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Some new aspects in the application of perfluoroalkyl halides in the synthesis of fluorine-containing organic compounds

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Contents

I. Introduction 491
II. The use of perfluoroalkyl halides in the synthesis of partially fluorinated compounds 492
III. Reactions of perfluoroalkyl halides with organic substrates occurring by a single-electron transfer mechanism 496
IV. Conclusion 517

Abstract. The approaches to the activation of perfluoroalkyl halides used as intermediates in the synthesis of partially fluorinated compounds are considered. The conditions for reactions of organic compounds with perfluoroalkyl iodides in the presence of reductants ($Na_2S_2O_4$, $HOCH_2SO_2Na$), metals and metal salts, redox systems ($Na_2S_2O_8$, Bu^tOOH, $Pb(OAc)_4$, $H_2O_2-FeSO_4$, $Ce(SO_4)_2$) and transition metal complexes are described. The generation of perfluoroalkyl radicals by a single-electron transfer mechanism are discussed. The introduction of perfluoroalkyl groups into aromatic and unsaturated organic compounds and functionalisation of perfluoroalkyl iodides, particularly, their transformation into perfluoroalkanesulfinic and perfluoroalkanecarboxylic acids and aldehydes, are considered. The bibliography includes 442 references.

I. Introduction

The introduction of fluorine atoms into the molecules of organic compounds not only changes their physical and chemical properties but also forms the basis for the development of new synthetic procedures, sometimes unusual for organic chemistry, for the generation of C–C bonds and cyclic systems.[1–6]

Partially fluorinated organic compounds, particularly those containing perfluoroalkyl groups, find wide application in the synthesis of novel materials, in the design of medicinal and agricultural preparations and in different branches of technology.[7–24] This, in turn, stimulates the development of novel, and the perfection of the existing methods for the introduction of polyfluorinated fragments into organic substrates. The interest of investigators in the possibility of direct introduction of such fragments into organic molecules is determined by diverse applicability of fluorine-containing compounds and unique physical and biological properties imparted to these compounds by fluorine, because regioselective substitution of a perfluoroalkyl group for the hydrogen atom in aromatic or heterocyclic systems may significantly influence their properties.

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The introduction of perfluoroalkyl groups, in the first place, of CF_3, into organic molecules is based on three main types of chemical transformations, *viz*., those involving electrophilic (see, *e.g*., Refs 2, 25, 26), nucleophilic[27] and radical[28–30] species. Thus, the availability of perfluoroalkyl iodides and the feasibility of their use in the synthesis of organometallic compounds made it possible to develop novel procedures for the generation of perfluoroalkyl radicals and to study their reactions.[28–30]

The addition of perfluoroalkyl halides to alkenes and alkynes is one of the most fundamental procedures for introducing perfluoroalkyl groups into the molecules of organic substrates. Perfluoroalkyl radicals are traditionally generated photochemically,[31–41] thermally[42] or electrolytically,[43,44] *viz*., by:

(i) photolysis or thermolysis of perfluoroalkyl halides, perfluoroalkanesulfonyl chlorides and organometallic compounds containing perfluoroalkyl substituents;[45–50]

(ii) decomposition of polyfluorinated acyl peroxides of the general formula $(C_nF_{2n+1}COO)_2$[51–64] and electrolysis of perfluoroalkanecarboxylic acids.[65–69]

These methods have successfully been used in the perfluoroalkylation of alkenes, aromatic, natural and heterocyclic compounds. Their advantages and disadvantages have been described in detail.[45,65–68] To the main disadvantages of these methods one may relate the difficulty in their implementation under conditions of large-scale manufacture, low selectivity and low yields of the target products. Moreover, the preparation of the starting building blocks, which are often toxic and expensive, demands special conditions.[19] These circumstances together have made it necessary to develop efficient methods for introducing perfluoroalkyl groups† into organic molecules. The main emphasis in these studies was laid on their direct incorporation by *in situ* generation of perfluoroalkyl radicals. This, in turn, required simple, available and inexpensive reagents and simplification of the procedure of direct introduction of perfluoroalkyl groups into organic molecules.

This search culminated in the development of novel approaches to the generation of perfluoroalkyl radicals from perfluoroalkyl halides in reactions occurring by a single-electron transfer mechanism. A variety of initiators for such reactions are currently known. The ease of performance and high efficiency of the perfluoroalkylation reaction as well as high accessibility of the reagents leave hope that this reaction will be very efficient in the synthesis of fluoroorganic compounds. The present work is an overview of the published data concerning perfluoroalkylation

† The electrophilic nature of the perfluoroalkyl radical was reported by Baum *et al*.[70]

reactions, it highlights the key events in the methodology of introduction of perfluoroalkyl groups into organic compounds.

II. The use of perfluoroalkyl halides in the synthesis of partially fluorinated compounds

Perfluoroalkyl iodides and bromides have recently received considerable attention owing to their accessibility, high reactivity and ability to be used in perfluoroalkylation reactions, including new ones.

These reactions can be initiated in various ways, *viz*., thermally,[42,71–74] electrochemically,[43,44] photolytically,[31–41,75,76] or in the presence of free radical inducers, *e.g*., hydrogen peroxide,[77] α,α-azobis(dimethylpentanonitrile),[78–80] α,α-azobis(cyclohexanecarbonitrile)[81] and α,α-azobis(isobutyronitrile) (AIBN).[79–85] By selecting appropriate reaction conditions (*viz*., solvent, temperature, reaction time), one may carry out perfluoroalkylation of various organic compounds.

These reactions are accompanied by the cleavage of C—I and C—Br bonds, but not of C—F bonds because the latter possess greater strength. Under certain conditions, perfluoroalkyl halides act as radical reagents, which perfluoroalkylate unsaturated organic compounds. This approach was repeatedly used in the chemistry of fluoroorganic compounds.[36,86–93]

Perfluoroalkyl iodides (R_FI) are widely used as a source of perfluoroalkyl radicals, their addition to alkenes[46] and reactions with aromatic hydrocarbons under thermolysis conditions have been described, *e.g*.:

$$R_F^{\bullet} + CH_2{=}CHR \longrightarrow [R_FCH_2CHR]^{\bullet},$$

$$[R_FCH_2CHR]^{\bullet} + R_FI \longrightarrow R_FCH_2CHIR + R_F^{\bullet},$$

$$ArH + 2\,R_FI \xrightarrow{190-250\,^{\circ}C} ArR_F + R_FH + I_2.$$

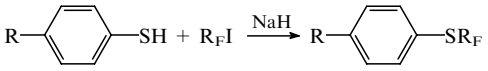
1. Reactions of perfluoroalkyl iodides with organic substrates in the presence of nucleophilic agents

This methodology was first used[94–102] in reactions of alkene- and arene-thiols with perfluoroalkyl iodides in liquid ammonia upon UV-irradiation. The corresponding aryl perfluoroalkyl sulfides were isolated in high yields.

$$PhSNa + n\text{-}C_8F_{17}I \xrightarrow[DMF,\ 25\ ^{\circ}C]{NH_3(liquid)} n\text{-}C_8F_{17}SPh + NaI \quad (92\%)$$

Reactions with perfluoroalkyl bromides and diiodoperfluoroalkanes were conducted in a similar way, this was further extended to selenium and tellurium derivatives and representatives of other classes.[103–108]

Later, it was shown that reactions of perfluoroalkyl iodides with trialkylammonium and sodium salts of benzenethiols (Table 1)[102] or sodium benzothiazole-2-thiolate[108,109] do not always require UV-irradiation. These reactions may occur in bipolar aprotic solvents at room temperature and are characterised by high yields.

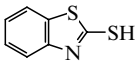


R	R_F	Yield (%)	R	R_F	Yield (%)
H	C_4F_9	66	NO_2	C_6F_{13}	93
Me	C_4F_9	77	NO_2	C_8F_{17}	93
OH	C_4F_9	30	NO_2	$C_4F_9(CH_2)_2$	90
Cl	C_4F_9	83	NO_2	$C_6F_{13}(CH_2)_2$	68
NO_2	C_4F_9	99			

Alkali metal benzenethiolates are convenient reagents, but in this case substitution reactions occur only on irradiation.[110–112] Nitrobenzene can be used as an initiator of this reaction. For example, the reactions of perfluorohexyl bromide with potassium benzenethiolates in DMF in the presence of nitrobenzene result in aryl perfluorohexyl sulfides.[113]

Table 1. Reactions of perfluoroalkyl iodides with triethylammonium arenethiolates.[102]

$$ArS^{-}\overset{+}{N}HEt_3 + R_FI \xrightarrow{Et_3N} \underset{\mathbf{A}}{ArSR_F} + \underset{\mathbf{B}}{ArSSAr}$$

Ar	Reaction conditions			Yield (%)		
	solvent	T /°C	t /h	**A**	**B**	other products
Ph	DMF	19–20	2	83	3	–
4-$MeO_2CNHC_6H_4$	DMF	0–5	3	17	12	30
	DMF	0–22	5	30	7	54
	MeCN	21–22	0.5	98	traces	–
		21–22	2	82	2	–
	THF	21–22	1.5	64	10	–
	HMPA[a]	21–22	3	75	3	–
2-$NH_2C_6H_4$	MeCN	21–30	0.5	84	–	–
	DMF	23–24	1.5	66	7	–
4-$MeOC_6H_4$	MeCN	22–40	2	88	6	–
4-ClC_6H_4	DMF	22	2	72	3	–
	MeCN	21–22	4	40	12	9
4-$HO_2CC_6H_4$	DMF	22–30	0.5	72	traces	traces
4-$MeO_2CC_6H_4$	DMF	20	3	39	13	–
4-$NO_2C_6H_4$	DMF	50–55	5	traces	6	80
	DMF	20–22	48	traces	traces	87
	DMF	20–22	120	58.8		20
	DMF	20–22	24	72.2	3.8	–

[a] HMPA is hexamethylphosphoramide.

$$ArSK + R_FBr \xrightarrow{PhNO_2} ArSR_F$$

Ar	R_F	Yield (%)	Ar	R_F	Yield (%)
Ph	C_2F_5	33	4-$MeOC_6H_4$	CF_3	83
Ph	n-C_6F_{13}	72	3-$MeOC_6H_4$	CF_3	40
4-MeC_6H_4	CF_3	75	3-$NH_2C_6H_4$	CF_3	23
4-MeC_6H_4	n-C_6F_{13}	77	4-ClC_6H_4	CF_3	34
Ph	CF_3	45	4-$CF_3C_6H_4$	CF_3	13

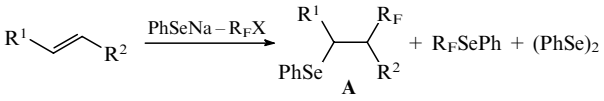
The reaction of $CF_3(CF_2)_9I$ with sodium 4-fluorobenzenethiolate in DMF at 30–45 °C gives 4-$FC_6H_4S(CF_2)_9CF_3$ (yield 94%).[114] On the other hand, benzenethiol,[115,116] benzeneselenol[117–119] and benzenetellurol[120,121] anions, which are known to be strong nucleophiles, generate the corresponding perfluoroalkyl radicals from perfluoroalkyl iodides introduced into the reaction with alkenes. In this way, efficient perfluoroalkylselenylation (Table 2)[117–119] and perfluoroalkyltellurylation (Table 3)[120,121] of a series of alkenes were carried out.

In PhSeNa—R_FX and PhTeNa—R_FI systems, perfluoroalkyl radicals are generated from perfluoroalkyl halides at room temperature. This property was used in the development of a new approach to the generation of perfluoroalkyl radicals at low temperatures.

The yields of perfluroalkyl phenyl sulfides (R_FSPh) depend on the length of the alkyl chain. In the case of $C_nF_{2n+1}I$, where $n = 4$, 6 and 8, the yields are 78%, 84% and 86%, respectively. Perfluoroalkyl radicals add to the multiple bond regioselectively.[1]

A procedure for the synthesis of aryl perfluoroalkyl sulfides from perfluoroalkyl halides and benzenethiols was proposed by

Table 2. Perfluoroalkylselenylation of alkenes.[117–119]



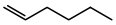
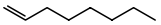
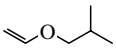
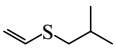
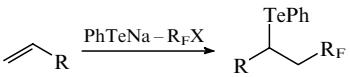
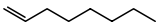
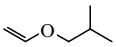
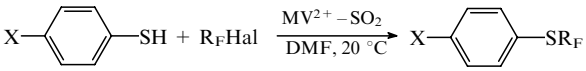
Alkene	R_FX	Yield (%)		
		A	R_FSePh	$(PhSe)_2$
	$C_8F_{17}I$	63	25	15
	$C_6F_{13}I$	55	20	19
	$C_8F_{17}I$	59	19	21
	$C_6F_{13}I$	57	17	13
	CF_3Br	26	34	31
	$C_8F_{17}I$	86	7	traces
	$C_6F_{13}I$	84	6	
	CF_3Br	38	32	20
	$C_8F_{17}I$	66	traces	30
	$C_8F_{17}I$	15	60	17
	$C_8F_{17}I$	39	42	9

Table 3. Perfluoroalkyltellurylation of alkenes.[120, 121]



Alkene	Yields for different R_FX (%)		
	CF_3Br	C_4F_9I	$C_8F_{17}I$
	57	81	59
	44	58	39
$CH_2{=}CH_2$	44	63	47
	30	64	54

Koshechko *et al.*[105] who used $MV^{2+}-SO_2$ (MV^{2+} is methylviologen, *N,N′*-dimethyl-4,4′-bipyridinium salt) and I_2-SO_2 systems as electron carriers.



$R_F = CF_3$, Hal = I: X = H (91.2%), $NHCO_2Me$ (88.5%), Cl (53%), NO_2 (9.2%);[104]

$R_F = CF_3$, Hal = Br: X = H (74%), Me (41%);[105]

$R_F = CFCl_2CF_2$, Hal = Cl, X = H (34%);[105]

$R_F = CF_3$, Hal = Br: X = $NHCO_2Me$ (94%), H (78%), Br (64%), Cl (60%), NO_2 (24%) (reaction with benzenethiols).[107]

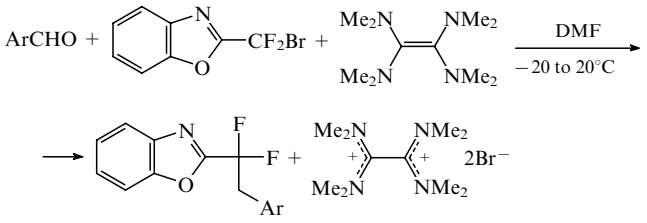
This reaction was studied in detail using spectrophotometry and cyclic voltamperometry [105] and provided conclusive evidence for the intermediate formation of the $^{\bullet}CF_3$ radical. Kinetic studies revealed that this reaction is of the second order with respect to the reagents, *i.e.*, $v = k_2[ArSH][MV^{2+}2I^-]$. The k_2 values for PhSH and 4-MeC_6H_4SH were equal to 4.6 and 7.1 litre mol^{-1} s^{-1}, respectively, at 30 °C.

After addition of SO_2 to the system, the reaction is controlled by the radical anion $SO_2^{-\bullet}$ generated from SO_2 by the radical cation $MV^{+\bullet}$, which, in turn, is generated upon action of ArS^- on MV^{2+}. The interaction of the intermediate radical anion $[CF_3SPh]^{-\bullet}$ with MV^{2+} gives the reaction product and $MV^{+\bullet}$.

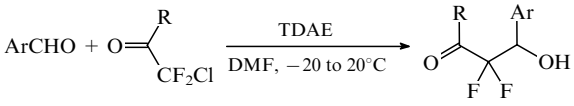
It is noteworthy that SO_2 is an efficient electron carrier in the electrochemical cathode trifluoromethylation of benzenethiols with trifluoromethyl bromide.[106, 107]

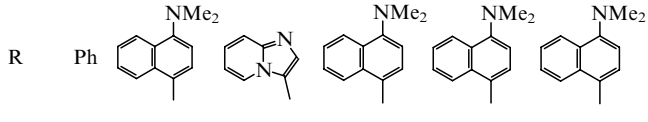
Tetrakis(dimethylamino)ethylene (TDAE) proved to be an efficient reductant initiating the cleavage of C–I and C–Br bonds in reactions with unsaturated compounds. Thus TDAE forms a complex (*e.g.*, with CF_3I), which can act as a nucleophilic trifluoromethylating agent in polar solvents. The ionisation potential of TDAE is equal to 6.13 eV,[122] being close to that of zinc, which is known to be a potent reductant [the standard electrode potential (E°) of zinc is −0.763 V]. TDAE is also known to be a very potent electron donor; its ionisation energy (591 kJ mol^{-1}) is lower than that of zinc (906 kJ mol^{-1}) and is close to that for lithium (521 kJ mol^{-1}). Electrochemical oxidation of TDAE in acetonitrile occurs in two reversible single-electron steps and results in $[TDAE]^{+\bullet}$ and $[TDAE]^{2+}$ ($E^\circ = -0.78$ and −0.61 V, respectively).[123]

Later, this methodology was used in the synthesis of dialkyl(trifluoromethyl)amines by the reaction of CF_2Br_2 with secondary amines in the presence of TDAE [124] and in reactions of 2-(bromodifluoromethyl)benzooxazole [125] and chlorodifluoromethyl ketones with aromatic aldehydes in the presence of TDAE.[126]



Ar	Ph	4-FC_6H_4	4-PhC_6H_4	4-$CF_3C_6H_4$	4-CNC_6H_4
Yield (%)	62	67	45	63	61

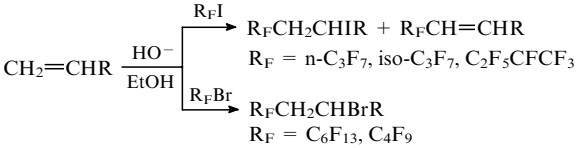




Ar	Ph	Ph	Ph	4-$CF_3C_6H_4$	4-FC_6H_4	
Yield (%)	55	45	55	58	55	57

The acyldifluoromethyl anion generated from chlorodifluoromethyl ketone reacts with aromatic aldehydes to give the corresponding hydroxy ketones containing a CF_2 fragment in the α-position.[126]

In the presence of alcoholates, perfluoroalkyl iodides and -bromides react with alkenes to yield the addition products.[127–131] This suggests that alcoholates, as is the case with the Cannizzaro reaction with aldehydes, act as reducing agents rather than induce splitting of perfluoroalkyl halides by the haloformic pathway.



