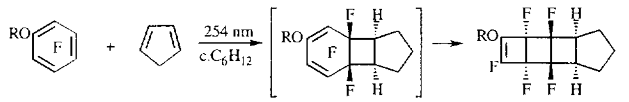
(109)



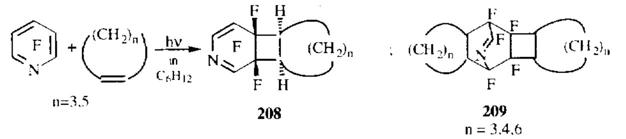
Scheme 102.



Scheme 103.



Scheme 104.



Scheme 105.

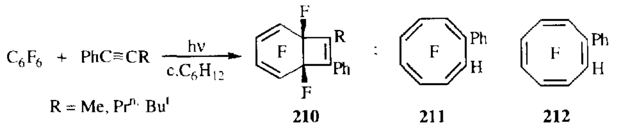
Cyclopentene and cycloheptene in cyclohexane gave only the 1:1 adducts (**208**) with C_5F_5N [761], but in the absence of solvents, 1:2 adducts (**209**) were obtained for the alkenes shown in Scheme 105 [762].

The photochemical reaction of 3-chlorotetrafluoropyridine with ethylene proceeded via an insertion reaction to give the 3-CH_2CH_2Cl derivative, whereas with cyclo-pentene and -hexene, 3-cycloalkyltetrafluoropyridines were formed [763].

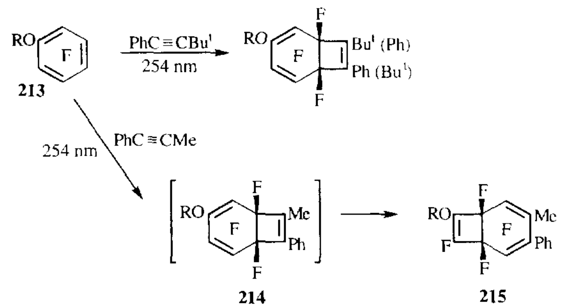
3.13.2.2. With alkynes

Irradiation of solutions of C_6F_6 and 1-phenyl-2-alkylethyne in cyclohexane resulted in the formation of the [2+2] addition product (**210**), but with phenylethyne, only the ring-opened products, the isomeric cyclooctatrienes (**211**) and (**212**), were formed (Scheme 106) [764].

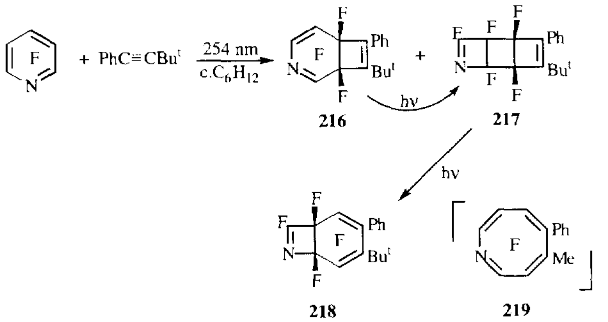
Regiospecific photo-addition of 1-phenyl-2-alkylethyne to positions 3 and 4 in the ethers C_6F_5OR ($R=Me, Et, Pr^i$) (**213**) in cyclohexane gave products which depended only on the alkyl group in the ethyne derivative (Scheme 107) [764].



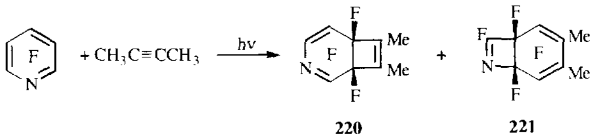
Scheme 106.



Scheme 107.



Scheme 108.



Scheme 109.

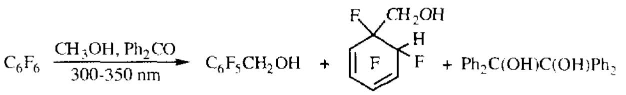
In the reaction involving 1-phenylpropyne, the presumed intermediate (**214**) was not detected during the formation of (**215**).

Pentafluoropyridine reacted regiospecifically at positions 3 and 4 with 1-phenyl-2-*t*-butylethyne to give three products; (**216**), (**217**) and (**218**) (Scheme 108) [765].

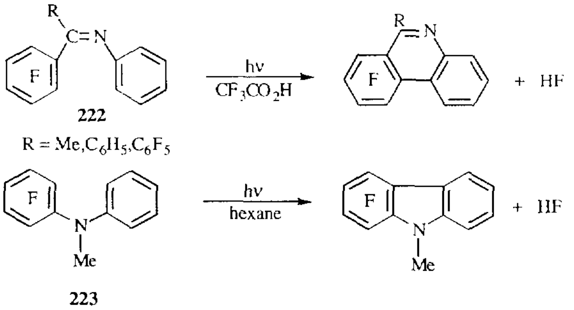
The related reaction using 1-phenylpropyne also gave three products, two of which were the Me analogues of (**216**) and (**217**), but the third product was (**219**). Earlier work with pentafluoropyridine and but-2-yne gave two 1:1 regiospecific products (**220**) and (**221**), related via ring-opened azacyclooctatetraenes analogous to (**219**) Scheme 109 [766].

3.13.3. Photosubstitution reactions

Hexafluorobenzene has been irradiated in methanol in the presence of benzophenone to give products which showed that a radical reaction had taken place (Scheme 110) [589]. Other examples of photosubstitution reactions are presented in Tables 9 and 10.



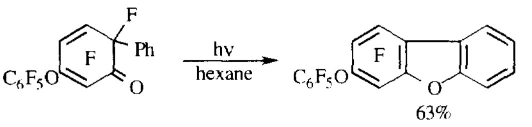
Scheme 110.



Scheme 111.

Photo-induced cyclisations of the Schiff's bases (**222**) in trifluoroacetic acid [767] and of diarylamines (**223**) in hexane [543], by loss of HF, provided novel routes to heterocyclic systems (Scheme 111).

Aromatisation of 2,4-cyclohexadienone ring systems bearing a 6-aryl substituent has been shown to occur on irradiation, with the formation of dibenzo[*b*]furan derivatives, one example of which is shown in Eq. (110) [768].