R = n-C_5H_{11}, CH_2OH.

Phosphines [PPh_3, PBu^n_3, $P(NEt_2)_3$, $P(OEt)_3$] are used as activators in the reaction of perfluoroalkyl iodides with alkenes.[132–145]

$$CH_2{=}CHR + R_FI \xrightarrow[70-75\ ^\circ C,\ 4\ h]{PPh_3} R_FCH_2CHIR$$

R = n-C_4H_9, n-C_6H_{13}.

R_F	Yield (%)	R_F	Yield (%)
C_6F_{13}	79	C_8F_{17}	72
$Cl(CF_2)_4$	81	$FSO_2(CF_2)_2O(CF_2)_2$	28
$Cl(CF_2)_6$	83	$FSO_2(CF_2)_2O(CF_2)_8$	87

In the presence of $P(NEt_2)_3$, perfluoroalkyl iodides $R(CF_2)_nI$ (R = CF_3, $n = 4-7$) react with alkenes[140] or benzoyl chloride derivatives[141] with the formation of addition products at the multiple bond and the corresponding ketones (yields 32%–43%). The hexamethyldisiloxane–sodium methoxide system in THF is also effective to this goal.[142]

The reaction of perfluoroalkyl iodides with nucleophiles manifests the features of a $S_{RN}1$ reaction[44,146] and proceeds smoothly under relatively mild conditions. The stereochemistry of the reaction of perfluoroalkyl iodides with alkenes suggests that it is the perfluoroalkyl radical that initially attacks the alkene. Presumably, the initiation consists in electron transfer from the nucleophile to the perfluoroalkyl iodide resulting in the generation of the radical anion $[R_FI]^{-\bullet}$;[147,148] the process is exothermic. The radical anion formed must be rapidly decomposed into the perfluoroalkyl radical and the iodide ion. The efficiency of the free-radical chain growth in the reaction with alkenes is provided under conditions such that the decomposition of the radical anion $[R_FI]^{-\bullet}$ is a fast reaction; apparently, the polar effect in the translocation of the iodine favours the decomposition:

$$R_F^{\delta-}\cdots I\cdots R_H^{\delta+}.$$

The radical anion $[CF_3I]^{-\bullet}$ has been detected in a solid state as a stable species at 77 K. At 100 K, it dissociates into the trifluoromethyl radical and the iodide ion.[149–155] The reaction of the perfluoroalkyl radical with an anionic substrate generates a radical anion which further reacts with perfluoroalkyl iodide to give $[R_FI]^{-\bullet}$ according to the $S_{RN}1$ mechanism.[152–155] A more detailed description of these reactions is given in Refs 116, 156–160. Further transformations of the radical anion $[R_FX]^{-\bullet}$ may proceed in two pathways (routes *a* and *b*), which depends on thermodynamic factors.

$$[R_FX]^{-\bullet} \xrightarrow{a} X^- + R_F^{\bullet} \xrightarrow{Nu^-} [R_FNu]^{-\bullet} \xrightarrow{RX} [R_FR]^{-\bullet} + NuX$$
$$[R_FX]^{-\bullet} \xrightarrow{b} R_F^- + X^{\bullet}$$

Nu is nucleophile.

It was shown[47] that the $R_F^{\bullet}$ and I fragments (but not the radical anions $[R_FI]^{-\bullet}$) are formed in polar solvents. Hence a question arises about the pathways of generation of the radical $R_F^{\bullet}$. It is quite probable that only the C–I bonds are involved in the formation of donor–acceptor complexes with perfluoroalkyl iodides, which favours the manifestation of electrophilic properties of R_FI in solvents of the hexamethylphosphoramide (HMPA) and DMF type. Presumably, the translocation of the radical anion centre to R_FI followed by the generation of the $R_F^{\bullet}$ radical is the limiting step in this reaction.

The formation of radicals from perfluoroalkyl halides by the $S_{RN}1$ mechanism is one of the most characteristic features of electron transfer reactions in organic chemistry.[161] The $S_{RN}1$ mechanism is especially favourable for perfluoroalkyl halides, since the latter manifest very low activity in nucleophilic reactions of the S_N1 and S_N2 type. Studies of perfluoroalkyl halides reactions occurring *via* the $S_{RN}1$ mechanism were begun in the 1970's.[162–170]

$$RS^- + R_FI \longrightarrow [R_FI]^{-\bullet} + RS^{\bullet},$$
$$[R_FI]^{-\bullet} \longrightarrow R_F^{\bullet} + I^-,$$
$$R_F^{\bullet} + RS^- \longrightarrow [RSR_F]^{-\bullet},$$
$$[RSR_F]^{-\bullet} + R_FI \longrightarrow RSR_F + [R_FI]^{-\bullet}.$$

The values of the radical formation energy (E) in the gas phase were found to be as follows:[89]

Radical	E /eV	Radical	E /eV
$\dot{C}F_3$	2.10	$F^{\bullet}$	3.39
$CF_3\dot{C}F_2$	2.10	$Cl^{\bullet}$	3.61
$(CF_3)_2\dot{C}F$	2.65	$Br^{\bullet}$	3.37
$(CF_3)_3C^{\bullet}$	3.40	$I^{\bullet}$	3.06

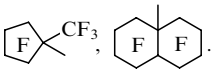
Therefore, route *a* in the transformation of radical anions is probable for compounds CF_3X, C_2F_5X, $(CF_3)_2CFX$ (but not for X = I), while route *b* is probable for $(CF_3)_3CX$ (at all values of X) and R. The direction of a reaction in solution depends on the value of free energy of solvation (ΔG). For example, in water ΔG has the following values:

Anion	ΔG /kJ mol^{-1}	Anion	ΔG /kJ mol^{-1}
F^-	−472	I^-	−283
Cl^-	−347	R_F^-	−200
Br^-	−321		

In this case, route *a* seems to be preferable for all R_FX [probably, with the exception of $(CF_3)_3CCl$] and, perhaps, $(CF_3)_2CFI$.

The transfer of electrons from the charged nucleophile to Bu^tBr leads to the formation of a radical anion–radical pair; its further transformations differ from those for an analogous pair in the case of R_FBr, which is decomposed by the route *b*, resulting in the radical anion $[R_FX]^{-\bullet}$. Quantum-chemical calculations using the AM1 method revealed that the formation of the radical anion generating the ternary perfluoroalkyl carbanion $(CF_3)_3C^-$ and the radical $Br^{\bullet}$ (see Refs 146, 165) is due to higher electronegativity of the tertiary group of the perfluoroalkyl radical. The enthalpy of formation of this anion and the $Br^{\bullet}$ radical (ΔH_1) is 17.6 kcal mol^{-1}, whereas that of the tertiary perfluoroalkyl radical and the bromide ion (ΔH_2) is much higher, *i.e.*, 57.9 kcal mol^{-1} (see Ref. 166).

$$[(R_F)_3CBr]^{-\bullet} \xrightarrow{R_F = CF_3} [(R_F)_3C]^{\bullet} + Br^-$$
$$[(R_F)_3CBr]^{-\bullet} \longrightarrow [(R_F)_3C]^- + Br^{\bullet}$$

R_F = $(CF_3)_3C$, $C_3F_7(CF_3)_2C$, .

The occurrence of this reaction through the formation of a radical anion was confirmed experimentally.[166] The reactions of $(R_F)_3CBr$ with nucleophiles, *e.g.*, Na_2S, NaSH, KSCN, KCN, R_4NX (X = Cl, Br, I), in organic solvents (*e.g.*, MeCN, DMF, CH_2Cl_2, EtOAc) result in the quantitative formation of mixtures of $(R_F)_3CH$ and perfluoroalkene. This can be attributed to the reaction of the perfluoroalkyl halide with the proton from the medium as well as to stabilisation of the perfluoroalkyl carbanion due to elimination of the fluorine anion from the CF_2 fragment in the α-position.

$$C_3F_7(CF_3)_2CBr + Nu^- \xrightarrow{Solv} C_3F_7(CF_3)_2CH + C_2F_5CF{=}C(CF_3)_2$$

Nu is nucleophile, Solv is solvent.

The electron transfer from the reductant to perfluoroalkyl halide resulting in the formation of the corresponding radical anions is highly efficient, since free σ^*-orbitals of the C–Hal bonds (Hal = Cl, Br, I) lie fairly low on the energy axis. Active generation of such radical anions requires a reductant the standard reduction potential (E°_{red}) of which is higher than that of the

alkyl halide involved in the reaction. Depending on the structure of the alkyl fragment and the nature of the halogen, the reducing potentials ($E_{1/2}$ relative to SCE) of perfluoroalkyl halides (Pt electrode in MeCN) vary from −1.10 to +0.71 V.[171]

R_FHal	$E_{1/2}$ /V	R_FHal	$E_{1/2}$ /V
CF_3I	−1.10	$(CF_3)_3CBr$	−0.14
C_3F_7I	−1.00	$C_3F_7CBr(CF_3)_2$	−0.09
$I(CF_2)_4I$	−0.96	1-bromo-1-methylperfluoro-	0.12
$(CF_3)_2CFI$	−0.66	cyclopentane	
cyclo-$C_6F_{11}I$	−0.36	1-bromoperfluorobicyclo-	0.71
I_2	0.10	[4.4.0]decane	
$(CF_3)_3CI$	0.14	1-chloro-1-methylperfluoro-	−1.02
$C_3F_7CI(CF_3)_2$	0.32	cyclopentane	
$C_3F_7CCl(CF_3)_2$	−0.97	1-chloroperfluorobicyclo-	−0.95
$(CF_3)_2CFBr$	−1.05	[4.4.0]decane	

Consequently, the presence in the reaction mixture of a compound with a higher (in comparison with perfluoroalkyl halide) value of E°_{red} makes possible the generation of the radical anion $[R_FX]^{-\cdot}$; its decomposition results in the perfluoroalkyl radical. The latter can be further involved in reactions with organic compounds. In the subsequent sections, this process will be exemplified with both classical reductants and redox systems.

2. Sulfinylation of perfluoroalkyl iodides

The addition of perfluoroalkyl halides to the C=C bond of alkenes is the most promising approach to the generation of C−C bonds in the synthesis of polyfluorinated compounds. Numerous synthetic procedures for perfluoroalkylation of alkenes, especially by R_FI, have been developed. One of them includes thermal or photochemical induction of free-radical reactions.

This approach was developed by a group of Chinese investigators who studied sulfinatodehalogenation of halogen-containing hydrocarbons. Thus it was demonstrated for the first time[54,172–177] that perfluoroalkyl iodides react with sodium dithionite ($Na_2S_2O_4$) to yield sulfinic acid derivatives. The chemistry of perfluoroalkanesulfinates including their synthesis, properties, reactions and applications is described in the reviews (see Refs 158–160).

The inexpensive reducing agent $Na_2S_2O_4$ can be used for the preparation of perfluoroalkanesulfinic acid salts from perfluoroalkyl halides (R_FX, where X = Br, I, or R_FCCl_3) under relatively mild conditions. This method is widely employed in reactions of these salts with alkenes, dienes, alkynes and aromatic compounds. On the other hand, this system is efficient mostly for polyfluorinated alkyl halides.[172] Bromine and iodine atoms in the perfluorinated carbon chain are easily substituted and the target product is formed in a high yield. More recent studies confirmed the efficacy of this approach.[178–192]

$$Cl(CF_2)_4I \xrightarrow[MeCN,\ 85\ ^\circ C,\ 9\ h]{Na_2S_2O_4-NaHCO_3} Cl(CF_2)_4SO_2Na \quad (84\%)$$

Later, it was found that other nucleophilic sulfur derivatives also react with perfluoroalkyl iodides to give salts of perfluoroalkanesulfinic acid (Table 4).[22,143,144,184]

Presumably, these reactions occur *via* a single-electron transfer (SET) mechanism as can be evidenced from the trapping of perfluoroalkyl radicals by alkenes and nitroso compounds.[54]

$$S_2O_4^{2-} \rightleftharpoons 2\,SO_2^{-\cdot}$$

$$SO_2^{-\cdot} + R_FI \longrightarrow [R_FISO_2]^{-\cdot}\ (\text{or } [R_FI]^{-\cdot}) \longrightarrow$$

$$\longrightarrow R_F^{\cdot} + I^- + SO_2 \xrightarrow{S_2O_4^{2-}} R_FSO_2^- + SO_2^{-\cdot}$$

$$\xrightarrow{Bu^tNO} R_F-N(Bu^t)-O^{\cdot}$$

$$\xrightarrow{\text{alkene}} \text{adduct (1 : 1)}$$

The sulfonylation with sodium dithionite gives an access to perfluoroalkanesulfonic acids, which are valuable intermediates in the synthesis of surfactants, without recourse to electrochemical fluorination and using accessible perfluoroalkyl iodides.[134,173,184,185,193] For example, $I(CF_2)_2O(CF_2)_2SO_3Na$ can be prepared from $I(CF_2)_2O(CF_2)_2I$ using phase-transfer catalysis in polyethylene glycols-200 and -600 or in acetonitrile, ethanol or diglyme.

Perfluoroalkyl bromides also react with sodium dithionite.[172–176,194,195] Thus, CF_3Br gives sodium trifluoromethanesulfinate in 90% yield, and sulfinylation products are formed from 1,1,1-trichloroperfluoroalkanes in yields of 90% and higher.

$$RCCl_3 \xrightarrow[MeCN-H_2O]{Na_2S_2O_4-NaHCO_3} RCCl_2SO_2Na \xrightarrow{Cl_2} RCCl_2SO_2Cl$$

R = Cl, F, CF_3, $Cl(CF_2)_2$, $Cl(CF_2)_4$, $Cl(CF_2)_6$.

The reactions of α,ω-diiodoperfluoroalkanes[183] and α,ω-dibromoperfluoroalkanes[189] with 1 or 2 equiv. of $Na_2S_2O_4$ in aqueous MeCN in the presence of sodium hydrogencarbonate result in sulfinates, *e.g.*, $I(CF_2)_nSO_2Na$ and $NaSO_2(CF_2)_nSO_2Na$, which in turn give the corresponding sulfonyl chlorides, *e.g.*, $I(CF_2)_nSO_2Cl$ and $ClSO_2(CF_2)_nSO_2Cl$ (n = 3, 4, 6) upon chlorination at 0 °C (Table 5).

Table 4. Synthesis of sodium perfluoroalkanesulfinates.

Nucleophile	R_FX	Reaction conditions		Product	Yield (%)
		solvent	T /°C		
$Na_2S_2O_4$	$F(CF_2)_8I$	MeCN–H_2O	80–85	$F(CF_2)_8SO_2Na$	95
	$F(CF_2)_8Br$	MeCN–H_2O	20	$F(CF_2)_8SO_2Na$	91
	CF_3CCl_3	MeCN–H_2O	25	$CF_3CCl_2SO_2Na$	73
	$I(CF_2)_2OCF_2CO_2Na$	H_2O	85	$NaSO_2(CF_2)_2OCF_2CO_2Na$	96
$HOCH_2SO_2Na$	$Cl(CF_2)_6I$	MeCN–H_2O	85	$Cl(CF_2)_6SO_2Na$	65
	$Cl(CF_2)_8I$	MeCN–H_2O	85	$Cl(CF_2)_8SO_2Na$	75
$NaHSO_3-K_3Fe(CN)_6$	$Cl(CF_2)_8I$	DMF–H_2O	70–80	$Cl(CF_2)_8SO_2Na$	88
$NaHSO_3-FeCl_3$	$F(CF_2)_6I$	DMF–H_2O	70	$F(CF_2)_6SO_2Na$	63
$Na_2S_2O_5$	$Cl(CF_2)_4I$	DMF–H_2O	80	$Cl(CF_2)_4SO_2Na$	85
	$Cl(CF_2)_6Br$	DMF–H_2O	80	$Cl(CF_2)_6SO_2Na$	79
$NaHSO_3$	$I(CF_2)_2O(CF_2)_2SO_2F$	DMF–H_2O	70–80	$NaSO_2(CF_2)_2O(CF_2)_2SO_2Na$	95
	$F(CF_2)_6Br$	DMF–H_2O	70–80	$F(CF_2)_6SO_2Na$	90
K_2SO_3	$I(CF_2)_2O(CF_2)_2SO_2F$	dioxane–H_2O	70	$KSO_2(CF_2)_2O(CF_2)_2SO_2F$	90

Table 5. Sulfinylation with subsequent chlorination of α,ω-diiodoperfluoroalkanes $I(CF_2)_nI$.[183, 189]

n	$I(CF_2)_nI$: : $Na_2S_2O_4$ (see [a])	MeCN : : H_2O (see [a])	Product	Yield (%) [b]
3	1 : 1	10 : 3	$I(CF_2)_3SO_2Cl$	28 (80)
4	1 : 1	10 : 3	$I(CF_2)_4SO_2Cl$	25 (90)
6	1 : 1	20 : 3	$I(CF_2)_6SO_2Cl$	39 (84)
3	1 : 2	1 : 1	$ClSO_2(CF_2)_3SO_2Cl$	73 (100)
4	1 : 2	1 : 1	$ClSO_2(CF_2)_4SO_2Cl$	83 (100)
6	1 : 2	1 : 1	$ClSO_2(CF_2)_6SO_2Cl$	75 (> 95)

[a] Molar ratio. [b] The figures in parentheses correspond to the yields according to ^{19}F NMR spectroscopy data.

$$I(CF_2)_nI \xrightarrow[MeCN-H_2O,\ 20\ ^\circ C]{Na_2S_2O_4-NaHCO_3} I(CF_2)_nSO_2Na \text{ and/or } NaO_2S(CF_2)_nSO_2Na \xrightarrow[0\ ^\circ C]{Cl_2,\ H_2O} I(CF_2)_nSO_2Cl \text{ and/or } ClO_2S(CF_2)_nSO_2Cl$$

One should bear in mind that dimerisation of a perfluoroalkyl radical is also possible. For example, heating of perfluoroalkyl iodide in the presence of the $Na_2S_2O_4-NaHCO_3$ system in MeCN for 48 h gives a dimeric product.[93]

$$2\ R_FI \xrightarrow[MeCN,\ \Delta]{Na_2S_2O_4-NaHCO_3} R_FR_F$$

The sulfinatodehalogenation reaction has opened up new opportunities for the synthesis of perfluoroalkanesulfinic and -sulfonic acids and their derivatives, since it permits direct transformation of perfluoroalkyl halide into perfluoroalkyl sulfinate and thus eliminates the necessity for the intermediate step, *i.e.*, the synthesis of an organometallic derivative. There is no doubt that this approach holds great promise for wide-scale technological application.[172–175, 178–181, 189, 195]

III. Reactions of perfluoroalkyl halides with organic substrates occurring by a single-electron transfer mechanism

The addition of perfluoroalkyl iodides to alkenes and alkynes is one of the most important methods for the synthesis of commercially valuable fluorohydrocarbons used as intermediates in the preparation of novel materials and products.[20] In this Section, we shall consider a novel approach to the functionalisation of the accessible perfluoroalkyl iodides, which consists in the involvement of an intermediate perfluoroalkyl radical generated under the action of various initiators. This reaction is described by a well-known mechanism, $S_{RN}1$. The possibility to alter the direction of the reaction by varying reaction conditions and using appropriate initiators permits one to perform directed synthesis of fluorinated compounds of various compositions.