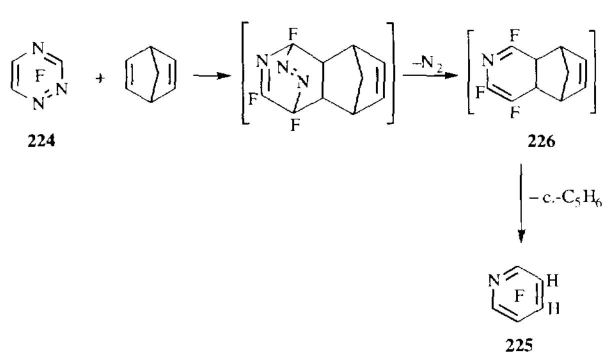


(110)

3.14. Polyfluoroheteroaromatic compounds as diene sources

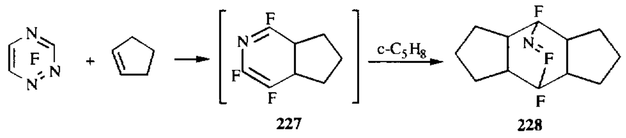
Trifluoro-1,2,4-triazine (**224**) has been reacted with bicyclo[2.2.1]hepta-2,5-diene to give 2,3,6-trifluoropyridine (**225**) [769]. The course of the reaction was interpreted in terms of an initial regiospecific [4+2] cycloaddition to the triazine, loss of nitrogen to give the dihydropyridine derivative (**226**), followed by a second retro-Diels–Alder reaction (Scheme 112).

However, the intermediate dihydropyridine derivative (**227**) formed from the triazine and cyclopentene reacted



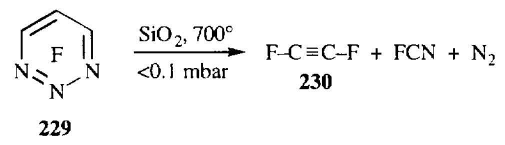
Scheme 112.

further with the alkene to produce the tetracyclic compound **228** (Scheme 113) [769]; *Z*-cyclooctene and bicyclo-[2.2.1]hept-2-ene reacted similarly.



Scheme 113.

The vacuum pyrolysis of trifluoro-1,2,3-triazine (**229**) resulted in the first synthesis of pure difluoroacetylene (**230**), which was characterised by ^{19}F NMR and gas-phase IR spectroscopy (Scheme 114) [770].

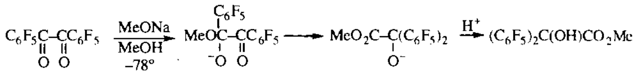


Scheme 114.

3.15. Rearrangement reactions

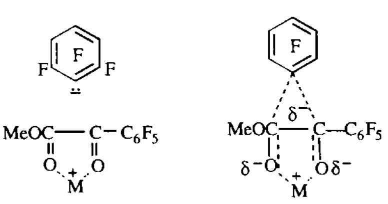
3.15.1. Benzil–benzilic ester rearrangement

The perfluoro equivalent of this reaction is shown in Scheme 115 [651]. What is remarkable about the rearrangement is the speed with which it takes place compared with that of benzil, which required reflux in methanol (64°C) to achieve the analogous transformation. A transition state involving a tight ion pair where the fluorines ortho to the charge in the pentafluorophenyl anion exercise a powerful stabilising effect, or even partial charge localisation on the aryl group (Scheme 116), has been proposed to account for the enormous activity of the system, estimated as ≥ 10^5 compared with the all-hydrogen case.



$C_6F_5C(O)C(O)C_6F_5 \xrightarrow[\text{MeOH, }-78^\circ]{\text{MeONa}} MeOC(O^-)(C_6F_5)C(O)C_6F_5 \longrightarrow MeO_2C\text{–}C(C_6F_5)_2O^- \xrightarrow{H^+} (C_6F_5)_2C(OH)CO_2Me$

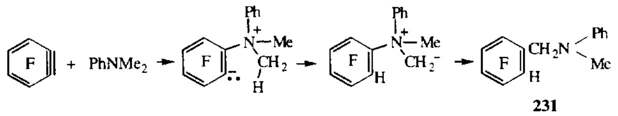
Scheme 115.



Scheme 116.

3.15.2. Stevens rearrangement

The first example ever recorded of an aryl group migrating in a Stevens rearrangement reaction has involved a tetrafluorophenyl group, and accounted for the formation of one of the products (**231**) (13%) found in decomposition of pentafluorophenyllithium in ether (tetrafluorobenzyne formation) in the presence of excess dimethylaniline (Scheme 117) [771,494b].



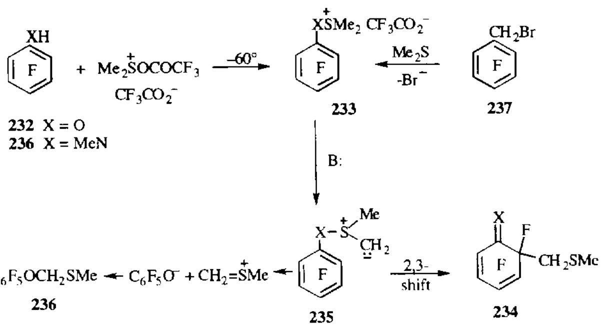
Scheme 117.

3.15.3. Smiles rearrangement

This rearrangement, found to take place during the synthesis of polyfluorophenoxazines using nucleophilic replacement of fluorine by nitrogen as the intended ring closure reaction, is discussed in Section 3.2.1.2.

3.15.4. Sommelet–Hauser rearrangements (2,3-sigmatropic reactions)

Treatment of dimethyl sulphoxide with trifluoroacetic anhydride at −60°C followed by pentafluorophenol (**232**) gave the salt (**233**), which with triethylamine (B:) rearranged to the dienone (**234**) (69%) via the intermediate ylide (**235**), the fluorine at position 2 in (**234**) preventing rearomatisation (Scheme 118) [772]; a small amount of the ether (**236**) was formed concurrently. Other phenolic compounds participating in the rearrangement included heptafluoro-2-naphthol, 2- and 3-OH derivatives of polyhalogenated pyridines (but not tetrafluoropyridine-4-ol) and trifluoropyrimid-4-ol [772]. In cases involving other C_6F_5X compounds, the ylides (**235**) containing a nitrogen atom (from 2,3,4,5,6-pentafluoro-*N*-methylaniline (**236**)) and a carbon atom (from 2,3,4,5,6-pentafluorobenzyl bromide (**237**)) bonded to the aromatic ring, rearranged smoothly under mild conditions to give products which underwent further reactions [773].



Scheme 118.

It is noteworthy that C_6Cl_5OH failed to undergo 2,3-rearrangements of the type reported above [624].