Reactions of perfluoroalkyl iodides with organic substrates can be initiated in three different ways, *viz.*:

(1) by treating perfluoroalkyl iodides with reductants. The key steps in this process are the initial formation of the intermediate radical anion of perfluoroalkyl iodide and its dissociation into the perfluoroalkyl radical and the iodide anion;

(2) by treating perfluoroalkyl iodides with oxidants. As a result the reactant, possessing electrophilic properties, generates a radical cation. The latter reacts with perfluoroalkyl iodide to generate a radical anion $[R_FI]^{-\cdot}$, which is further decomposed to give a perfluoroalkyl radical;

(3) by treating perfluoroalkyl iodides with systems which generate alkyl or any other radicals themselves. The reaction of the latter with perfluoroalkyl iodide yields perfluoroalkyl radicals by-passing the formation of radical anions.

A vast body of experimental evidence on each of these approaches provides a guideline for new applications of perfluoroalkyl iodides. It seems therefore expedient to lay the main emphasis on these particular pathways of chemical transformations of perfluoroalkyl halides and sodium perfluoroalkanesulfinates.

1. Reactions of perfluoroalkyl iodides in the presence of reducing systems

The presence of an appropriate reductant is a main requirement for the activation of perfluoroalkyl halides and the intermediate formation of perfluoroalkyl radicals. Its specific function consists primarily in the generation of the corresponding radical anions from perfluoroalkyl halides.

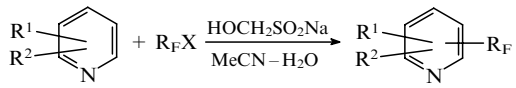
Various systems have been tested for this purpose, *viz.*, (1) formaldehyde–sodium sulfoxylate;[190] (2) sodium dithionite; (3) thiourea dioxide;[170, 185] (4) metals and metal salts; (5) transition metal complexes. Each of these systems has characteristic features of its own; therefore, their effects must be considered in more detail.

a. The formaldehyde–sodium sulfoxylate system

The formaldehyde–sodium sulfoxylate system or rongalite ($HOCH_2SO_2Na$), is widely used in industry as a reductant. Its reaction with perfluoroalkyl iodides and bromides gives the corresponding salts of sulfinic acids. It was found that under special conditions this reagent can generate perfluoroalkyl radicals from both perfluoroalkyl iodides and perfluoroalkanesulfinic acid salts.

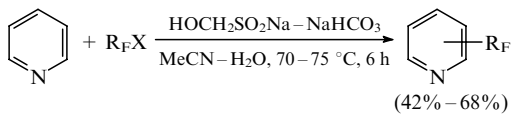
The reaction of perfluoroalkyl iodides and bromides with ethylene, ethylene derivatives and acetylene in polar solvents in the presence of compounds containing the SO_2^- anion (*e.g.*, $Na_2S_2O_4$, $HOCH_2SO_2Na$, *etc.*) (3 h, room temperature) yields addition products at the multiple bond in nearly quantitative yields.[101]

Rongalite was used for perfluoroalkylation of pyridine derivatives under the action of perfluoroalkyl iodides.[191, 192, 196, 197]



X = I, Br;
R^1 = H: R^2 = H, 3-Me, 4-Me, 4-NH_2; R^1 = 3-Me, R^2 = 5-Me;
R^1-R^2 = 2,3-CH=CHCH=CH (quinoline);
R^1-R^2 = 3,4-CH=CHCH=CH (isoquinoline).

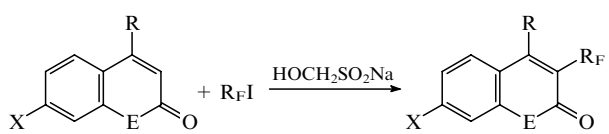
It is worth noting that the reaction of the perfluoroalkyl iodides R_FI with pyridine in the presence of the $Na_2S_2O_4$–$NaHCO_3$ system does not result in the formation of perfluoroalkylation products in acceptable yields, whereas an addition of $HOCH_2SO_2Na$ affords a mixture of α-, β- and γ-perfluoroalkylpyridines in sufficiently good yields.[191, 192]



(42%–68%)

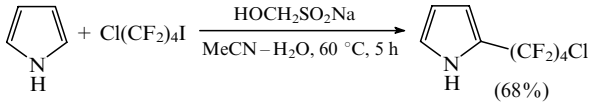
R_FX = $C_6F_{13}I$, $C_7F_{15}I$, $C_8F_{17}I$, $ClC_8F_{16}I$, $C_7F_{15}Br$, $ClC_6F_{12}Br$.

This reaction applied to coumarin gives 3-perfluoroalkylcoumarin; its S- and N-analogues can also be prepared in good yields.[198, 199] However, in the case of the $Na_2S_2O_4$–cetyltrimethylammonium bromide (CTMAB) system the yield of the target product is low.[62]



E = O (63%), S, NH; R_F = $F(CF_2)_6$; X = H, OH.

Polyfluorination of pyrrole in the presence of rongalite was carried out in a similar way.[192]



Reactions involving rongalite occur in accordance with the following tentative scheme:

$$HOCH_2SO_2^- \longrightarrow HSO_2^- + CH_2O,$$

$$R_FI + HSO_2^- + OH^- \longrightarrow R_F^{\bullet} + SO_2^{-\bullet} + I^- + H_2O.$$

Perfluoroalkyl halides react with disulfides in the presence of reductants, *e.g.*, $HOCH_2SO_2Na$, $Na_2S_2O_4$, formate – SO_2, to give perfluoroalkyl thioethers.[62, 200, 201] For example, the reaction of diphenyl disulfide with bromotrifluoromethane in the presence of $Na_2S_2O_4$ in DMF containing Na_2HPO_4 at 20 °C gives trifluoromethyl phenyl sulfide in 65% yield.

The reaction of polyfluoroalkyl iodides and -bromides containing 3 to 12 carbon atoms, *viz.*, $Cl(CF_2)_nI$ ($n = 4, 6, 8$), $CF_3(CF_2)_nI$ ($n = 5-7$) and $Cl(CF_2)_nNBr$ ($n = 4, 6$), with the rongalite – $NaHCO_3$ system in bipolar aprotic solvents (MeCN, DMF) results in the formation of sodium polyfluorocarboxylates in high yields.[185, 201–205] This approach is more convenient than the conventional method based on electrochemical fluorination of carboxylic acids and their derivatives.

$$CF_3(CF_2)_nHal \xrightarrow[80-85\ ^\circ C,\ 15-22\ h]{HOCH_2SO_2Na - NaHCO_3} CF_3(CF_2)_{n-1}CO_2^- \xrightarrow{H^+} CF_3(CF_2)_{n-1}CO_2H$$

n	Hal	Yield (%)	*n*	Hal	Yield (%)
2	I	74	6	I	82
	Br	80		Br	70
3	I	82	7	I	70
	Br	–		Br	86
5	I	79	11	I	51
	Br	84		Br	–

These results gave an impetus to further investigations of perfluoroalkylation of various organic substrates using perfluoroalkyl iodide – reductant systems.[206–210]

b. The use of sodium dithionite

Reactions of perfluoroalkyl iodides with ethylene and acetylene in polar solvents induced by sodium dithionite ($Na_2S_2O_4$) also permit the introduction of the perfluoroalkyl group into organic molecules. Thus the reaction of $Cl(CF_2)_6I$ with ethylene in the presence of the $Na_2S_2O_4 - NaHCO_3$ system (3 h, room temperature) gives an addition product at the multiple bond, $Cl(CF_2)_6CH_2CH_2I$, in a nearly quantitative yield.[186, 187, 211, 212] A similar reaction involves secondary perfluoroalkyl iodides, such as $CF_3CFI(CF_2)_4SO_2F$, $CF_3CFI(CF_2)_nCl$ ($n = 2, 4$), $CF_3CFI(CF_2)_2O(CF_2)_2SO_3Na$ and $CF_3(CF_2)_2OCFICF_3$.[213–215]

$$R^1CH{=}CR^2R^3 + R_FI \xrightarrow[MeCN]{Na_2S_2O_4} R_FR^1CHICR^2R^3$$

$R^1 = R^2 = H$: $R^3 = (CH_2)_4Me$, $(CH_2)_2CH{=}CH_2$, CH_2OH, OAc, $(CF_2)_4Cl$, $CH_2OCH_2CH{=}CH_2$; $R^1 = H$, $R^2 = R^3 = F$;
$R^1 - R^2 = (CH_2)_4$, $R^3 = H$.

In the presence of sodium dithionite, perfluoroalkyl bromides react vigorously with alkenes in aqueous isopropyl alcohol at 60–70 °C to give addition products in good yields.[215]

$$CH_2{=}CHR + R_FBr \xrightarrow[Pr^iOH-H_2O]{Na_2S_2O_4} \underset{SO_2Na}{\overset{R_F\quad R}{\diagup\!\diagdown}} \xrightarrow{Cl_2} \underset{SO_2Cl}{\overset{R_F\quad R}{\diagup\!\diagdown}}$$

(64%–74%)

$R = H, (CH_2)_3Me, (CH_2)_5Me, (CH_2)_7Me$;
$R_F = H(CF_2)_6, F(CF_2)_8, Cl(CF_2)_4, Cl(CF_2)_6$.

The reaction of perfluoroalkyl iodides ($R_FI = CF_3I$, $Cl(CF_2)_2I$, $Cl(CF_2)_4I$) with aryl isocyanides (RC_6H_4NC) in the presence of the $Na_2S_2O_4 - NaHCO_3$ system results in polyfluoroalkylimidoyl iodides $RC_6H_4N{=}CIR_F$.[216]

Dibromodifluoromethane is used as the starting compound in the synthesis of compounds containing the bromodifluoromethyl group.

In the presence of sodium dithionite, rongalite or thiourea dioxide, CF_2Br_2 and CHF_2I react with terminal alkenes in aqueous acetonitrile or *tert*-butyl alcohol at room temperature or on cooling to give the corresponding adducts.[196, 217, 218]

$$CH_2{=}CHBu^n + CHF_2I \xrightarrow[MeCN-H_2O,\ 20\ ^\circ C,\ 14\ h]{Na_2S_2O_4 - NaHCO_3} CHF_2CH_2CHIBu^n \quad (86\%)$$

$$CH_2{=}CHC_6H_{13} + CF_2Br_2 \xrightarrow[Bu^tOH,\ 20\ ^\circ C,\ 24\ h]{HOCH_2SO_2Na,\ CuCl} CBrF_2CH_2CHBrC_6H_{13} \quad (68\%)$$

Compounds containing different halogen atoms can also be used as fluoroalkylating reagents in the presence of the $Na_2S_2O_4 - NaHCO_3$ system. For example, Freon-113 reacts with alkenes, dienes and hex-1-yne at moderate temperatures resulting in fluoroalkylation products, albeit, in low yields.[219]

$$CF_2ClCFCl_2 \xrightarrow[MeCN-H_2O]{Na_2S_2O_4 - NaHCO_3}$$

$CH_2{=}CH(CH_2)_3Me$, 40–45 °C, 20 h → $CF_2ClCFCl(CH_2)_5Me$

$CH_2{=}CH(CH_2)_nCH{=}CH_2$ → $CF_2ClCFClCH_2CHCl(CH_2)_nCH{=}CH_2$ ($n = 2$ (48%), 4 (56%))

$HC{\equiv}C(CH_2)_3Me$, 40–45 °C, 20 h → $CF_2ClCFClCH{=}CH(CH_2)_3Me$

In the presence of sodium dithionite, CF_2Br_2 reacts with diethylallyl malonate, alkenes and alkynes; in the latter case, mixtures of *E*- and *Z*-isomers are formed in moderate yields (Table 6).[196, 220]

$$CF_2Br_2 \xrightarrow{Na_2S_2O_4 - NaHCO_3}$$

$CH_2{=}CHCH_2CH(CO_2Et)_2$ → $CF_2BrCH_2CHBrCH_2CH(CO_2Et)_2$

$HC{\equiv}CR$ → $CF_2BrCH{=}CRBr$

$R = (CH_2)_3Me$ (55%), $(CH_2)_4Me$ (53%), $(CH_2)_5Me$ (50%).

The reaction of difluorodiiodomethane with alkenes in the presence of iron at 40–50 °C gives compounds carrying the ICF_2 group.[221, 222]

CF_2I_2 (Fe)

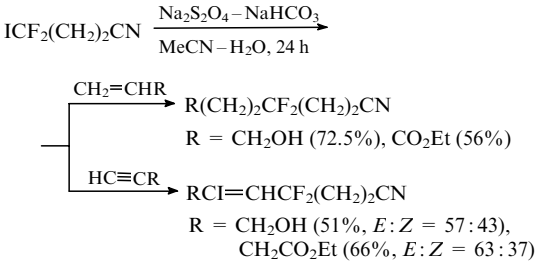
$CH_2{=}CH(CH_2)_3Me$ → $ICF_2CH_2CHI(CH_2)_3Me$ (73%)

$CH_2{=}CHCN$ → $ICF_2(CH_2)_2CN$ (57%)

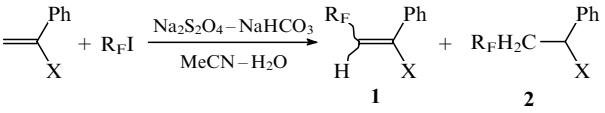
The latter also react with alkenes and alkynes in $MeCN - H_2O$ in the presence of the $Na_2S_2O_4 - NaHCO_3$ system at 30 °C, resulting in the formation of addition products at the multiple bond.[222]

Table 6. Reactions of alkenes and alkynes with CF_2Br_2 induced by reductants.

Substrate	Reductant	Yield (%)
Hex-1-ene	$HOCH_2SO_2Na$	85
	$(NH_2)_2C=SO_2$	80
	$Na_2S_2O_4$	92
Oct-1-ene	$HOCH_2SO_2Na$	87
	$Na_2S_2O_4$	88
Cyclohexene	$HOCH_2SO_2Na$	70
	$(NH_2)_2C=SO_2$	75
	$Na_2S_2O_4$	75
Cyclooctene	$Na_2S_2O_4$	80
Styrene	$HOCH_2SO_2Na$	50
Diallyl ether	$Na_2S_2O_4$	85
α-Pinene	$Na_2S_2O_4$	68
β-Pinene	$Na_2S_2O_4$	75
Diethyl allylmalonate	$Na_2S_2O_4$	80
Hex-1-yne	$Na_2S_2O_4$	55
Hept-1-yne	$Na_2S_2O_4$	53
Oct-1-yne	$Na_2S_2O_4$	50
2,3-Dihydrofuran	$Na_2S_2O_4$	78
3,4-Dihydro-2*H*-pyran	$Na_2S_2O_4$	72
3,4-Dihydro-2*H*-pyran (excess)	$Na_2S_2O_4$	76

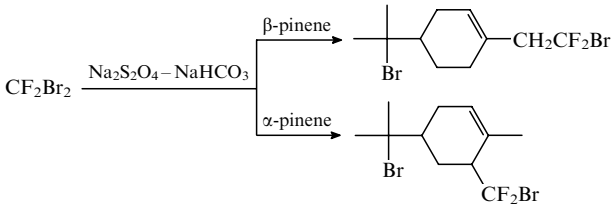


The reaction of $Cl(CF_2)_4I$ with α-phenylstyrene in aqueous MeCN induced by the $Na_2S_2O_4-NaHCO_3$ system (4 h, 40 °C) gives the products **1** and **2** which contain no iodine atom.[223]

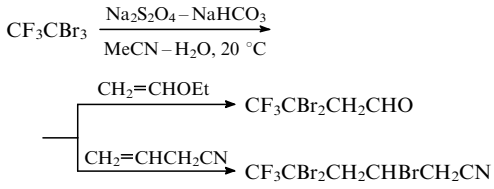


R_F	X	Yield (%)	
		1	**2**
$Cl(CF_2)_4$	Ph	33	30
$Cl(CF_2)_6$	Ph	36	35
$Cl(CF_2)_2$	Ph	24	26
$CF_3(CF_2)_5$	Ph	31	32
$Cl(CF_2)_4$	4-$MeOC_6H_4$	19	18
$Cl(CF_2)_4$	Bu^t	36	38
$Cl(CF_2)_4$	H	68	

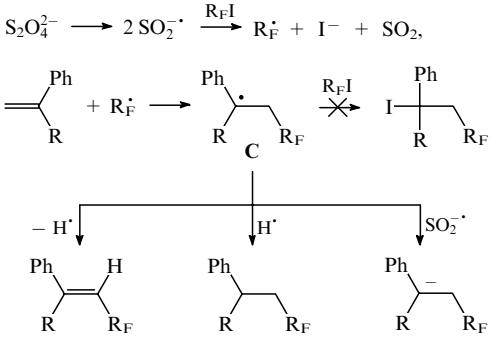
However, if styrene is used as a substrate, fluorine-containing oligomers are formed together with compound **1**.[196] Cyclohexene and cyclooctene manifest similar behaviour.[196] Under these conditions, CF_2Br_2 also reacts with α- and β-pinenes.[196, 220]



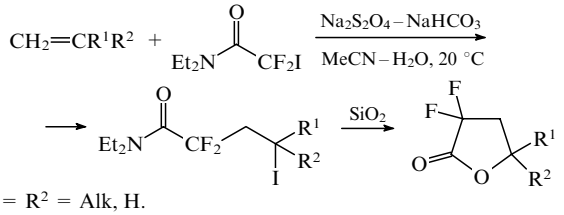
It was shown[224–229] that the use of compounds containing different halogen atoms in the reaction of 1,1,1-tribromotrifluoroethane with alkenes yields addition products at the multiple bond.



The mechanism of generation of perfluoroalkyl radicals under the action of sodium dithionite and its subsequent reaction with alkenes is now well-established.[158] The transformations of the intermediate radical **C** were shown to occur in three different ways.



The reaction of perfluoroalkyl iodides with alkynes under sulfinatodehalogenation conditions gives a mixture of *E*- and *Z*-adducts in very high yields.[230] A similar reaction with alkenes was used in the synthesis of an α,α-difluoro-γ-lactone.[231]



$R^1 = R^2$ = Alk, H.

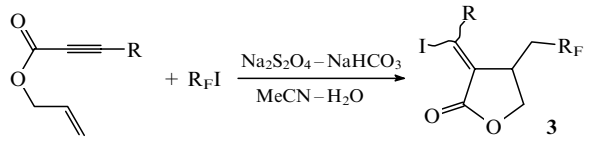
The reaction of $CF_2=CFCF_2Cl$ with allyl alcohol in aqueous acetonitrile in the presence of the $Na_2S_2O_4-NaHCO_3$ system affords an adduct (1 : 1); treatment of the latter with zinc at 130–140 °C in ethylene glycol results in 1,1,2,3,3-pentafluoro-1,5-hexadiene,[232] which is further used in the synthesis of polyfluorinated polymers.

In the presence of sodium dithionite, perfluoroalkyl iodides react also with allyl alcohol and unsaturated carboxylic acids to give addition products at the multiple bonds in high yields.[233]

A convenient and efficient procedure was developed for the direct introduction of the perfluoroalkyl group into unsaturated compounds which is based on the reaction of perfluoroalkyl iodides with alkene and alkyne derivatives induced by sulfur-containing systems. The main advantages of this method are its simplicity, high variability of functional groups, easy isolation of reaction products and regioselectivity. Moreover, these reagents

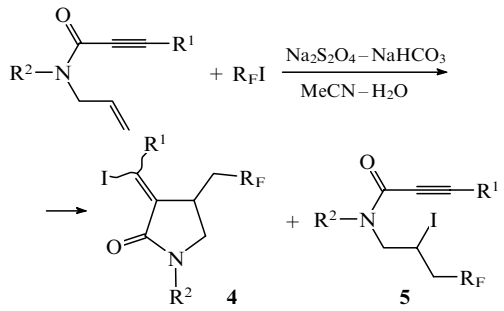
are neither toxic nor explosive, which makes them environmentally safe.

The presence of two multiple bonds in the substrate molecule favours the addition of R_F and I fragments to the alkene and the formation of a five-membered heterocycle of the type **3**. This reaction is regioselective.[201] Its strategy consists in the generation of a radical centre due to the cleavage of the F_2C-I bond, the addition of the radical formed at the double bond and subsequent cyclisation involving the radical centre and the multiple bond as a donor. Polyfluoroalkylated 3-iodoalkylidenetetrahydrofuran-2-one is formed as a result of generation of the perfluoroalkyl radical initiated by the reaction of R_F with $Na_2S_2O_4$ and subsequent formation of a five-membered heterocycle. This reaction occurs with high regioselectivity.[201]



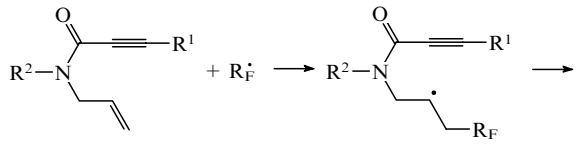
R	R_F	Yield (%)	*E*:*Z*
H	CF_3	44	32:68
H	$Cl(CF_2)_2$	47	60:40
H	$Cl(CF_2)_4$	50	52:48
Me	CF_3	80	95:5
Me	$Cl(CF_2)_2$	83	>97:3
Me	$Cl(CF_2)_4$	82	>97:3
n-C_8H_{17}	$Cl(CF_2)_2$	92	>97:3

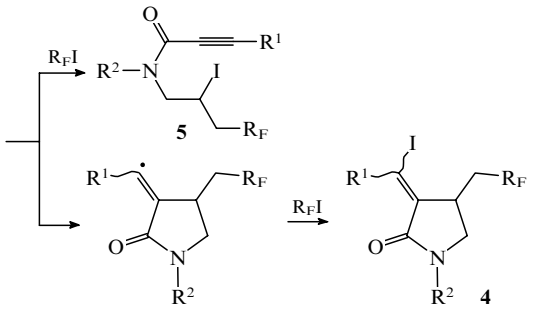
Similarly, perfluoroalkyl derivatives of 3-iodoalkylidene-2-pyrrolidone **4** and the acyclic amide **5** are formed in the perfluoroalkylation of *N*-allylprop-2-en- and *N*-allylbut-3-enamides by perfluoroalkyl iodides (or by polyfluorohalogenalkyl iodides) in the presence of the $Na_2S_2O_4-NaHCO_3$ system.[201,211]



R^1	R^2	R_F	Yield (%)		*E*:*Z*
			4	**5**	
Me	Me	$Cl(CF_2)_2$	53	19	>97:3
Me	Bn	$Cl(CF_2)_2$	50	35	>97:3
Me	Bn	$Cl(CF_2)_4$	49	29	>97:3
Pr^n	Bn	$Cl(CF_2)_2$	41	23	>97:3
Pr^n	Bn	$Cl(CF_2)_4$	43	27	>97:3
H	MeCO	$Cl(CF_2)_2$	46	0	52:48
Me	PhCO	$Cl(CF_2)_2$	70	0	>97:3
Me	PhCO	$Cl(CF_2)_4$	60	0	>97:3
Me	OTs	CF_3	72	0	>97:3
Me	OTs	$Cl(CF_2)_4$	83	0	>97:3

Presumably, this reaction occurs by the following scheme:

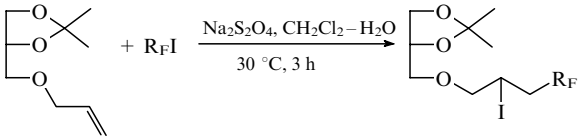




Cyclisation induced by the intermediate radical is successfully used for the construction of cyclic systems.[234]

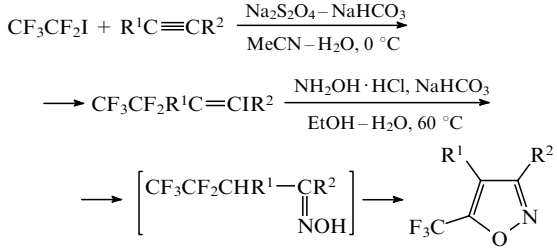
It is worth noting that in reactions with alkynes perfluoroalkyl iodides form mixtures of *E*- and *Z*-adducts in the presence of sodium dithionite, whereas perfluoroalkyl bromides and trichloro-1,1,1-trifluoroethane yield exclusively sulfinates.[230]

Generally, if the starting compound contains a double bond, its treatment with perfluoroalkyl iodides in the presence of the $Na_2S_2O_4-NaHCO_3$ system results in the formation of addition products as is the case in the reaction of perfluoroalkyl iodides with *O*-allyl-*O*-isopropylideneglycerol and crown ethers containing multiple bonds in a $CH_2Cl_2-H_2O$ mixture.[235,236]



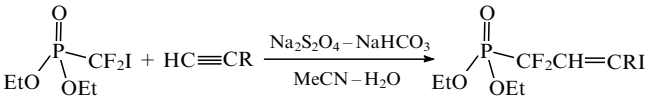
R_F = $F(CF_2)_8$ (72%), $F(CF_2)_6$ (59%), $Cl(CF_2)_6$ (55%), $Cl(CF_2)_8$ (68%).

The addition products of perfluoroalkyl iodides at the triple bond can be used in the synthesis of heterocyclic compounds, *e.g.*, 5-perfluoroalkyl-substituted isoxazoles.[237,238]

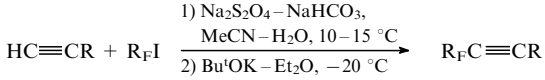


R^1 = H, R^2 = CH_2OH.

Diethyl difluoroiodomethylphosphonate was also introduced in the reaction with alkynes[222] to give a mixture of isomers the ratio of which depends on the nature of the substituent at the triple bond (Table 7).



Perfluoroalkyl derivatives of alkynes are formed in the reaction of alkynes with perfluoroalkyl iodides and subsequent treatment with a base as a result of elimination of HI from the adducts formed.[235–240]



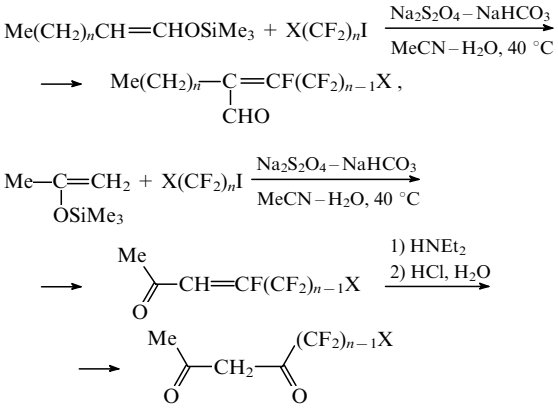
R_F	R	Yield (%)	R_F	R	Yield (%)
$Cl(CF_2)_2$	n-C_6H_{13}	47	$Cl(CF_2)_4$	$n^z{}_5H_{11}$	73
$Cl(CF_2)_2$	n-C_8H_{17}	74	$Cl(CF_2)_4$	$(CH_2)_6OH$	76
$Cl(CF_2)_2$	$(CH_2)_9OH$	82	$Cl(CF_2)_8$	Pr^n	78
$Cl(CF_2)_4$	Pr^n	52			

Table 7. The reaction of diethyl difluoroiodomethylphosphonate with alkynes HC≡CR in the presence of the $Na_2S_2O_4-NaHCO_3$ system in $MeCN-H_2O$.[222]

R	*t* /h	Yield (%)	*E*:*Z*
$(CH_2)_3Me$	3	79	82:18
	0.17	41	52:48
CH_2OH	3	74	50:50
CO_2Me	4	65	100:0
CO_2Et	4	67	100:0
	0.17	26	100:0
CH_2OMe	3	75	57:43
Ph	3	62	72:28
CH_2OEt	3	72	59:41
$CONMe_2$	4	56	100:0

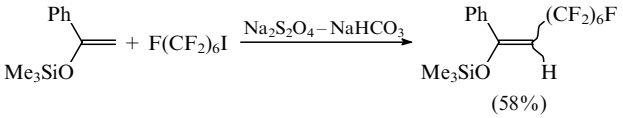
Note. The $ICF_2P(O)(OEt)_2:HC\equiv CR:Na_2S_2O_4:NaHCO_3$ ratio is 1:2:1:1.

The reaction of silylenol ethers with perfluoroalkyl iodides in the presence of the $Na_2S_2O_4-NaHCO_3$ system results in the formation of perfluoroalkylated α,β-unsaturated aldehydes and ketones.[241–245] Heating of the latter with $HNEt_2$ (or piperidine) and acid hydrolysis give the corresponding β-dicarbonyl compounds.



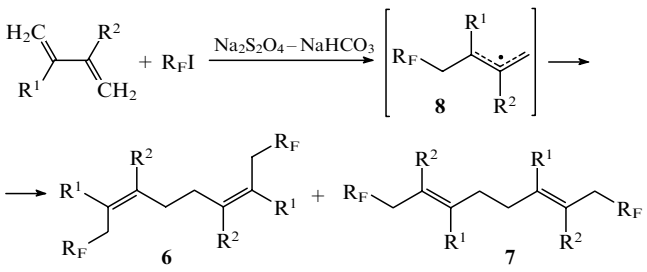
X = Cl: *n* = 4, 6, 8; X = F: *n* = 6, 8.

Trimethylsilyl ethers of the enol forms of acetophenone and methyl vinyl ketone react with perfluoroalkyl iodides in the presence of the $Na_2S_2O_4-NaHCO_3$ system to give hydrogen substitution products at the double bond.[242]



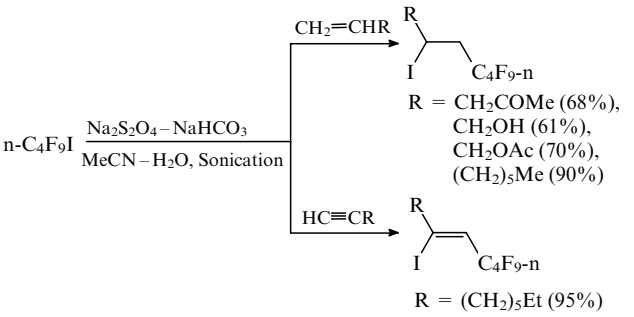
(58%)

It should be noted that the intermediate radical is capable of dimerisation; thus the dimeric products **6** and **7** are formed from butadiene derivatives in reactions involving allylic radicals **8**.[246]

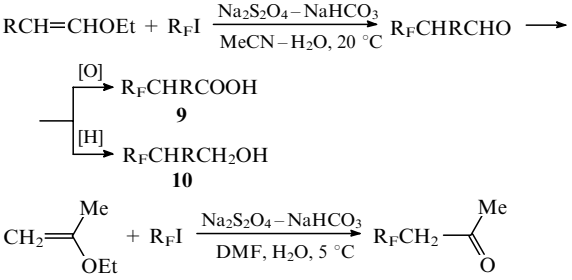


$R_F = Cl(CF_2)_n$ (*n* = 2, 4), $CF_3(CF_2)_3$; $R^1 = R^2 = H$, Me.

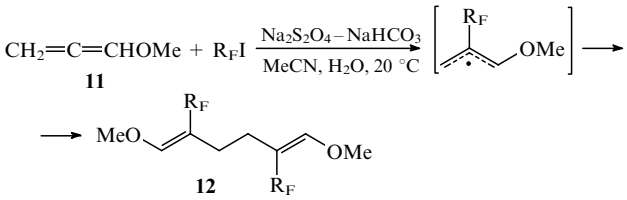
The rates of reactions of perfluoroalkyl halides with alkenes and alkynes can be increased by sonication.[206, 235]



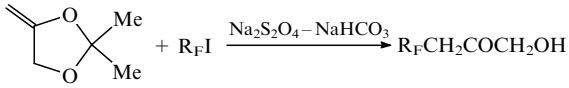
α-Perfluoroalkyl derivatives of aldehydes formed as intermediate products in the synthesis of valuable fluorine-containing blocks[226] are further used in the synthesis of heterocyclic compounds.[227, 240] Polyfluorinated aldehydes or ketones are formed in reactions of vinyl ethers with perfluoroalkyl iodides and are further transformed into either the corresponding acids **9** or alcohols **10**.[247]



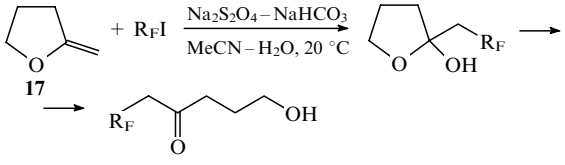
Compound **11** containing the allene group, like dienes, form an intermediate radical in the reaction with perfluoroalkyl iodides; its dimerisation yields the diether **12**.[236]



Perfluoroalkyl iodides n-$C_6F_{13}I$ and $Cl(CF_2)_nI$ (*n* = 2, 4, 6, 8) react with 4-methylenedioxolane in the presence of the $Na_2S_2O_4-NaHCO_3$ system resulting in ring opening.[248]



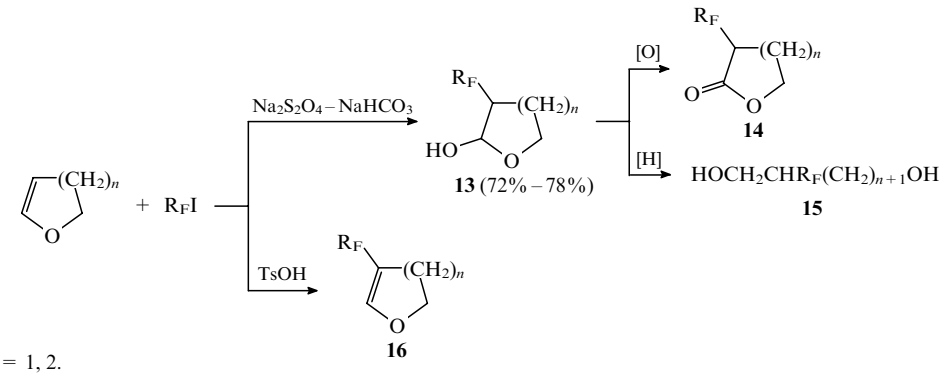
Cyclic ethers (2,3-dihydrofuran and 3,4-dihydro-2*H*-pyran) react with R_FI [$R_F = Cl(CF_2)_n$, where *n* = 4, 6, 8; $F(CF_2)_n$, where *n* = 6, 8][226] or with CF_2Br_2[196, 225] in the presence of the $Na_2S_2O_4-NaHCO_3$ system to produce 2-polyfluoroalkylhemiacetals **13** which can be oxidised to the corresponding lactones **14** or reduced to the diols **15**.[226, 249] On the other hand, the hydrogen substitution product at the multiple bond **16** is formed in the presence of *p*-toluenesulfonic acid (Scheme 1).



R_F = n-C_6F_{13}, $Cl(CF_2)_n$ (*n* = 2, 4, 6, 8).

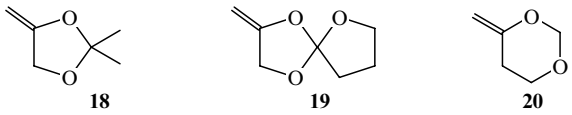
Perfluoroalkyl iodides react with heterocyclic compounds **17**–**20** containing an α-methylene substituent in the presence of

Scheme 1

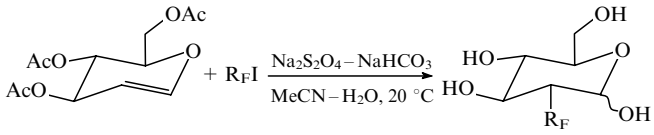


n = 1, 2.