3.15.5. 3,3-Sigmatropic reactions

The action of heat on a wide variety of prop-2-enyl and prop-2-ynyl ethers (Claisen rearrangements) has proved to be a fruitful area of polyfluoro-aromatic and -heteroaromatic chemistry giving, in some cases, products which had no analogues in the hydrocarbon field.

Simple Claisen rearrangement products were isolated from the 1-prop-2-enyl ether of the isoquinoline (**238**) [774]; from the 2-prop-2-enyl ethers of the naphthalene (**239**) [775] and the quinoline (**240**) [774]; and from the 4-prop-2-enyl ethers of the quinoline (**241**) [774] and the pyrimidine (**242**) [776] (Scheme 119).

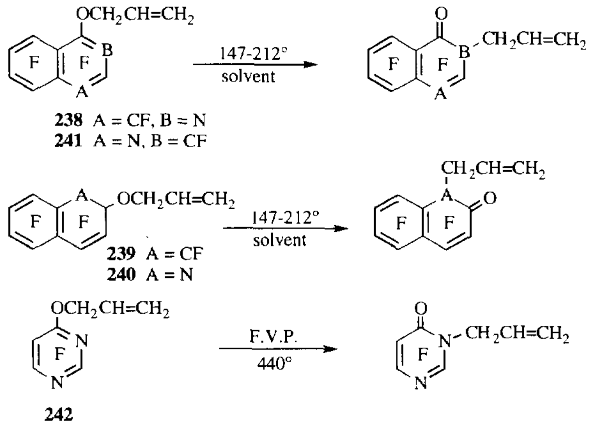
Flash vapour-phase pyrolyses of the pentafluorophenyl ethers (**243**) and (**244**) at 310–365°C resulted in the formation of the 2,5-cyclohexadienone derivatives (**245**) [777] and (**246**) [778] respectively, via a Claisen followed by a Cope rearrangement, whereas at higher temperatures (410–480°C), isomerisations also occurred via the corresponding internal Diels–Alder intermediates (**247**) to the bicyclic compounds (**248**) [779] and (**249**) [778] respectively (Scheme 120).

Also isolated from FVP reactions of (**250**) and (**251**) carried out at the higher temperatures were the 1-fluorovinyl ketones (**252**) [780] and (**253**) [778], formed via the other structurally possible internal Diels–Alder adduct (**254**) (Scheme 121). Thermolysis reactions carried out with (**250**) and (**251**) under milder conditions at 137–160°C in the vapour phase for 13–15 days resulted in the formation of (**255**) and (**256**), compounds which possess a plane of symmetry (Scheme 121) [781]. The actual internal Diels–Alder adduct (**254**, R = H) implicated in the transformation with (**250**) was later isolated [782]. Nitrogen-containing analogues of (**254**) were the sole tricyclic products obtained from similar reactions with ethers of tetrafluoropyridin-3-ol (**257**) and -4-ol (**258**) [783].

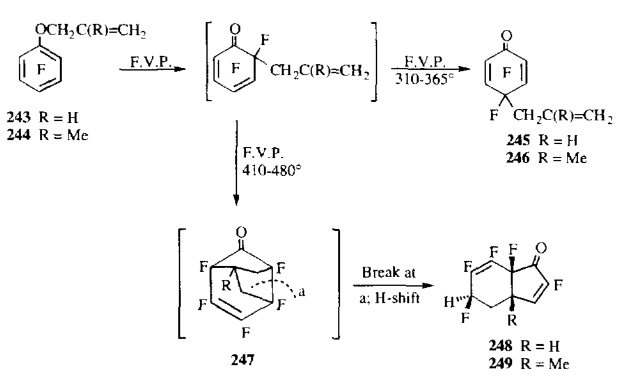
The course of the thermolysis reactions of prop-2-enyl ethers (**259**), (**260**) and (**261**) was altered by the introduction of KF into the system carried out in refluxing dimethylformamide (Scheme 122) [784]. Dehydrofluorination of the rearranged material occurred to form (**262**) which electrocyclised to the corresponding fused 2-*H*-pyran derivatives (**263**).

Thermally induced reactions of pentafluorophenyl prop-2-enyl sulphide (**264**) [785] and heptafluoro-2-naphthylprop-2-enyl sulphide (**265**) [786] gave heterocycles (in very low yield from (**264**)) via an initial thio-Claisen rearrangement (Scheme 123). There was evidence to suggest that the solvent played a vital role in bringing about the reduction of the rearranged materials (**266**) to compounds (**267**) which aromatised and cyclised to the five- (**268**) and six-membered rings (**269**) as shown.

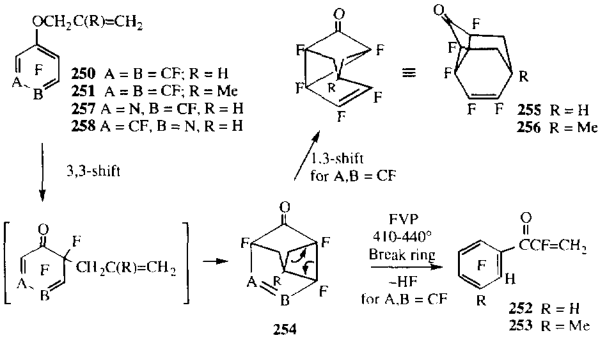
Prop-2-ynyl ethers (**270**) and (**271**) and sulphides (**272**) and (**273**) of polyfluoroaromatic compounds were converted to benzo- and naphtho[*b*]furan and benzo- and naphtho[*b*]thiophene derivatives, respectively, on thermol-



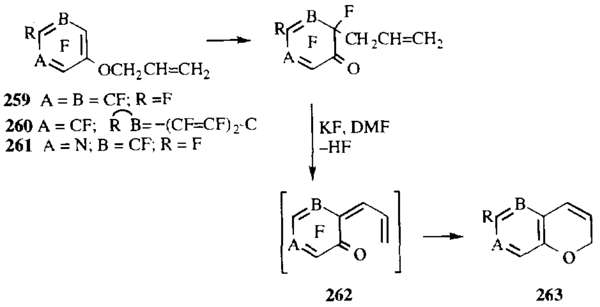
Scheme 119.