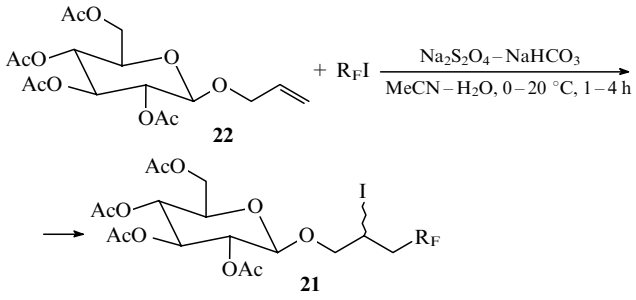
the $Na_2S_2O_4-NaHCO_3$ system with the formation of ring-opening products.[250]



Carbohydrates containing perfluoroalkyl substituents, *e.g.*, 2-R_F-2-deoxy-D-glucose, are prepared by perfluoroalkylation of glycals by perfluoroalkyl iodides induced by the $Na_2S_2O_4-NaHCO_3$ system.[197,207,251–258]

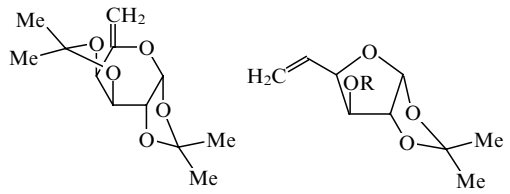


Perfluoroalkyl-substituted carbohydrates, *e.g.,* 2-iodo-3-perfluoroalkylpropyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (**21**), can be synthesised by perfluoroalkylation of allyl glucopyranoside **22**. These compounds were found to be useful intermediates and can be used as surfactants and emulsifiers.[250,259–266]

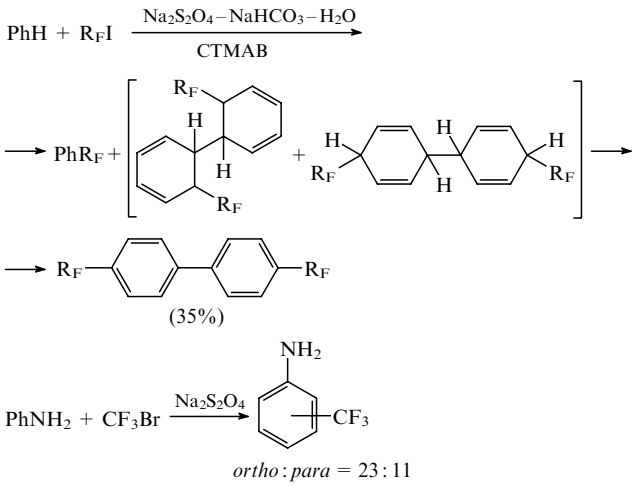


R_F = C_4F_9 (86%), C_6F_{13} (83%), C_8F_{17} (78%), $C_{10}F_{21}$ (71%).

Perfluoroalkyl iodides add at the multiple bond of hex-5-enopyranose and -furanose (R = CH_2Ph, Me) in the presence of $Na_2S_2O_4$.[262]



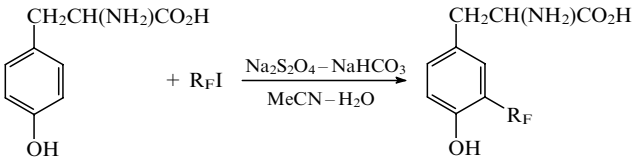
Under ordinary conditions, benzene does not react with perfluoroalkyl iodides; however, under conditions of phase-transfer catalysis with CTMAB it yields perfluoroalkylation products and dimerisation products of intermediate cationic σ-complexes.[212,267–269] Perfluoroalkylation of aromatic compounds containing amino or hydroxy substituents with bromotrifluoromethane or long-chain perfluoroalkyl iodides occurs at the *ortho*- and *para*-positions.[212,267–269]



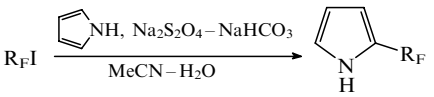
ortho : *para* = 23 : 11

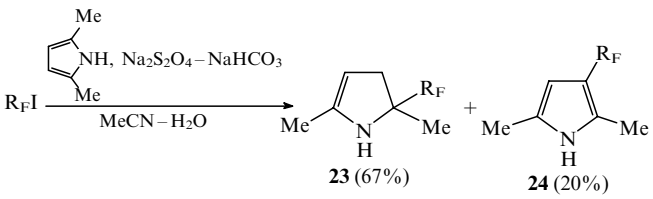
Ortho- and *para*-perfluoroalkylphenols can easily be prepared from phenol[270] and its *para*-substituted derivatives[252,271] in the presence of an alkali. For example, in the presence of NaOH *p*-cresol reacts with $Cl(CF_2)_6I$ in DMF containing $Na_2S_2O_4-NaHCO_3$ to give 2-ω-chloroperfluorohexyl-*p*-cresol in 60% yield.[270] 2,6-Diperfluoroalkyl derivatives can also be formed.[271]

The $Na_2S_2O_4-NaHCO_3$ system was efficient in the perfluoroalkylation of biologically active compounds containing a phenolic fragment. A procedure was developed for introducing perfluoroalkyl substituents into the aromatic ring of tyrosine.[272]



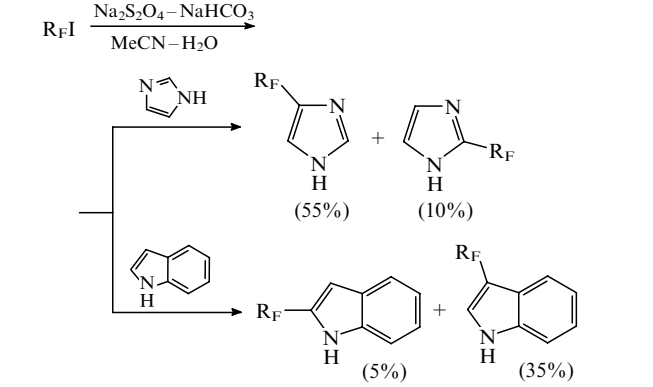
α-Perfluoroalkyl-substituted derivatives are formed in high yields upon treatment of pyrrole with perfluoroalkyl iodides in the presence of the $Na_2S_2O_4-NaHCO_3$ system.[273] However, high hydrolytic lability of the fluorine atoms of the α-CF_2 group should be kept in mind. It is of note that 2,5-dimethylpyrrole yields both addition (**23**) and substitution products of the hydrogen atom of the pyrrole ring (**24**).[274–277]





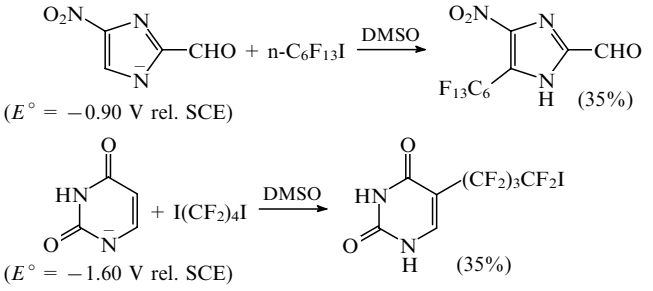
23 (67%) **24** (20%)

Perfluoroalkylation of other nitrogen-containing heterocyclic compounds is also possible.[273]



Perfluoroalkyl sulfones are synthesised in the reaction of alkenes $H_2C=CHR$ (R = CN, MeCO) with sodium perfluoroalkanesulfinates R_FSO_2Na ($R_F = C_4F_9$, ClC_4F_8) obtained by treatment of perfluoroalkyl iodides with sodium dithionite.[188]

It may thus be concluded that perfluoroalkyl radicals can be formed from perfluoroalkyl halides under the action of other radical anions capable of generating radical anions of perfluoroalkyl halides. Indeed, Medebielle *et al.*[239] who studied the reduction of CF_3Br, n-C_4F_9I, n-$C_6F_{13}I$ and $I(CF_2)_4I$ using terephthalonitrile, nitrobenzene and 4-nitropyridine *N*-oxide as messengers ($E^\circ = -1.60$, -1.10 and -0.79 V rel. SCE, respectively) demonstrated the efficiency of perfluoroalkylation of N-anions of the heterocyclic series (*e.g.*, imidazole, adenine, xanthine, uracil, cytosine, barbituric acid, lumazine, theophylline) by intermediate perfluoroalkyl radicals.



This reaction occurs in accordance with the following scheme. The initial electrochemically generated 4-nitropyridine *N*-oxide (P) radical anion induces the reduction of perfluoroalkyl halide to the corresponding radical anion which is further transformed into the perfluoroalkyl radical. The latter reacts with the N-anion to yield a new radical anion which ultimately yields the final product and the radical anion of the 'messenger', *viz.*,

$$P + e^- \rightleftharpoons P^{-\cdot},$$

$$P^{-\cdot} + R_FI \longrightarrow R_F^{\cdot} + I^- + P,$$

$$R_F^{\cdot} + Nu^- \longrightarrow R_FNu^{-\cdot},$$

$$R_FNu^{-\cdot} + P \rightleftharpoons R_FNu + P^{-\cdot}.$$

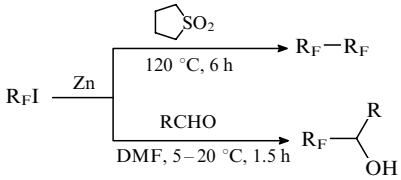
In the case of perfluoroalkyl halides, the reaction mechanism represents a modified version of the classical $S_{RN}1$ mechanism where the electron transfer occurs without the intermediate formation of the substrate radical anion. The perfluoroalkyl radical thus generated attacks the carbon atom of the N-anion of the heterocyclic compound, eventually resulting in the formation of the reaction product.

This methodology describes the perfluoroalkylation of organic substrates by perfluoroalkyl halides as a reduction in the presence of catalysts of the 4-nitropyridine *N*-oxide type.

c. Reactions of perfluoroalkyl iodides and -bromides catalysed by transition metals and their derivatives

Catalytic effects of metals and their salts. Various initiators of addition reactions of perfluoroalkyl iodides and -bromides to the multiple bonds C=C are presently known. An important role in the generation of perfluoroalkyl radicals is played by transition metal derivatives (mostly, zero-valent compounds)[278,279] and their complexes[180,280–283] used as both reagents and catalysts of diverse reactions.[180,278,282,283] Reactions of perfluoroalkyl iodides with alkenes and alkynes are especially efficient in the presence of Ru, Ni, W, Mo,[180,282,283] Sn,[284,285] Fe,[286,287] Mg,[288,289] Cu,[290–294] Raney Ni (RaNi),[295–297] Pt^0,[298,299] Mn^{II}, Hg^I,[300] Ru^{II},[301] Rh,[302] Me_3Al,[217] Et_3B,[303–308] Zn,[197,309] and Pd^0 (see Refs 197, 278, 310) and result in the formation of addition products at the multiple bond.[278,279] Reactions of perfluoroalkyl iodides with benzene in the presence of metals (Rh, Pd, Pt, Ru, Cu, RaNi, Co) and aqueous potassium hydrogencarbonate give perfluoroalkylbenzenes.[311,312] It is noteworthy that disubstitution occurs with low yields.

The role of metals consists in reductive generation of the radical $R_F^{\cdot}$ from R_FI. Further transformations depend on the type of the substrate and may occur either as subsequent addition of the radical $R_F^{\cdot}$ at the multiple bond (C=C) or as substitution of a halogen or hydrogen atom at the carbon atom of the multiple bond. Thus perfluoroalkyl iodides give perfluoroalkanes in the presence of zinc in sulfolane or in H_2O;[313] in DMF they react with aldehydes to give the corresponding alcohols.[314]

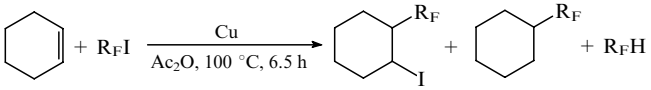


The reaction of bromotrifluoromethane with aldehydes and zinc in *N*-methylpyrrolidone yields alcohols;[315] trifluoroacetaldehyde is formed from DMF under conditions of cathode synthesis.[316]

It should be noted that reactions of perfluoroalkyl iodides and -bromides with electrophiles can also be catalysed by other metals. Thus the reaction of bromotrifluoromethane with chlorotrimethylsilane in the presence of aluminium powder in *N*-methylpyrrolidone yields trimethyl(trifluoromethyl)silane (yield 62%).[317] In the presence of cadmium, perfluoroalkanes are formed in 72% to 90% yield.[318] The reaction of $Cl(CF_2)_4I$ with $Bu^nCH=CH_2$ in the presence of Mg results in the addition product $Bu^nCHICH_2(CF_2)_4Cl$ in high yield, the reaction with $Bu^nC\equiv CH$ yields a mixture of (*E*)- and (*Z*)-$Cl(CF_2)_4CH=CIBu^n$ (Ref. 288).

Various reactions of perfluoroalkyl iodides with aromatic compounds (Table 8) and alkenes in the presence of copper have been described.[319–322] In these reactions, diethylene glycol, acetonitrile and acetic anhydride are used as solvents.

The reaction of perfluoroalkyl iodides with cyclohexene in the presence of catalytic amounts of copper gives addition products at the multiple bond and reduction products.



$R_F = (CF_2)_4Cl$, $(CF_2)_4O(CF_2)_2SO_2F$, $(CF_2)_2O(CF_2)_2SO_2F$.

Table 8. Reactions of bromo- and iodoaromatic compounds with perfluoroalkyl iodides R_FI in the presence of copper.[321]

ArHal	R_F	Reaction conditions			Product	Yield (%)
		solvent	T /°C	t /h		
PhI	n-C_7F_{15}	DMSO	125	23	n-$C_7F_{15}Ph$	78
	n-C_8F_{17}	DMSO	130	15	n-$C_8F_{17}Ph$	83
$C_{10}H_7Br$	n-C_7F_{15}	DMSO	125	34	n-$C_7F_{15}C_{10}H_7$	45
$C_{10}H_7I$	n-C_7F_{15}	DMSO	125	48	n-$C_7F_{15}C_{10}H_7$	89
	n-C_8F_{17}	C_5H_5N	120	16	n-$C_8F_{17}C_{10}H_7$	96

The reactions catalysed by metals (*e.g.*, Zn, Cd) seem to occur *via* the intermediate formation of organometallic compounds, *viz.*, an organozinc compound of the $CF_3ZnBr \cdot L_n$ type (see Ref. 314) or an organocadmium compound,[318] which further generate perfluoroalkyl radicals.

$$Cd + R_FI \xrightarrow[80\ ^\circ C,\ 2-5\ h]{MeCN} \left[(R_F)_2Cd + CdI_2 \rightleftharpoons 2\,R_FCdI\right] \longrightarrow R_F{-}R_F \quad (72\%-90\%)$$

R_F = $F(CF_3)_2C(CF_2)_6$, n-C_6F_{13}, n-C_8F_{17}, $F(CF_3)_2CO(CF_2)_2$, $F(CF_3)_2CO(CF_2)_8$, $EtOC(O)(CF_2)_4O(CF_2)_2$.

Hence the initiation of the cleavage of the C—Hal bond under the action of metals is one of the simplest and convenient methods for the activation of reactions of R_FI with alkenes and alkynes.[288]

It would be natural to expect that a similar effect will be produced by a combination of transition metal salts and zero-valent metals. Indeed, the $NiCl_2 \cdot 6\,H_2O$—Al system efficiently initiates the reactions of R_FI with $R_FCH{=}CH_2$ resulting in the formation of addition products at the multiple bond, albeit, in moderate yields.[323] For example, the yields of the adducts formed in the reaction of alkenes with R_FI in MeCN in the presence of 20 mol. % of $NiCl_2 \cdot 6\,H_2O$ and 2 equiv. Al (25–30 °C, 12 h) (Table 9) were 45%–60%.[323] Zinc can replace aluminium in this reaction.[324]

$$CH_2{=}CHCF_2R_F^1 + R_F^2I \xrightarrow[MeCN,\ 25-30\ ^\circ C]{NiCl_2 \cdot H_2O,\ Al} R_F^2CH_2CHICF_2R_F^1$$

R_F^1 = C_3F_6Cl, $C_5F_{10}Cl$, C_3F_7; R_F^2 = ClC_4F_8, ClC_6F_{12}, ClC_8F_{16}.

An interesting transformation occurred when perfluoroalkyl iodides, -bromides and -chlorides were heated in DMF in the presence of aluminium-promoted Sn^{II} ($SnCl_2$—Al)[325] or Pb^{II} ($PbBr_2$—Al).[326–329] This reaction resulted in the formation of perfluoroalkylaldehyde monohydrates.[325–329]

$$R_FX \xrightarrow[a\ \text{or}\ b]{Me_2NCHO} R_FCH(OH)_2 \xrightarrow{P_2O_5} R_FCHO$$

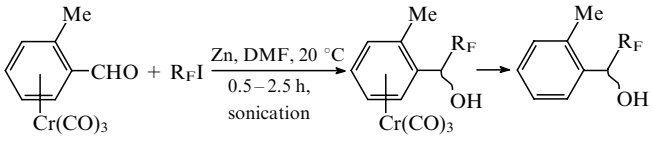
Reagents and conditions	R_FX	Yield (%)	Reagents and conditions	R_FX	Yield (%)
(*a*) $SnCl_2$, Al, 20 °C, 10 h	$Cl(CF_2)_4I$	80	(*b*) $PbCl_2$, Al	$H(CF_2)_4Cl$	80
	$Cl(CF_2)_6I$	97		$H(CF_2)_6Cl$	85
	$Cl(CF_2)_8I$	88		$H(CF_2)_8Cl$	88
	C_4F_9I	90		$CH_2{=}CH(CF_2)_4Cl$	82
	$C_6F_{13}Br$	84		$CH_2{=}CH(CF_2)_6Cl$	86
	$C_8F_{17}Br$	89		$Bu^nCHICH_2(CF_2)_4Cl$	91
				$Bu^nCHICH_2(CF_2)_6Cl$	93

The yields of reaction products and reaction conditions are listed in Tables 10 and 11.