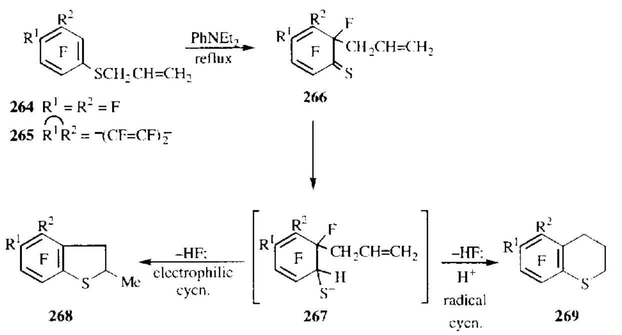
Scheme 120.



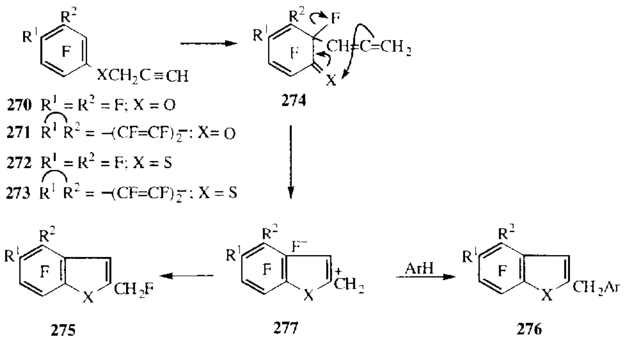
Scheme 121.



Scheme 122.

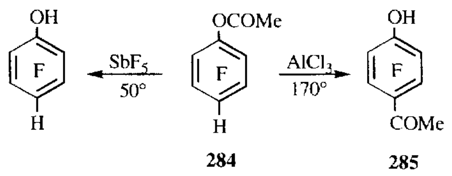


Scheme 123.



Scheme 124.

ysis (Scheme 124). In one case, from heptafluoro-2-naphthyl prop-2-ynyl ether (**271**) the simple rearranged compound (**274**) was obtained [787]. Isomerisations to 2-fluoromethyl derivatives (**275**) (X=O, [788–790]; X=S, [791]) have been carried out under both FVP conditions and in $CF_2ClCFCl_2$ as solvent in nickel apparatus. Reactions of the ethers and sulphides in aromatic solvents gave the 2-benzyl derivatives (**276**) [788,791] respectively. The ethers were also reacted with alkenes to give substitution products [789]. A mechanism involving a tight ion pair (**277**) was proposed for the course of these reactions, which accounted for the high yields of isomerised products (**275**) in the vapour phase reactions, where the fluorine undertakes an overall 1,4-shift [791].



Scheme 126.

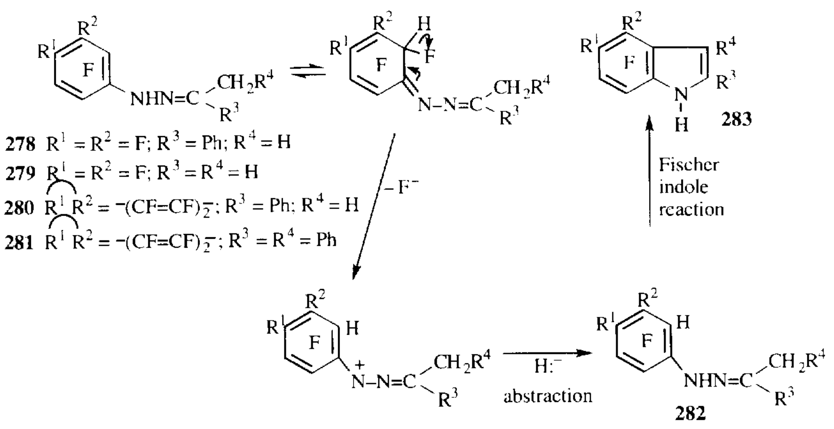
The Fischer indole synthesis, which proceeds via a 3,3-sigmatropic shift of the tautomeric enehydrazine, has been accomplished with a variety of pentafluoro- (**278**, **279**) and heptafluoro-2-naphthylhydrazones (**280**, **281**) [792,793] even though fluorine is present in both sites ortho to the nitrogen. The isolation of the *ortho*-hydrogen compound (**282**) (3%) along with the indole (**283**) from the reaction with acetophenone heptafluoro-2-naphthylhydrazone (**280**) provided the clue to the mechanism of these unexpected reactions (Scheme 125) [794]. The ring-closing reaction was, therefore, a conventional Fischer indole synthesis on a substrate with an *ortho*-hydrogen, formed by the process shown (see Section 3.10.2 for another ring–side-chain tautomerism reaction).

3.15.6. The Fries rearrangement

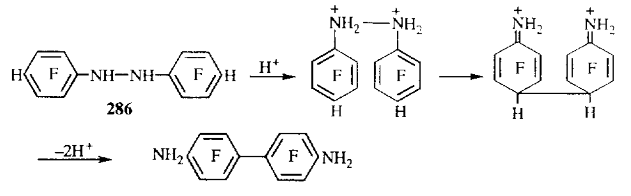
One example of this reaction has been mentioned in a review [523]: the conversion of 2,3,5,6-tetrafluorophenyl acetate (**284**) to 4-hydroxy-2,3,5,6-tetrafluoroacetophenone (**285**) using $AlCl_3$; no ketone was formed with SbF_5 (Scheme 126).

3.15.7. The benzidine rearrangement

The treatment of 2,2′,3,3′,5,5′,6,6′-octafluorohydrazobenzene (**286**) with strong acids resulted in its conversion into 4,4′-diaminooctafluorobiphenyl (**287**) (Scheme 127) [795], along with products of disproportionation, 2,2′,3,3′,5,5′,6,6′-octafluoroazobenzene and 2,3,5,6-tetrafluoroaniline, the experimental conditions influencing the relative incidence of the two processes. The acid systems



Scheme 125.

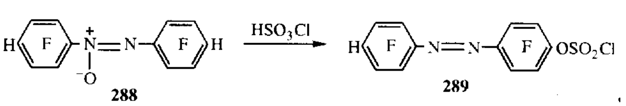


Scheme 127.

HF–SbF_5 (1:1) and HSO_3F–SbF_5 (1:1) were used in these investigations.

3.15.8. The Wallach rearrangement

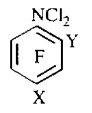
Chlorosulphonic acid promoted the conversion of 2,2′,3,3′,5,5′,6,6′-octafluoroazoxybenzene (**288**) to 2,2′,3,3′,5,5′,6,6′-octafluorobenzene 4-chlorosulphonate (**289**) (Eq. (111)) [796].