The perfluoroalkylation of DMF by perfluoroalkyl iodides and α,ω-dibromoperfluoroalkanes in the presence of Al—$SnCl_2$ or Al—$PbBr_2$ is strongly accelerated by sonication[330] which has recently found wide application in the activation of organic reactions.[331–333] Thus the reaction occurring under normal conditions usually lasts from 4 to 24 h, whereas that subjected to sonication is completed within 0.25–3 h. The possibility of performing perfluoroalkylation with perfluoroalkyl iodides in the presence of metals (*e.g.*, zinc, magnesium, *etc.*) using sonication has been demonstrated.[255, 334–337]

The reaction of cyclohexanone with C_4F_9I in hexane catalysed by magnesium and activated by sonication results in 1-perfluorobutylcyclohexanol (yield ~ 81%).[336]

Perfluoroalkylation occurs in the presence of zinc in THF and is catalysed by the triphenylphosphine–palladium complex. In the absence of catalysts, the reactions of perfluoroalkyl iodides with compounds containing a carbonyl group are carried out using zinc in DMF. For example, the reaction of perfluoroalkyl iodides with the *o*-tolualdehyde–chromium tricarbonyl **25** complex yields the corresponding alcohols **26** which eliminate $Cr(CO)_3$ to give the alcohols **27**.[338]



25 **26** (85%) **27**

Table 9. Reactions of fluorine-containing alkenes $CH_2{=}CHCF_2R_F^1$ with perfluoroalkyl iodides R_F^2I (25–30 °C, 12 h, molar ratio $R2_FI : NiCl_2 : 6\,H_2O$ = 2.0 : 1.0 : 0.2 or 5.0 : 1.0 : 0.2).[323]

R_F^1	R_F^2	Product	Yield (%)
C_3F_6Cl	ClC_4F_8	$ClC_4F_8CH_2CH{=}CFC_3F_6Cl$	55
	ClC_6F_{12}	$ClC_6F_{12}CH_2CH{=}CFC_3F_6Cl$	56
	ClC_8F_{16}	$ClC_8F_{16}CH_2CH{=}CFC_3F_6Cl$	55
$C_5F_{10}Cl$	ClC_4F_8	$ClC_4F_8CH_2CH{=}CFC_5F_{10}Cl$	58
	ClC_6F_{12}	$ClC_6F_{12}CH_2CH{=}CFC_5F_{10}Cl$	60
	ClC_8F_{16}	$ClC_8F_{16}CH_2CH{=}CFC_5F_{10}Cl$	59
C_3F_7	ClC_6F_{12}	$ClC_6F_{12}CH_2CH{=}CFC_3F_7$	45
	ClC_8F_{16}	$ClC_8F_{16}CH_2CH{=}CFC_3F_7$	50

Table 10. The reaction of perfluoroalkyl iodides with DMF in the presence of the SnE_2—Al system.[325]

R_FX	SnE_2	Reaction conditions		Product	Yield (%)
		T /°C	t /h		
$Cl(CF_2)_4I$	$SnCl_2$	16	6	$Cl(CF_2)_4CHO$	80
	$SnCl_2$	15	10	$Cl(CF_2)_4CHO$	88
	$SnBr_2$	15	6	$Cl(CF_2)_4CHO$	83
$Cl(CF_2)_6I$	$SnCl_2$	15	8	$Cl(CF_2)_6CHO$	97
	$SnBr_2$	15	9	$Cl(CF_2)_6CHO$	75
	SnF_2	15	5	$Cl(CF_2)_6CHO$	85
$Cl(CF_2)_8I$	$SnBr_2$	15	10	$Cl(CF_2)_8CHO$	79
$F(CF_2)_4I$	$SnCl_2$	15	8	$F(CF_2)_4CHO$	90
$F(CF_2)_6Br$	$SnCl_2$	15	12	$F(CF_2)_6CHO$	84
$F(CF_2)_8Br$	$SnCl_2$	15	12	$F(CF_2)_8CHO$	89
	$SnBr_2$	15	15	$F(CF_2)_8CHO$	74
	SnF_2	15	6	$F(CF_2)_8CHO$	90

Table 11. The synthesis of polyfluorinated aldehydes and their monohydrates from perfluoroalkyl halides and DMF in the presence of aluminium-activated salts with and without sonication.[330]

R_FX	Sonication	Time /h	Product	Yield (%)
Catalyst — $SnCl_2$				
C_4F_9I	+	0.25	C_4F_9CHO	41
$C_6F_{13}I$	–	24	$C_6F_{13}CH(OH)_2$, $C_6F_{13}CHO$	80, 65
	+	0.25	$C_6F_{13}CH(OH)_2$, $C_8F_{17}CHO$	60, 65
$C_8F_{17}I_2$	+	0.25	$C_8F_{17}CH(OH)_2$, $C_8F_{17}CHO$	78, 65
$BrC_8F_{16}Br$	+	3	$(HO)_2CHC_8F_{16}CH(OH)_2$, $OCHC_6F_{12}CHO$	90, 69
Catalyst — $PbBr_2$				
C_4F_9I	+	0.25	C_4F_9CHO	50
$C_6F_{13}I$	–	16	$C_6F_{13}CH(OH)_2$, $C_6F_{13}CHO$	74, 65
	+	0.25	$C_6F_{13}CH(OH)_2$, $C_6F_{13}CHO$	70, 62
$C_8F_{17}I$	+	0.25	$C_8F_{17}CH(OH)_2$, $C_8F_{17}CHO$	70, 60
$BrC_6F_{12}Br$	–	4	$(HO)_2CHC_6F_{12}CH(OH)_2$, $OCHC_6F_{12}CHO$	80, 65
	+	1.5	$(HO)_2CHC_6F_{12}CH(OH)_2$, $OCHC_6F_{12}CHO$	87, 60
$BrC_8F_{16}Br$	+	1.5	$(HO)_2CHC_8F_{16}CH(OH)_2$, $OCHC_8F_{16}CHO$	83, 60

More recent studies [338] demonstrated that sonication can be used in reactions of perfluoroalkyl iodides and -bromides with various carbonyl compounds and alkyl halides in the presence of $MnCl_2-Na$ and $AgBr-Li$ systems.[339] This finding has led to the development of a simple procedure for the synthesis of perfluorocarboxylic acids and partially fluorinated secondary alcohols using carbon dioxide and aldehydes, respectively. In this case, sodium and lithium are used as reductants for the formation of active metals (manganese and silver), which yield reactive organometallic derivatives with perfluoroalkyl halides. The organometallic derivatives enter into the reaction with the carbonyl compound.

$$R_FX \xrightarrow[MnCl_2,\ 2\ equiv.\ Na,\ DMF,\ sonication]{1)\ CO_2;\ 2)\ H_3O^+} R_FCO_2H$$

R_FX	i-C_3F_7I	n-C_4F_9I	n-C_4F_9Br	n-$C_6F_{13}I$	n-$C_8F_{17}I$	n-$C_8F_{17}Br$
Yield (%)	41	52	39	62	61	46

$$R_FX \xrightarrow[MnCl_2,\ 2\ equiv.\ Na,\ DMF,\ sonication]{RCHO} R_F\underset{OH}{\overset{R}{C}}$$

R_FX	CF_3I	n-C_4F_9Br	n-C_4F_9I	n-$C_8F_{17}Br$
R	Ph	Ph	C_5H_{11}	Et
Yield (%)	52	51	32	38

The activity of perfluoroalkyl halides decreases in the following order: $R_FI > R_FBr \gg R_FCl$.

The $Sn-AgOAc$ and $Sn-Cu_2Cl_2$ systems effectively catalyse reactions of perfluoroalkyl iodides with alkenes under relatively mild conditions.[284] Methanol is the most suitable solvent for these reactions. Joint use of metallic Sn and Al produces the same effect.

$$CH_2{=}CHR + R_FI \xrightarrow[MeOH,\ 20\ ^\circ C,\ 24\ h]{Sn^0} R_FCH_2CHIR$$

R = $Me(CH_2)_5$, $MeO(CH_2)_2$, $HOCH_2$, $PhCH_2$, $HO(CH_2)_4$, $(EtO_2C)_2CHCH_2$, Me_2CHCH_2; R_F = n-C_4F_9, n-C_6F_{13}.

It was found that the copper acetate–hydrazine hydrate system catalyses reactions of perfluoroalkyl iodides with alkenes and alkynes;[340] the yields of the target products vary from 65% to 90%.

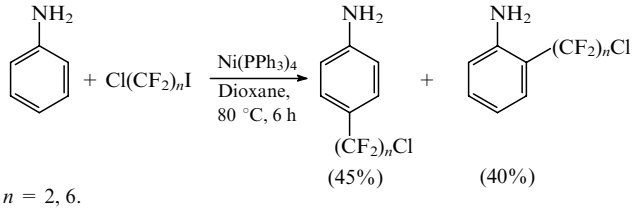
$$R_FI \xrightarrow[Pr^iOH]{Cu(OAc)_2-H_2NNH_2\cdot H_2O} \begin{cases} \xrightarrow{CH_2=CHR} R_FCH_2CHIR \\ \xrightarrow{HC\equiv CR} R_FCH{=}CIR \end{cases}$$

R_F = C_2F_5, n-C_3F_7, iso-C_3F_7, n-C_6F_{13}, $C_3F_7OCFCF_3$
R = CH_2OH, Bu^n, n-C_6F_{13}.

R_F = n-C_3F_7, iso-C_3F_7,
R = CH_2OH.

The $KI-CuSO_4$ system is also active in these reactions.[341] In the presence of this system, cupric perfluoroalkanesulfinates react with alkenes with the formation of addition products at the multiple bond, *viz.*, $R_FSO_2CH_2CHIR$.

Nickel complexes effectively catalyse the perfluoroalkylation of aromatic compounds under the action of polyfluoroalkyl iodides.[342]



n = 2, 6.

It was found [343] that the Cp_2TiCl_2-Fe system catalyses the reactions of perfluoroalkyl iodides XCF_2CF_2I (X = Cl, Br) with alkenes and alkynes which yield 1 : 1 adducts.[343–345] The use of octa-1,7-diene (**28**) as an alkene results in the involvement of only one multiple bond and the formation of the adduct **29**.

$$CH_2{=}CH(CH_2)_4CH{=}CH_2 + R_FI \xrightarrow[50-65\ ^\circ C,\ 8-15\ h]{Cp_2TiCl_2-Fe} \underset{\mathbf{28}}{} \longrightarrow \underset{\mathbf{29}}{R_FCH_2CHI(CH_2)_4CH{=}CH_2}$$

R_F = ClC_4F_8 (87%), C_4F_9 (88%), $(CF_2)_2CF$ (92%), CF_2ClCF_2 (90%).

In the presence of 30 mol.-equiv. of Fe and 2 mol.-equiv. of Cp_2TiCl_2, 1,2-dihalogenotetrafluoroethane CF_2BrCF_2X (X = I, Br) reacts with alkenes in EtOH under a nitrogen atmosphere to give addition products in excellent yields (Table 12). The experimental results provide support for a radical mechanism of this reaction. In the perfluoroalkylation induced by CF_2BrCF_2X in the presence of Cp_2TiCl_2 as a catalyst, 2-bromotetrafluoroethyl radical can be formed, apparently according to the following scheme:[346, 347]

$$Ti^{IV} + Fe^0 \longrightarrow Ti^{III} + Fe^I,$$

$$Ti^{III} + CF_2BrCF_2X \longrightarrow CF_2BrCF_2X^{-\bullet} + Ti^{IV}$$

$$\downarrow$$

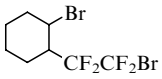
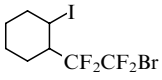
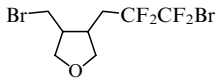
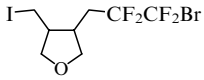
$$CF_2BrC^{\bullet}F_2 + X^-,$$

$$CF_2BrC^{\bullet}F_2 + R^1CH{=}CHR^2 \longrightarrow CF_2BrCF_2CHR^1C^{\bullet}HR^2 \xrightarrow{CF_2BrCF_2X}$$

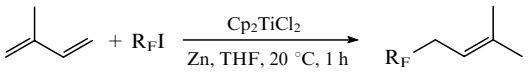
$$\longrightarrow CF_2BrCF_2CHR^1CHXR^2 + CF_2BrC^{\bullet}F_2\,.$$

Table 12. Reactions of alkenes with 1,2-dihalogenotetrafluoroethane induced by the Cp_2TiCl_2-Fe system.[345]

$CF_2BrCF_2X + R^1CH{=}CHR^2 \longrightarrow CF_2BrCF_2CHR^1CHXR^2$

Alkene	R_FX	T /°C	t /h	Product	Yield (%)
Oct-1-ene	CF_2BrCF_2I	55	10	$CF_2BrCF_2CH_2CHIC_6H_{13}$	96
	CF_2BrCF_2I	25	15	$CF_2BrCF_2CH_2CHIC_6H_{13}$	91
	CF_2BrCF_2Br	55	15	$CF_2BrCF_2CH_2CHBrC_6H_{13}$	95
Hex-1-ene	CF_2BrCF_2Br	60	15	$CF_2BrCF_2CH_2CHBrC_4H_9$	93
Hexa-1,5-diene	CF_2BrCF_2Br	60	26	$CF_2BrCF_2CH_2CHBr(CH_2)_2CH{=}CH_2$	78
Cyclohexene	CF_2BrCF_2Br	70	36		92
	CF_2BrCF_2I	65	24		92
Allyl alcohol	CF_2BrCF_2I	65	13	$CF_2BrCF_2CH_2CHICH_2OH$	96
Diallyl ether	CF_2BrCF_2Br	60	8		95
	CF_2BrCF_2I	55	7		94

Dichlorobis(cyclopentadienyl)titanium(IV) catalyses the perfluoroalkylation of isoprene by perfluoroalkyl iodides in the presence of zinc in THF or DMF at room temperature, resulting in the reductive addition product at one multiple bond.[334] This reaction is activated by sonication.



Zinc used as a catalyst in the reaction of perfluoroalkyl iodides with alkenes initiates addition and reduction reactions as well as dimerisation of transient radicals.[335] The ratio of reaction products changes when the reaction is carried out in CH_2Cl_2. As in the case with AIBN, only the addition product is formed in the presence of iron in DMF.

$$CH_2{=}CH(CH_2)_mR + R_FI \longrightarrow$$

$$\xrightarrow[H^+]{Zn} R_FCH_2CH_2(CH_2)_mR + R_FCH_2\underset{\displaystyle R_FCH_2CH(CH_2)_mR}{\underset{|}{C}}H(CH_2)_mR$$

$$\xrightarrow[DMF]{Fe} R_FCH_2CHI(CH_2)_mR$$

$R_F = C_6F_{13}, C_8F_{17}$; R = CO_2H, CH_2OH; m = 0, 2, 8.

The cyclopentanedienyldicarbonyl iron dimer is yet another efficient catalyst of the reaction of perfluoroalkyl iodides with alkene derivatives.[348, 349]

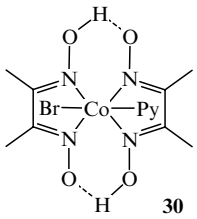
$$CH_2{=}CHR + R_FI \xrightarrow[Et_3N,\ EtOH,\ 25\ ^\circ C]{[CpFe(CO)_2]_2} R_FCH_2CH_2R$$

$R_F = F(CF_2)_n$ (n = 4, 6, 8), $Cl(CF_2)_6$; R = CO_2Et, CN, COMe.

$$CH_2{=}CHOEt + CF_3(CF_2)_5I \xrightarrow[Et_3N,\ EtOH,\ 25\ ^\circ C]{[CpFe(CO)_2]_2} CF_3(CF_2)_5CH_2CH_2OEt \quad (63\%-95\%)$$

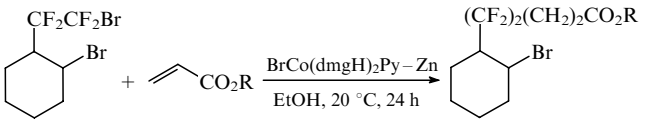
$R_F = C_8F_{17}, C_3F_7, CF(CF_3)_2$.

Successful perfluoroalkylation of alkenes containing electron-accepting substituents (*e.g.*, acrylates, acrylonitrile, methyl vinyl ketone, *etc.*) was carried out with Zn-bis(dimethylglyoxymate)-pyridinecobalt(II) bromide [$BrCo(dmgH)_2Py$, **30**] in ethanol as a catalyst (Table 13).[205, 256, 259, 343, 350–354] This reaction also involved ozone-destroying bromoperfluoroalkanes (bromofreons), which are now prohibited for use. Owing to relatively mild reaction conditions, this method is especially convenient for the synthesis of carboxylic acid esters, nitriles and ketones containing a perfluoroalkyl fragment. Zinc powder was used as a reductant in the reaction catalysed by $BrCo(dmgH)_2Py$ (**30**).[205, 343]



30

The system **30**–Zn was found to be efficient in reactions of $BrCF_2CF_2CH{=}CHCH_2X$ (X = Cl, AcO) with alkynes $HC{\equiv}CR$ (R = Ph, CH_2OH, C_5H_{11}). The yield of the cyclisation products, *viz.*, 4,4,5,5-tetrafluoro-3-vinylcyclopentenes, varied from 40% to 50%.[343] In the presence of this system, cyclic polyfluoroalkyl bromides react smoothly with alkenes.