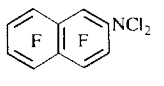
(111)

3.15.9. Isomerisation reactions of N,N-dichloramines

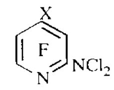
Stable *N,N*-dichloramines of polyfluorobenzenes (**290**) [797], (**291**) [798], (**292–295**) [799], polyfluoronaphthalene (**296**) [800], polyfluoropyridines (**297–299**) [801] and pentafluoro-*N*-chloro-*N*-methylamine (**300**) [799], prepared from the corresponding amino compounds with *t*-butyl hypochlorite, have been isomerised on treatment with a crystal of iodine (Scheme 128).



290 X = Y = F
291 X = H, Y = F
292 X = CF_3, Y = F
293 X, Ph, Y = F
294 X = F, Y = Cl
295 X = Cl, Y = F



296



297 X = H
298 X = Cl
299 X = $(CF_3)_2CF$

300

The mechanism proposed to explain the isomerisation is shown in Scheme 129.

N,N-Dichloropentafluoroaniline (**290**) has also been isomerised under acidic conditions which allowed an intermediate (**301**) to be purified (Scheme 130) [802].

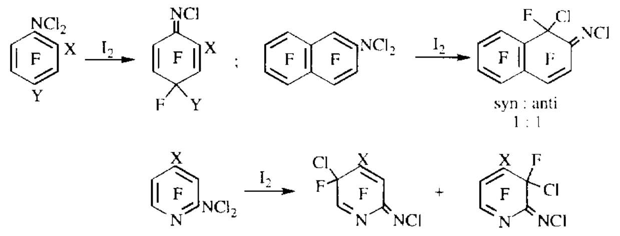
The dichloronaphthylideneamine (**302**) was speculated to be a precursor to the nitrene (**303**) since it was converted by a ring-contraction process to the 2-cyanoindene derivative (**304**) (45%) on flow pyrolysis, and the same product was obtained in low yield (5%) from 2-azidoheptafluoronaphthalene (**305**) (Scheme 131) [803].

3.15.10. A rearrangement via an internal Diels–Alder/retro-Diels–Alder reaction

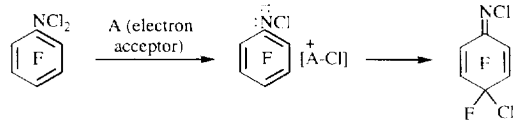
Heptafluoro-2-naphthyl propynoate (**306**) reacted quite differently from pentafluorophenyl propynoate [631] (see Section 3.6.2.4) on flash vacuum pyrolysis [804]. The products (**307**), (**308**) and (**309**) were accounted for via the formation of initial Diels–Alder adducts (**310**) and (**311**) followed by a retro-Diels–Alder reaction to give the isomer (**312**), which in turn cyclised and decarbonylated (Scheme 132).

3.16. Reactions with oxidising agents

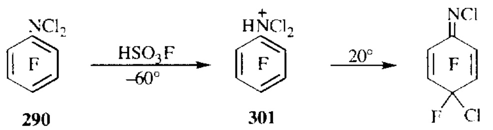
Pentafluorophenol (**313**) is oxidised by lead tetraacetate in ether to a mixture of two compounds (**314**) and (**315**) in the ratio 1:2 respectively (Scheme 133) [805], whereas the derivatives (**316**) gave only the conjugated dienones (**315**) [806]. Using lead dioxide as oxidant, C_6F_5OH was again converted to (**314**) and (**315**) together with a third component (**317**) [805]. These processes were interpreted in terms



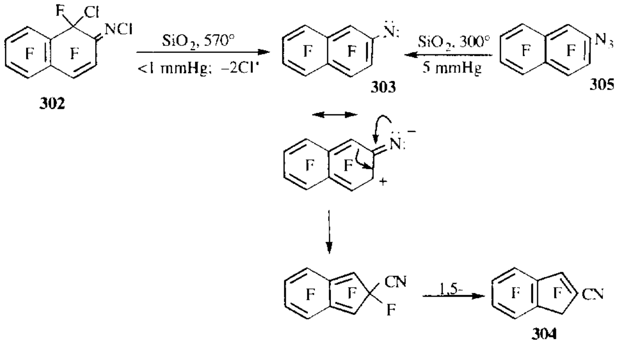
Scheme 128.



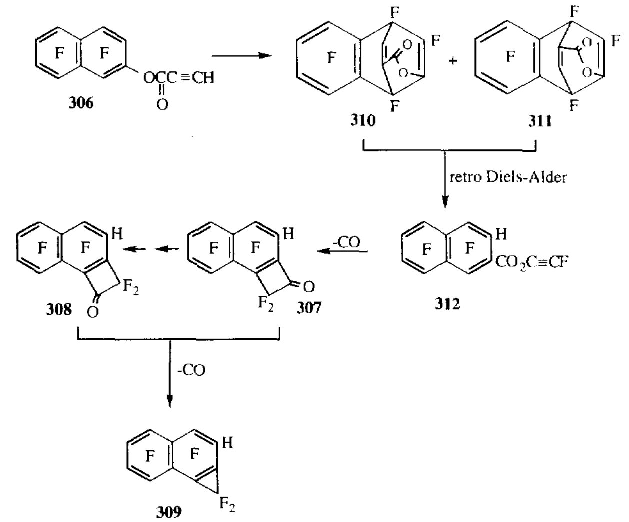
Scheme 129.



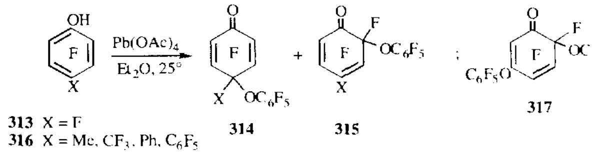
Scheme 130.



Scheme 131.



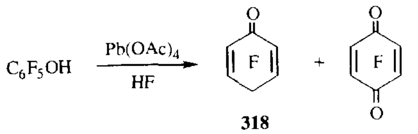
Scheme 132.



Scheme 133.

$$C_6F_5OH \xrightarrow[\text{or } PbO_2]{Pb(OAc)_4} C_6F_5O^{\bullet} \xrightarrow{x2} \underset{(X = F)}{314 + 315} \xrightarrow{C_6F_5OH} 317$$

Scheme 134.

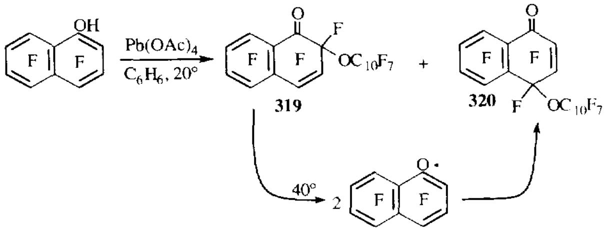


Scheme 135.

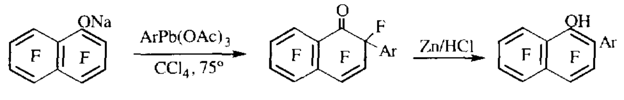
of initial free radical dimerisations of $C_6F_5O^{\bullet}$ and facile nucleophilic displacement of fluorine at position 3 in compound (**315**) (Scheme 134). When the oxidation with lead tetra-acetate was carried out in anhydrous HF, the radical dimers (**314**) and (**315**) were not formed: the 2,5-cyclohexadienone (**318**) was the main product, which suggested that an ionic mechanism had operated (Scheme 135) [807]. Related oxidations of heptafluoro-1- and -2-naphthols with $Pb(OAc)_4$ in benzene have also been investigated [808]. Two dimers from the 1-ol were identified, (**319**) and (**320**), compound (**319**) being isomerised to the thermodynamically more stable compound (**320**) under very mild conditions (Scheme 136).

Lead aryl triacetate brought about selective ortho-arylation of the sodium salts of pentafluorophenol and heptafluoro-1- and -2-naphthol [809]. The simplest of the reactions is shown in Scheme 137 with the 1-naphthoxide, along with a re-aromatisation process.

The electrochemical oxidation of C_6F_5OH in SbF_5/HF gave the radical dimer (**314**, X = F) and the 2,5-dienone (**318**) [810]. Peracetic acid converted C_6F_5OH to difluoromaleic acid at 80°C [811a]; the 1- and 2-naphthols $C_{10}F_7OH$, however, gave 1,4- and 1,2-diones respectively, among the products of their oxidation [811b]. Compound (**320**) was also formed from the 1-ol, and was accompanied by tetrafluorophthalic acid (the result of the rupture of the HO-substituted ring) and difluoromaleic acid from the overall breaking of both rings.



Scheme 136.



(Ar = Ph, p-MeC_6H_4, p-$MeOC_6H_4$)

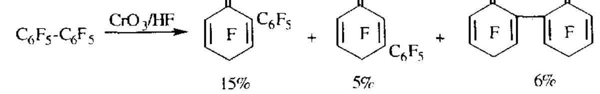
Scheme 137.

2,5-Cyclohexadienone derivatives were produced by the oxidation of perfluoroarenes with CrO_3/HF [812]. Scheme 138 shows the oxidation of decafluorobiphenyl.

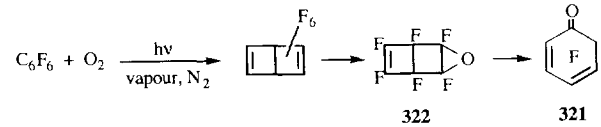
Hexafluorobenzene has been oxidised by 90% H_2O_2 to C_6F_5OH [610] (Section 3.5).

Ultraviolet irradiation ($\lambda > 200$ nm) of a gaseous mixture of C_6F_6, N_2 and O_2 is of interest since it led to the synthesis of hexafluorocyclohexa-2,4-dienone (**321**) [813]. Hexafluoro-Dewar-benzene was formed rapidly and was then converted slowly into the oxirane (**322**). When heated at 50°C over 7 days, compound (**322**) gave the 2,4-dienone (**321**) (Scheme 139). The oxirane (**322**) is a potential source of hexafluorobenzene oxide (**323**) which was prepared by a different route from C_6F_6 and shown to rearrange spontaneously to the dienone (**321**) in acetonitrile or acetone (Scheme 140) [63].

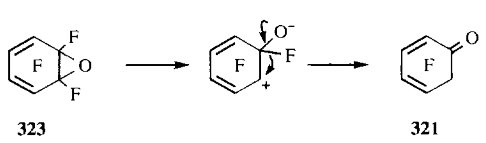
Heptafluoroquinoline (**324**) has been oxidised by 98% HNO_3 under different conditions to compound (**325**), the quinone (**326**) and the dicarboxylic acid (**327**) (Scheme 141) [814].



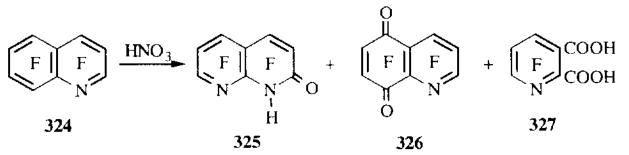
Scheme 138.



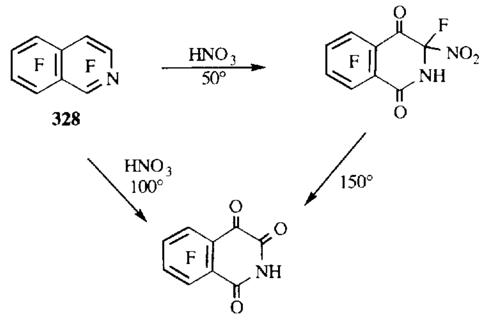
Scheme 139.



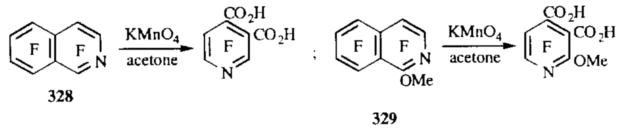
Scheme 140.



Scheme 141.



Scheme 142.



Scheme 143.

The analogous reaction with heptafluoroisoquinoline (**328**) at 50°C resulted from ipso attack by NO_2^+ at position 3 which was retained in the product, whereas further transformations occurred at higher temperatures (Scheme 142) [815].

Destruction of the benzenoid ring in the isoquinoline compounds (**328**) and (**329**) by potassium permanganate in acetone facilitated the determination of the site of substitution of fluorine by methoxide in heptafluoroisoquinoline (Scheme 143) [349].

3.17. Fluorination reactions

3.17.1. Use of fluorine

Hexafluorobenzene reacted smoothly in the liquid phase at 0°C with a mixture of fluorine and nitrogen (1:10) to give a mixture of products (Scheme 144) [816].

Reaction of fluorine with pentafluoropyridine took place at 40–100°C, with 1,3- and 1,4-azadienes being formed among the products (Scheme 145) [817]. Perfluoro-4-isopropylpyridine was converted in a similar way to perfluoro-1-aza-4-isopropylcyclohexa-1,3-diene [818].