Zinc itself can exert a pronounced effect on the reactions of alkenes with perfluoroalkyl iodides. For example, the reaction of $Me(CH_2)_4CH{=}CH_2$ with $CF_3(CF_2)_3I$ yielded 90% of $Me(CH_2)_4$. $.CHICH_2(CF_2)_3CF_3$.[351]

The system **30**–Zn was used for perfluoroalkylation of alkenes by perfluoroalkyl iodides and -bromides.[256, 259, 344] Thus perfluoroalkylation of various cyclic, linear, symmetric or asymmetric alkenes with Freon-2402 (1,2-dibromo-1,1,2,2-tetrafluoroethane) resulted in derivatives containing a CF_2CF_2 fragment.[354, 355] It may be noted that the activation of the C–Br bond, *e.g.*, in RCF_2CF_2Br, by cobalt in the low valent state generated *in situ* occurs with high efficiency, which made it possible to induce reactions of these compounds with unsaturated substrates.[259]

Table 13. Perfluoroalkylation of alkenes by perfluoroalkyl iodides in the presence of the catalytic system **30** – Zn.[354]

Alkene	R_FX	T /°C	t /h	Product	Yield (%) (E : Z)
$H_2C=CHCO_2Et$	$Cl(CF_2)_6I$	15	0.5	$R_FCH_2CH_2CO_2Et$	56
	$F(CF_2)_4I$	20	0.5	$R_FCH_2CH_2CO_2Et$	71
	$F(CF_2)_6I$	20	0.5	$R_FCH_2CH_2CO_2Et$	72
	$F(CF_2)_8I$	20	0.5	$R_FCH_2CH_2CO_2Et$	75
	CF_2ClCF_2I [a]	65	10	$R_FCH_2CH_2CO_2Et$	92
	CF_2BrCF_2Br	75	11	$R_FCH_2CH_2CO_2Et$	93
	$CF_2BrCFClBr$	50	10	$R_FCH_2CH_2CO_2Et$	90
	CF_2Br_2	70	24	$R_FCH_2CH_2CO_2Et$	90
$H_2C=CHCN$	$Cl(CF_2)_4I$	30	2	$R_FCH_2CH_2CN$	61
	CF_2BrCF_2I	65	10	$R_FCH_2CH_2CO_2Et$	93
	$C_6F_{13}I$	30	2.5	$R_FCH_2CH_2CN$	71
	$C_8F_{17}I$	30	3	$R_FCH_2CH_2CN$	69
	$C_6F_{13}Br$	30	3.5	$R_FCH_2CH_2CN$	75
	$C_8F_{17}Br$	30	4	$R_FCH_2CH_2CN$	70
$H_2C=CHC(O)Me$	$Cl(CF_2)_6I$	30	5	$R_FCH_2CH_2C(O)Me$	45
	C_4F_9I	25	4	$R_FCH_2CH_2C(O)Me$	49
	$C_6F_{13}I$	30	3.5	$R_FCH_2CH_2C(O)Me$	64
	$C_6F_{13}Br$	45	5	$R_FCH_2CH_2C(O)Me$	72
	$C_8F_{17}Br$	45	5	$R_FCH_2CH_2C(O)Me$	53
$HC\equiv CCO_2Et$	ClC_4F_8I	25	8	$R_FCH=CHCO_2Et$	85 (26 : 74)
	C_4F_9I	20	7	$R_FCH=CHCO_2Et$	73 (9 : 91)
	$C_6F_{13}Br$	30	7	$R_FCH=CHCO_2Et$	76 (30 : 70)
	$C_8F_{17}Br$	30	10	$R_FCH=CHCO_2Et$	65 (28 : 72)

[a] The reaction was carried out in the presence of the catalytic system Cp_2TiCl_2 – Fe.

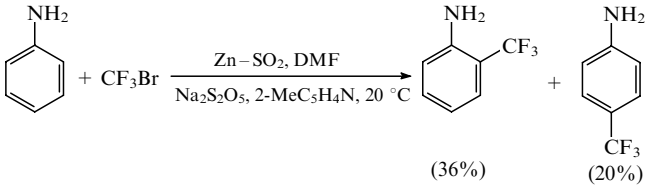
The (diethoxyphosphoryl)difluoromethyl group was successfully introduced into alkenes containing electron-withdrawing substituents by the reaction with $(EtO)_2P(O)CF_2Br$ in the presence of the system **30** – Zn.[344, 346–348]

$$CH_2{=}CHX \xrightarrow{\textbf{30}-Zn,\ (EtO)_2P(O)CF_2Br} (EtO)_2P(O)CF_2(CH_2)_2X$$

X = CO_2Et, CO_2H, CN, CH_2Cl, $CONH_2$, COMe, OAc, OEt, CO_2Me, Bu^n.

The yield of the reaction products increases after addition of 1 equiv. of $HCOONH_4$. Apparently, the surface of zinc is activated by ammonium ions. Other ammonium salts, *e.g.*, NH_4Cl, NH_4Br and NH_4OAc, can also be used for this purpose; however, the yields of the reaction products are lower.

Reduction of commercial Freon-1301 (bromotrifluoromethane) to the trifluoromethyl radical possessing electrophilic character using the Zn – SO_2 system in DMF in the presence of $Na_2S_2O_5$ and bases (Na_2HPO_4, 2-methylpyridine) was a step forward on the way to trifluoromethylation of aromatic and heterocyclic compounds.[138, 171, 267, 353, 355–357] Thus the reaction of CF_3Br with aniline in the presence of this system gives a mixture of *ortho*- and *para*-trifluoromethylanilines with the *ortho*-isomer prevailing.

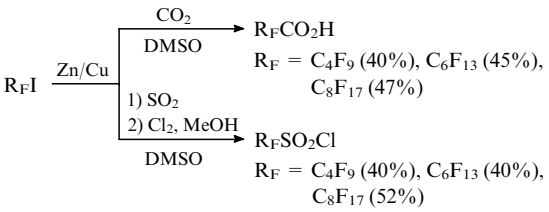


Trifluoromethylation of pyrrole and *N*-methylpyrrole occurs at position 2.

In the presence of this system, perfluoroalkyl iodides $F(CF_2)_nI$ (n = 1, 2, 4, 6, 8) efficiently react with aromatic compounds containing electron – donor substituents (phenols, anisole, anilines, aminophenols, toluene) and pyrrole.

$$ArH + R_FI \xrightarrow[B:]{Zn-SO_2} ArR_F + BH^{+\bullet}\,I^-$$

The reaction of perfluoroalkyl iodides with CO_2 in the presence of the Zn/Cu couple in DMSO results in perfluorinated carboxylic acid, this presents special interest.[358–360] An analogous reaction with SO_2 gives the corresponding perfluoroalkanesulfonyl chlorides.[360]



Some metal halides can effectively catalyse perfluoroalkylation reactions. Thus the redox system $CrCl_3$ – Fe in ethanol promotes the perfluoroalkylation of alkenes containing electron-withdrawing substituents[256, 347, 361, 362] under the action of CF_2Br_2 (Table 14),[205] CF_3Cl or $ICHFCO_2R$ (R = Me, Et) at 60 – 70 °C.[287]

$$CH_2{=}CHR^1 + ICHFCO_2R^2 \xrightarrow[EtOH]{CrCl_3-Fe\cdot 6H_2O} R^2O_2CCHFCH_2CH_2R^1$$

R^1 = CO_2Me (71%), CO_2Et (78%), CN (74%), COMe (75%);

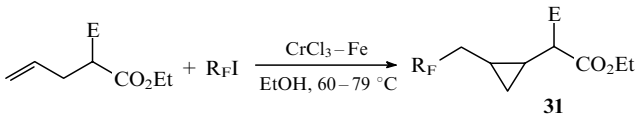
R^2 = Me, Et.

The $CrCl_3$ – Fe system is efficient in the reaction of perfluoroalkyl iodides $Cl(CF_2)_nI$ (n = 2, 4, 6, 8), C_4F_9I, $C_6F_{13}I$ and $C_8F_{17}I$ with methyl α-acetylaminoacrylate resulting in β-perfluoroalkyl-α-amino acid derivatives $R_FCH_2CH(NHAc)CO_2Me$ in 65% to 80% yields. The reaction of perfluoroalkyl iodides with diethyl allylmalonate and its analogues in the presence of the $CrCl_3$ – Fe system gives perfluoroalkylmethyl-substituted derivatives of

Table 14. Reactions of alkenes containing electron-withdrawing substituents with CF_2Br_2 in the presence of the $FeCrCl_3$ system in EtOH.[205]

Alkene	T /°C	t /h	Product	Yield (%)
$CH_2=CHCO_2Et$	60	20	$CF_2Br(CH_2)_2CO_2Et$	72
$CH_2=CHCO_2Me$	60	20	$CF_2Br(CH_2)_2CO_2Me$	62
$CH_2=C(Me)CO_2Et$	60	24	$CF_2BrCH_2CH(Me)CO_2Et$	80
$MeCH=CHCO_2Et$	75	24	$CF_2BrCH(Me)CH_2CO_2Et$	43
$CH_2=CHCO_2H$	65	20	$CF_2Br(CH_2)_2CO_2H$	64
$CH_2=CHCONH_2$	70	20	$CF_2Br(CH_2)_2CONH_2$	72
$CH_2=CHCN$	60	18	$CF_2Br(CH_2)_2CN$	62
$CH_2=CHCOMe$	60	20	$CF_2Br(CH_2)_2COMe$	60
$CH_2=CHBu^n$	60	10	$CF_2BrCH_2CHBrBu^n$	96
$CH_2=CHC_6H_{13}$-n	60	10	$CF_2BrCH_2CHBrC_6H_{13}$-n	84
$CH_2=CH(CH_2)_2CH=CH_2$	60	6	$CF_2BrCH_2CHBr(CH_2)_2CH=CH_2$	72
$CH_2=CH(CH_2)_2Ac$	60	13	$CF_2BrCH_2CHBr(CH_2)_2Ac$	64
$CH_2=CH(CH_2)_8CO_2Me$	60	8	$CF_2BrCH_2CHBr(CH_2)_8CO_2Me$	64
$CH_2=CHCH_2OAc$	60	12	$CF_2BrCH_2CHBrCH_2OAc$	30
	12	8	$CF_2BrCH_2CHBr(CH_2)_3Me$	74

cyclopropane **31** in high yields.[355, 356] Ethanol is the best solvent for this reaction.

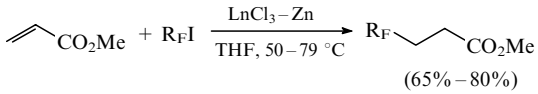


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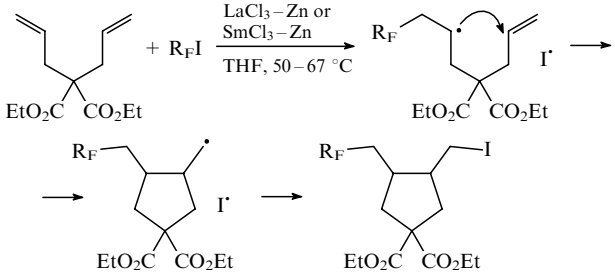
R_F	E	Yield (%)	R_F	E	Yield (%)
C_2F_5	CO_2Et	89	C_6F_{13}	COMe	92
C_6F_{13}	CO_2Et	92	C_4F_9	CN	76
C_8F_{17}	CO_2Et	85	C_8F_{17}	CN	70
C_4F_9	COMe	87	C_6F_{13}	CN	69
C_8F_{17}	COMe	85			

The $YbCl_3-Zn$ and $LnCl_3-Zn$ systems produce a similar effect.[138, 251, 254, 256] Thus the reaction of perfluorohexyl iodide with $CH_2=CHCH_2OAc$ in THF in the presence of the $YbCl_3-Zn$ system results in $F(CF_2)_6(CH_2)_3OAc$ in 95% yield. This can be explained by the fact that the primary addition product to the double bond undergoes reductive deiodination.

The efficiency of the $YbCl_3-Zn$ system in catalytic reactions of perfluoroalkyl iodides with alkenes was studied (Table 15).[250–256] This reaction is completed within several minutes in tetrahydrofuran but does not take place in EtOH or benzene.



The reaction of substituted hepta-1,6-diene with perfluoroalkyl iodide in the presence of the $LaCl_3-Zn$ or $SmCl_3-Zn$ system is accompanied by cyclisation involving the second double bond and results in a mixture of the corresponding *cis*- and *trans*-3-iodomethyl-4-perfluoroalkylmethyl-1,1-di(ethoxycarbonyl)cyclopentanes (4 : 1).[138]



$R_F = ClC_4F_8$, ClC_6F_{12}, C_6F_{13}, C_8F_{17}.

The $NiCl_2 \cdot 6\,H_2O-Zn$ system in THF proved to be efficient in the reaction of iodofluoroacetates with alkenes resulting in δ-iodo esters in good yields.[251–253] In the case of perfluoroalkyl chlorides, the hydrogen atom is substituted for chlorine.[252]

Activation of perfluoroalkyl iodides by transition metal complexes. Transition metal complexes can also efficiently activate perfluoroalkyl iodides.

Perfluoroalkanesulfonyl chlorides $F(CF_2)_nSO_2Cl$ ($n = 1-20$) and pentafluorobenzenesulfonyl chloride can replace perfluoroalkyl iodides in perfluoroalkylation and arylation reactions of aromatic and heterocyclic compounds and alkenes with $(Ph_3P)_3RuCl_2$ as a catalyst.[355, 363–367]

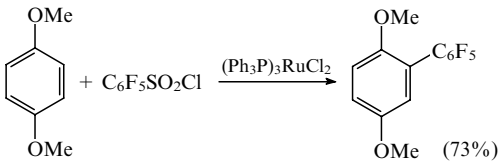


Table 15. Perfluoroalkylation of alkenes with perfluoroalkyl iodides in the presence of the $YbCl_3Zn$ system.[251]

Alkene	R_F	Time /min	Product	Yield (%)
$CH_2=CHCH_2OAc$	$F(CF_2)_6$	6	$F(CF_2)_6(CH_2)_3OAc$	95
$CH_2=CHCH_2OH$	$F(CF_2)_6$	7	$F(CF_2)_6(CH_2)_3OH$	56
$CH_2=CHCH_2P(O)(OEt)_2$	$F(CF_2)_6$	10	$F(CF_2)_6(CH_2)_3P(O)(OEt)_2$	60
$CH_2=CHC_6H_{13}$-n	$Cl(CF_2)_8$	10	$Cl(CF_2)_8(CH_2)_2C_6H_{13}$	58

Note: The alkene : R_FI : $YbCl_3$: Zn molar ratio is 1.00 : 1.00 : 0.05 : 0.50.

$$ArH + R_FSO_2Cl \xrightarrow[120\ ^\circ C,\ 19\ h]{(Ph_3P)_3RuCl_2} ArR_F + SO_2$$

R_F	Ar	Yield (%)	R_F	Ar	Yield (%)
CF_3	Ph	41	C_6F_{13}	Ph	44
CF_3	MeC_6H_4	36	C_6F_{13}	MeC_6H_4	54
CF_3	$MeOC_6H_4$	58	C_6F_{13}	$MeOC_6H_4$	59
CF_3	1,4-$Me_2C_6H_3$	63	C_6F_{13}	1,4-$Me_2C_6H_3$	41
C_6F_{13}	1,4-$(MeO)_2C_6H_3$	71			

The addition product to the double bond is formed in the reaction with alkenes.[301, 368, 369]

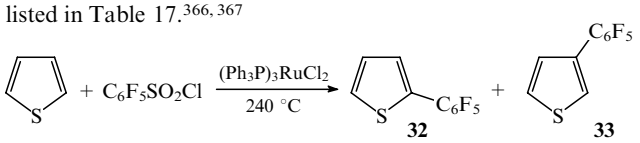
This catalytic system was effective in perfluoroalkylation of arenes [363, 364, 370, 371] and enol silyl ethers by perfluoroalkanesulfonyl chlorides (Table 16).[366]

Table 16. Reactions of aromatic compounds with pentafluorobenzenesulfonyl chloride in the presence of $(Ph_3P)_3RuCl_2$ at 240 °C.[366]

Substrate	Time /h	Product	Yield (%)
PhH	24	C_6F_5Ph	73
PhOMe	4	$C_6F_5C_6H_4OMe$ [б]	14
PhCl	8	$C_6F_5C_6H_4Cl$ [b]	87
PhCN	4	$C_6F_5C_6H_4CN$ [c]	39
p-$Me_2C_6H_4$	4	$C_6F_5C_6H_3Me_2$	59
p-$MeC_6H_4CHMe_2$	4	$MeC_6H_3(C_6F_5)CHMe_2$	14
p-$(MeO)_2C_6H_4$	2	$C_6F_5C_6H_3(OMe)_2$	5

[a] The ratio of the *ortho* : *meta* : *para* isomers is 43 : 16 : 41.
[b] The ratio of the *ortho* : *meta* : *para* isomers is 42 : 31 : 27.
[c] The ratio of the *ortho* : *meta* : *para* isomers is 27 : 43 : 30.

Perfluorophenylation of various thiophene derivatives by $C_6F_5SO_2Cl$ in the presence of the $(Ph_3P)_3RuCl_2$ complex was studied under similar conditions. The results of these studies are listed in Table 17.[366, 367]



32 **33**

Perfluoroalkyl iodides add to alkenes in the presence of the Wilkinson catalyst [tris(triphenylphosphine)rhodium chloride] at 80 °C.[298, 372] This catalyst ensures high chemoselectivity under mild reaction conditions.

$$CH_2{=}CHC_5H_{11} + Cl(CF_2)_4I \xrightarrow[PhH,\ 1.5\ h]{(Ph_3P)_3RhCl} Cl(CF_2)_4CH_2CHIC_5H_{11}\ (75\%)$$

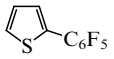
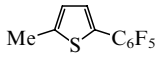
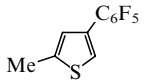
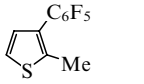
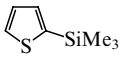
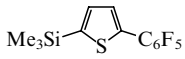
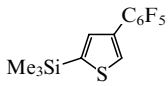
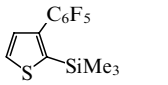
$$CH_2{=}CR^1R^2 + R_FI \xrightarrow{(Ph_3P)_3RhCl} R_FCH_2CIR^1R^2\ (80\%-95\%)$$

R_F = $Cl(CF_2)_4$, $F(CF_2)_4$, $Cl(CF_2)_6$, $Cl(CF_2)_2$;
R^1 = n-C_5H_{11}, n-C_6H_{13}, Bu^n, Me_2CHCH_2, Et; R^2 = H, Me.

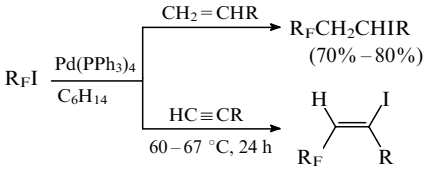
Perfluoroalkyl iodides R_FI [R_F = $Cl(CF_2)_4$, $Cl(CF_2)_6$, $CF_3(CF_2)_3$] react with alkenes and alkynes in the presence of $Ir(H)(CO)(PPh_3)_3$. The addition reaction to the triple bond yields predominantly *E*-isomers.[358]

The perfluoroalkyl radical $R_F^{\bullet}$ generated from perfluoroalkyl iodides in the presence of metals or transition metal complexes reacts smoothly with alkenes containing both electron-donor and electron-withdrawing substituents. As in the case of sulfinatodehalogenation, these complexes effectively catalyse the addition of perfluoroalkyl halides to both types of alkenes.