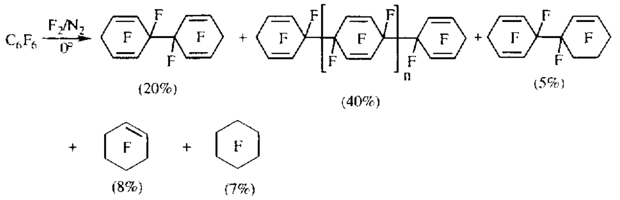
The formation of the dimeric compound (**330**) in the reaction with perfluoropyrimidine indicated the radical nature of the process (Scheme 146) [818].

3.17.2. Use of cobalt(III) fluoride with or without calcium fluoride

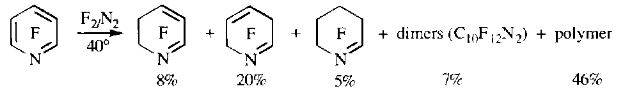
This fluorinating agent has enabled various degrees of unsaturation to be retained in the products, in a transformation which proceeded as shown in Scheme 147 for hexafluorobenzene [248,819]. The cyclic products obtained from the fluorination of penta- and polyfluorochloro-pyridines [819], as well as with $(CF_3)_2CF$ derivatives [818], are shown in Table 17.

Perfluoropyrimidine gave a dimer (**331a** or **331b**), whereas the 1,3-diene (**332**) was formed from perfluoropyrazine (Scheme 148) [819].

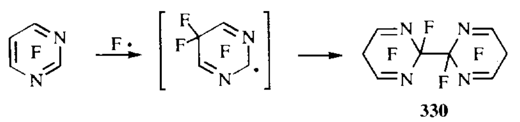
The fluorination of both perfluoro(4,6-diisopropylpyrimidine) (**333**) and perfluoro(2,5-diisopropylpyrazine) (**334**)



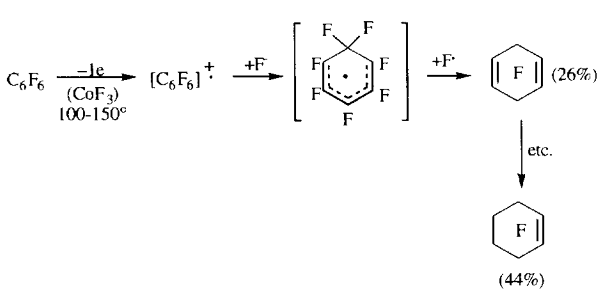
Scheme 144.



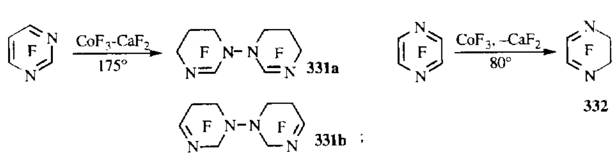
Scheme 145.



Scheme 146.

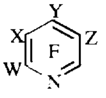
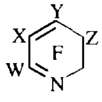
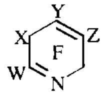
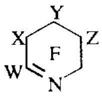
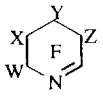


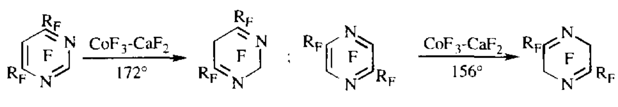
Scheme 147.



Scheme 148.

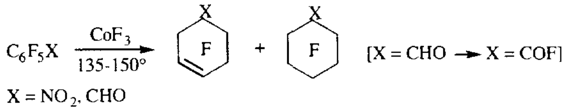
Table 17
Cyclic products from the fluorination of polyhalopyridines with CoF_3

Starting material	Products			
				
W,X,Y,Z = F	–	–	✓	–
X = Cl, W,Y,Z = F	–	–	✓	✓
W,X,Z = F, Y = Cl	✓	trace	✓	–
X,Y = Cl, W,Z = F	✓	–	✓	✓
X,Z = Cl, W,Y = F	–	–	✓	–
W,X,Z = F, Y = $(CF_3)_2CF$	60%	18%	–	–
W,Y = $(CF_3)_2CF$, X,Z = F	26%	26%	45%	–



333 83% 334 87%

Scheme 149.



Scheme 150.

gave high yields of 1,4-dienes (Scheme 149) (R^F = $(CF_3)_2CF$) [818]. No cyclic products were obtained from reactions with perfluoro(4,5- and 3,6-diisopropylpyridines [818].

The nitro group in pentafluoronitrobenzene survived the reaction with CoF_3, but the aldehyde functionality in pentafluorobenzaldehyde was transformed into acid fluoride (Scheme 150) [820].

3.17.3. Use of antimony pentafluoride, vanadium pentafluoride, xenon difluoride and bromine trifluoride

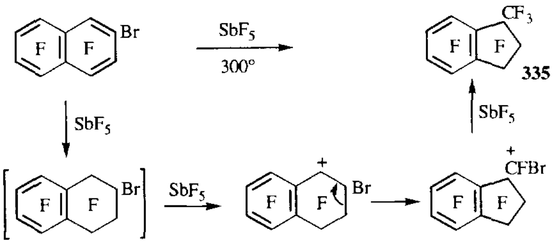
These four reagents have been used under a variety of conditions to bring about the overall addition of two fluorine atoms to unsaturated bonds in polyfluoro-aromatic or -heteroaromatic ring systems, the results of which are shown for monocyclic ring systems in Table 18 and for polyfluoronaphthalenes in Table 19. In many cases, fluorine first adds to give 1,4 dienes with the substituent group X on the 1-position. This was the case with BrF_3/Br_2 with substrates having electron-withdrawing substituents, though products with the substituent at the 3-position were found if it was electron donating [821].

It is known that SbF_5 interacts with polyfluoroaromatic compounds to give radical cations [721,722,822,823] and a similar situation exists using XeF_2/catalyst [824]. Radical cations from octafluoronaphthalene with BrF_3 (and ClF_3) have been detected by ESR studies [825] and have been suggested as key intermediates during the fluorination process [821]. The fluorination mechanism with vanadium pentafluoride remains even less clear, though a radical mechanism was considered unlikely [826].

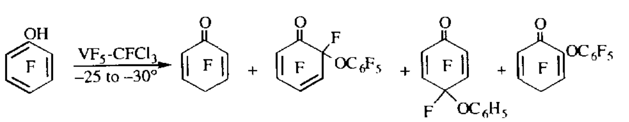
The 1-trifluoromethylindane derivative (**335**) was formed via a ring-contraction process during the fluorination of 2-bromoheptafluoronaphthalene with SbF_5 (Scheme 151) [827,828].

Pentafluorophenol has been converted by SbF_5 into perfluoro-2-cyclohexen-1-one [829], whereas reaction with vanadium pentafluoride took place under very mild conditions to give a complex product (Scheme 152) [830].

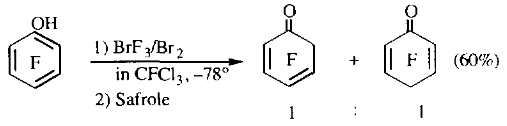
Perfluoro-2,4- and -2,5-cyclohexadienones were formed in equimolar amounts on fluorination of C_6F_5OH with BrF_3/Br_2 at low temperature and quenching the mixture with safrole (Scheme 153) [831]; CF_3OF also gave the same fluorination products, though less efficiently [831].



Scheme 151.



Scheme 152.



Scheme 153.

Table 18
Fluorination of monocyclic polyfluoroaryl compounds

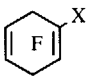
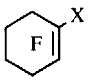
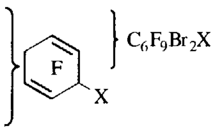
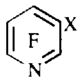
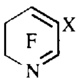
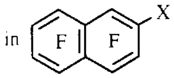
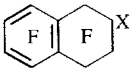
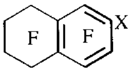
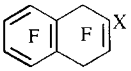
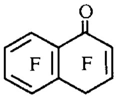
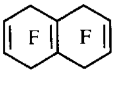
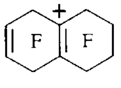
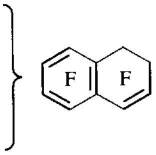
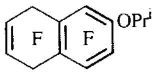
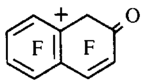
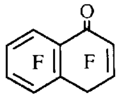
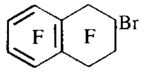
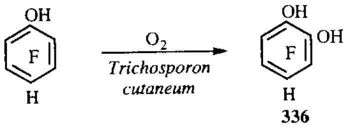
Substituent X in C_6F_5X	Fluorinating agent	Products		Other	Ref.
					
F	SbF_5, 140°C	–	✓	–	[829]
Br, I, Cl	SbF_5	–	✓	c-$C_6F_{11}X$; c-C_6F_{10}	[829]
C_6F_5	SbF_5	✓	–	[c-$C_6F_{11}X$]	[823,832]
F, CF_3, C_6F_5, I	VF_5/SO_2ClF	✓	✓	–	[826,833]
$CF_2CF{=}CF_2$ $CF{=}CFCF_3$	VF_5	✓ ($X = C_3F_7$)	✓ ($X = C_3F_7$)	$C_6F_5C_3F_7$	[834]
Me, CH_2F, CHF_2	VF_5	✓	✓	X = Me gives products obtained from $X = CH_2F$ and CHF_2	[835]
OMe	VF_5	–	✓	c-2,5-dienone (C_6F_6O); c-2-enone (C_6F_8O); c-$C_6F_{11}OMe$	[835]
$OCHF_2$	VF_5	✓	–	c-3X-1,4-diene; c-$C_6F_{11}X$	[835]
F, H, Cl, Br, C_6F_5	$XeF_2–BF_3/CH_2Cl_2$	✓	–		[836]
F, NO_2	XeF_2–HF or $XeF^+SbF_6^-/HF/SO_2ClF$	✓ ✓	– –		[837]
$SiMe_3$, $GeEt_3$	$XeF_2–BF_3/Et_2O$, CH_2Cl_2	✓	–	–	[838]
$Xe^+AsF_6^-$	XeF_2–HF	✓	✓	–	[839]
F	BrF_3; H_2O	✓	–	c-2,5-dione	[840]
F	$[BrF_2]^+SbF_6^-$	✓	–	–	[825]
H, CF_3, NO_2	$[BrF_2]^+BF_4^-$	✓ [+X(H)→X(Br)]	–	–	[825,840]
F, CF_3, Br	BrF_3/Br_2	✓	–	BrF adduct(s) of diene	[821]
Me	BrF_3/Br_2	✓	–	 $C_6F_9Br_2X$	[821]
MeO	BrF_3/Br_2	–	–		
MeO	BrF_3	–	–		
In 1,4-$C_6F_4(CF_3)_2$	BrF_3/Br_2	2,5-$(CF_3)_2$-1,4-diene		BrF adduct of diene	[821]
In  X = F, Cl	$[BrF_2]^+BF_4^-$			[825,840]	

Table 19
Fluorination of polyfluoronaphthalene compounds

Substituent X in 	Fluorinating agent	Products 			Other	Ref.
F	SbF_5, 300°C	✓	–	–	–	[832]
H, Cl	SbF_5, 300°C	✓ (X→F)	✓	–	–	[832]
CF_3	SbF_5, 300°C	–	✓	–	–	[832]
F	SbF_5 (radical cation); H_2O	–	–	✓		[823]
F	VF_5	✓	–	✓	 	[826]
F	XeF_2–HF/CH_2Cl_2 or XeF_2–WF_6	–	–	✓		[837]
	$[XeF]^+SbF_6^-$	–	–	✓		[837]
	XeF_2–BF_3/CH_2Cl_2	–	–	✓		[841]
OMe(OEt)	XeF_2–BF_3/CH_2Cl_2	–	–	✓	–	[841]
OPr^i	XeF_2–BF_3/CH_2Cl_2	–	–	–	 	[841]
F	BrF_3; H_2O	–	–	✓	 (I)	[840]
	BrF_3/Br_2	–	–	✓	 (II)	[842]
	$[BrF_2]^+SbF_6^-$; H_2O	–	–	✓	(I) and (II)	[825]
F	ClF_3/SO_2ClF, −50 to −60°C	–	–	✓	–	[825]

3.18. Biotransformations of fluoroaromatic compounds

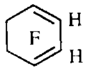
Biotransformations of polyfluoroaromatic compounds are relatively rare. Scheme 154, however, shows the novel microbiological oxidation of p-HC_6F_4OH to the catechol derivative (**336**) [843].



Scheme 154.

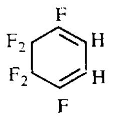
4. Notes on the formulae

In the majority of formulae given in this review, there is a symbol "F" within a ring, meaning that all unmarked substituents are the correct number of fluorine atoms. Thus:



4

is equivalent to



in Eq. (7)

Acknowledgements

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