Table 17. Reactions of thiophene and its derivatives with pentafluorobenzenesulfonyl chloride in the presence of $(Ph_3P)_3RuCl_2$.[366]

Substrate	Product	Yield (%)
		22
		6
		14
		5
		7
		39
		17
		11

Tetrakis(triphenylphosphine)palladium is also efficient in reactions of perfluoroalkyl iodides with alkenes and alkynes in hexane.[278, 302, 305, 310, 373–376]



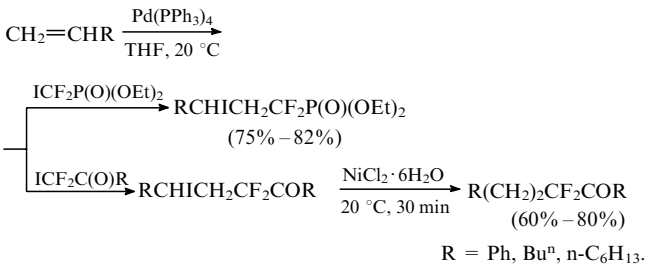
R_F = $CF_3(CF_2)_3$, $CF_3(CF_2)_2$, $CF_3(CF_2)_5$; R = $(CH_2)_2OH$, Ph, n-C_6H_{13}, $SiMe_3$, Bu^n, CH_2SiMe_3, $(CH_2)_2CO_2Me$, CH_2OH.

For example, chlorododecafluorohexyl iodide reacts with hept-2-ene in the presence of 0.5 mol.% Pd^0 (20 min, 20 °C) resulting in the addition product (yield 97%). An increase in temperature from 20 to 100 °C has little effect on this reaction.

The trialkylstannyl group at the carbon atom of the multiple bond can be replaced by the perfluoroalkyl group by treatment with perfluoroalkyl iodide in the presence of $Pd(PPh_3)_4$.[377] Thus the reaction of (*E*)-$PhCH{=}CHSnBu^n_3$ with perfluorobutyl iodide in the presence of $Pd(PPh_3)_4$ in hexane with boiling for 4 min results in (*E*)-$PhCH{=}CHC_4F_9$ in 68% yield.[297, 377]

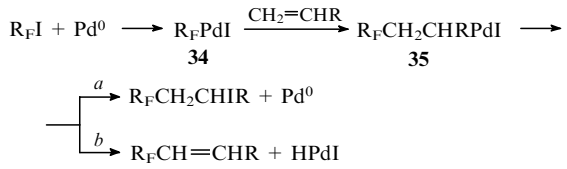
A mixture of *cis*- and *trans*-ethers $R_FCH{=}CHOR$ (yields 51%–86%) is formed in the reaction of R_FI (R_F = CF_3, C_3F_7, C_6F_{13}) with $CH_2{=}CHOR$ (R = H, Bu^n) in hexane in the presence of $Pd(PPh_3)_4$ and Et_3N.[378]

α,α-Difluoro-substituted esters of carboxylic and phosphonic acids are prepared by the reaction of iodo-substituted derivatives of these acids with alkenes in the presence of $Pd(PPh_3)_4$. Subsequent treatment of the iodo-substituted derivative with $NiCl_2 \cdot 6\ H_2O$ results in the formation of the reduction product.[158, 250–256]



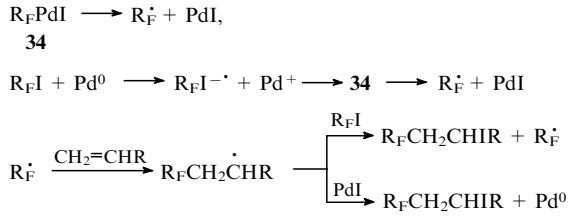
Zero-valent palladium also catalyses the reactions of aryl- or alkenyl halides with alkenes resulting in addition products.[379]

Most probably, the complex **34**, which is formed first, yields an organopalladium derivative **35** in reactions with alkene.[380] Its further transformations can include reduction of palladium to Pd^0 with the formation of an addition product to the multiple bond (route *a*) or elimination of the hydrogen atom from the β-position under the action of palladium eventually resulting in a new alkene (route *b*).



Palladium(0) is the only possible reagent in the formation of a radical anion of perfluoroalkyl iodide (reduction) which yields the perfluoroalkyl radical initiating further conversions. The formation of a cyclic system in the reaction of perfluoroalkyl iodide with diallyl ether in the presence of Pd^0 provides strong evidence in favour of the radical mechanism of this reaction.

On the other hand, this reaction may occur *via* the generation of the perfluoroalkyl radical upon decomposition of the complex **34**. The perfluoroalkyl radical further reacts with alkene to give the target product.

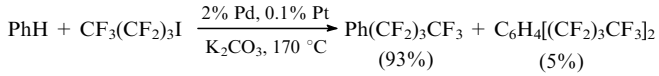


The EPR spectra of perfluoroalkyl radicals generated in these reactions could not be recorded because of their high reactivity and low concentration.[278] However, the use of *N*-benzylidene-*tert*-butylamine *N*-oxide as a spin trap made it possible to obtain well-resolved EPR spectra in which the trapped $[Cl(CF_2)_4]^{\bullet}$ radical could be detected as the radical $[Cl(CF_2)_4CH(Ph)N(O^{\bullet})Bu^t]$.[278] These findings provide evidence both for the electron transfer in this reaction and the oxidation of Pd^0 by perfluoroalkyl iodide resulting in the formation of a perfluoroalkyl palladium complex of the type **34** as occurring with the formation of a transient radical.

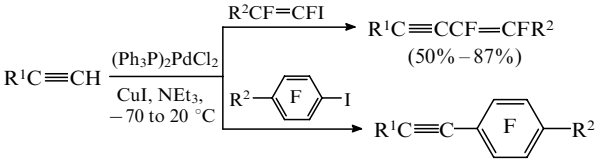
Fluorine-containing aliphatic mono- and dicarboxylic acids were obtained by the reaction of perfluoroalkyl iodides or -bromides with CO_2 in the presence of the Group VIII transition metal complexes and subsequent hydrolysis of the reaction products.[381,382] Thus $CF_3(CF_2)_7CO_2H$ was isolated in 40% yield upon hydrolysis of the reaction product of $CF_3(CF_2)_7I$ with CO_2 in DMF in an autoclave in the presence of $Pd(PPh_3)_4$ at 60 °C. This suggests the intermediate formation of the perfluoroalkyl radical which further reacts with carbon dioxide.

When the reaction is carried out in the presence of alkenes and a CO_2 source, the intermediate radical formed as the product of addition of the perfluoroalkyl radical to the multiple bond reacts further with CO_2 to yield a carboxylic acid. With alcohol as a solvent, this reaction gives the corresponding ester. Thus the reaction of hex-1-ene with $C_8F_{17}I$ in the presence of K_2CO_3 and dichlorobis(triphenylphosphine)palladium in ethanol (12 h, 80 °C) gives $C_8F_{17}CH_2CHBuCO_2Et$ in 67% yield.[383,384]

Perfluoroalkylation of aromatic compounds by perfluoroalkyl iodides can be carried out in the presence of zero-valent transition metals (*e.g.*, Rh, Pd, Pt, Ru, Cu, Ni, Re) and aqueous K_2CO_3.[385] The yields of disubstituted products are usually low.

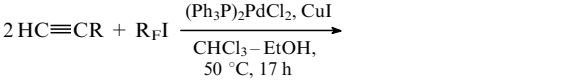


On the other hand, the reaction of perfluorovinyl- and polyfluoroaryl iodides with alkynes in the presence of the $(Ph_3P)_2PdCl_2-CuI$ complex results in the formation of addition products to the triple bond and elimination of HI.[361,373–376]



R^1 = OMe, NMe_2, F, Br; R^2 = $(CH_2)_nMe$ (n = 3–6), Ph, $(CH_2)_3CN$, CH_2OPh, CH_2OH, CH(OH)Me.

The reaction of perfluoroalkyl iodides with alkynes in the presence of a palladium catalyst and bases (*e.g.*, K_2CO_3, Et_3N) yields mixtures of enynes and alkenes.[386] The co-catalyst CuI increases the yield of enynes. The best results are attained when the $CHCl_3-EtOH$ mixture (5 : 1) is used as a solvent.



R_F	R	Yield (%)		
		36	**37**	**38**
n-C_8F_{17}	Bu^n	74	3	7
n-C_3F_7	$SiMe_3$	70	–	–

These reactions occur smoothly without complications and allow for high variability of functional groups without resorting to the use of toxic or hazardous reagents.

Palladium derivatives efficiently catalyse the reactions of perfluoroalkyl halides with allylic alcohols which occur in the presence of K_2CO_3 and result in the formation of polyfluoroalkyl-substituted oxiranes (Table 18).[386]

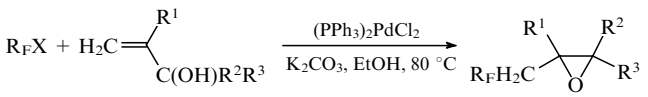
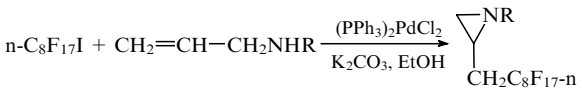


Table 18. Reactions of allylic alcohols $H_2C=CR^1C(OH)R^2R^3$ with perfluoroalkyl iodides R_FI in EtOH in the presence of $(Ph_3P)_2PdCl_2$.[386]

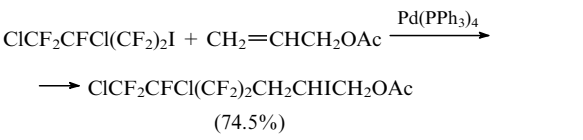
R^1	R^2	R^3	R_F	Yield of oxirane (%)
H	H	H	n-C_8F_{17}	70
H	H	Me	n-C_8F_{17}	71
H	Me	Me	n-C_8F_{17}	79
H	H	n-C_6H_{13}	CF_3	63
H	H	n-C_6H_{13}	C_2F_5	71
H	H	n-C_6H_{13}	n-C_3F_7	77
H	H	n-C_6H_{13}	n-C_4F_9	72
H	H	n-C_6H_{13}	n-C_6F_{13}	74
H	H	n-C_6H_{13}	$CF_2ClCFCl$	56

Similarly, perfluorooctylmethyl-substituted aziridines are obtained in the reaction of perfluorooctyl iodide with allylamines under identical conditions.

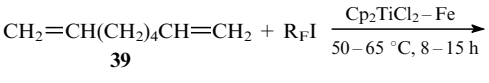


R = H (35%), Ph (41%).

On the other hand, the addition product to the multiple bond is formed in the reaction of perfluoroalkyl halides with allyl acetate in the presence of $Pd(PPh_3)_4$.[382]



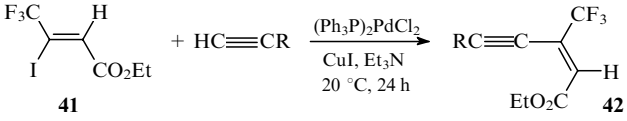
It was found [328] that the dichlorobis(η-cyclopentadienyl)titanium(IV)–iron system efficiently catalyses the reactions of perfluoroalkyl iodides and -bromides with octa-1,7-diene (**39**). This reaction gives addition products to one multiple bond (**40**).



R_F = ClC_4F_8 (87%), C_4F_9 (88%), $(CF_2)_2CF$ (92%), CF_2ClCF_2 (90%), CF_2BrCF_2 (91%), $CF_2ClCFCl$ (81%).

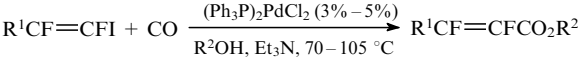
The Cp_2TiCl_2–Zn system is also efficient in reactions of allyl bromide with carbonyl compounds.[329]

Ethyl-4,4,4-trifluoro-3-iodo-(*Z*)-crotonate (**41**) is a valuable synthon in the synthesis of compounds containing the trifluoromethyl group. The reaction of alkynes with the ester **41** in the presence of $Pd(PPh_3)_2Cl_2$ results in compound **42** which contains a conjugated system of double and triple bonds in addition to the CF_3 group.[387, 388]



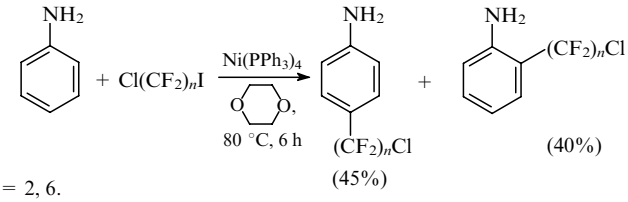
R = $SiMe_3$ (76%), Ph (87%), $(CH_2)_7Me$ (92%), 4-$MeOC_6H_4$ (93%), 4-$NO_2C_6H_4$ (88%), $(CH_2)_5Me$ (93%), $(CH_2)_3Me$ (91%).

The reaction of (*E*)- and (*Z*)-1,2-difluoro-1-iodoalkenes and (*E*)- and (*Z*)-α,β-difluoro-β-iodostyrenes with carbon monoxide in the presence of $Pd(PPh_3)_2Cl_2$ as the catalyst, an alcohol and trialkylamine on heating yields carboxylic acid esters.[389]



Configuration	R^1	Product	*T* /°C	Yield (%)
Z	Bu^t	(*E*)-$Bu^tCF=CFCO_2Bu$	105	85
Z	Bu^s	(*E*)-$Bu^sCF=CFCO_2Bu$	105	92
Z	Ph	(*E*)-$PhCF=CFCO_2Bu$	105	89
E	Bu^n	(*Z*)-$Bu^nCF=CFCO_2Et$	95	82
Z	4-$MeOC_6H_4$	(*E*)-4-$MeOC_6H_4CF=CFCO_2Bu$	80	86
Z	4-CNC_6H_4	(*E*)-4-$CNC_6H_4CF=CFCO_2Bu$	80	96
Z	4-$CF_3C_6H_4$	(*E*)-4-$CF_3C_6H_4CF=CFCO_2Bu$	80	89
E	4-$MeOC_6H_4$	(*Z*)-4-$MeOC_6H_4CF=CFCO_2Bu$	70	86

Nickel complexes also efficiently catalyse perfluoroalkylation of aromatic compounds.[342]



n = 2, 6.

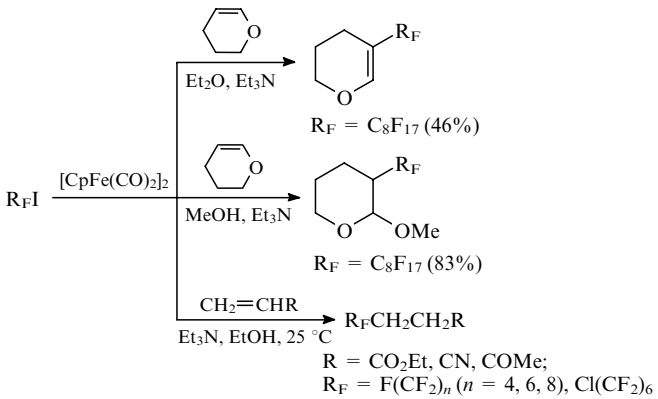
The search for novel methods for the synthesis of fluoroorganic compounds was based on the use of accessible carbonyls of zero-valent metals. It was found that carbonyl complexes of the Group VIII transition metals can efficiently catalyse the reaction of R_FI with alkenes and alkynes.[180, 382, 383] For example, perfluoroalkyl iodides react with phenylacetylene in the presence of transition metal carbonyls, *e.g.*, $Ni(CO)_2(PPh_3)_3$, resulting in β-perfluoroalkylstyrenes (yield 89%–96%) (Table 19).

Table 19. Reactions of phenylacetylene with perfluoroalkyl iodides.[180]

Catalyst	*T* /°C	*t* /h	Conversion (%)	Yield (%)
Ru/C	120	12	98.6	93
Pt/C	100	12	99.8	94
Ag/Al_2O_3	125	11	99.7	94.5
$Ni(CO)_2(PPh_3)_3$	70	6	100	96
$W(CO)_5[P(OEt)_3]$	90	5	95.7	89
$Mo(CO)_5(PPh_3)$	80	5	97.9	92

Depending on the reaction conditions, iron pentacarbonyl converts the primary perfluoroalkyl iodide into 1-iodoperfluoroalk-1-ene or to a perfluoroalkyl radical which both can further perfluoroalkylate aromatic compounds and alkenes.[233, 390, 391] The addition of $I(CF_2)_4I$ to $CH_2=CH_2$ in the presence of $Fe(CO)_5$ and $HOCH_2CH_2NH_2$ in an autoclave at 100 °C results in $ICH_2CH_2(CF_2)_4CH_2CH_2I$ (yield 78%).

Perfluoroalkyl iodides enter into addition or substitution reactions with alkenes [346, 348] and dihydropyran [348] in the presence of $[CpFe(CO_2)]_2$.



The reactions of trialkylsilyl derivatives of alkenes with perfluoroalkyl iodides in the presence of iron carbonyl, $Fe_3(CO)_{12}$ result in the substitution of the perfluoroalkyl group for the trialkylsilyl group.[392, 393]



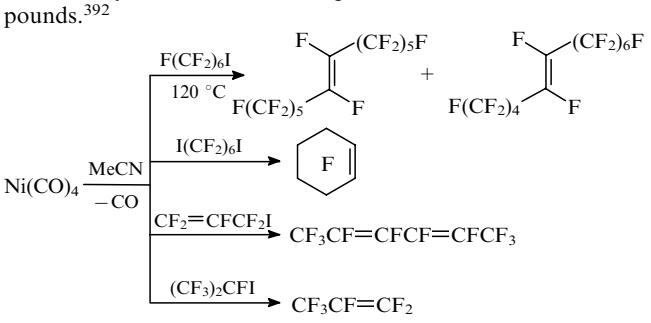
R_F = n-C_3F_7, n-C_8F_{17}, CF_2CF_2Br, $CFClCF_2Br$, $CFClCF_2Cl$, $CHFCF_2Cl$.

In the presence of $Fe(CO)_5$ in DMF, alkenes react with R_FI with the formation of addition products to the double bond.[281]

$$CH_2{=}CHR + R_FI \xrightarrow[DMF]{Fe(CO)_5} R_FCH_2CHIR$$

R_F = $(CF_3)_2CFCF{=}CFCF_2$, $NCCF_2$, $MeCO_2CF_2$, C_3F_7, $CF_3(CF_2)_4CF_2$, $FSO_2CF_2CF_2$, $(CF_3)_2CFOCF_2CF_2$; R = Bu^n, CO_2Me.

It was shown[394] that nickel carbonyls are efficient in the reaction of substitution of the perfluoroalkyl group of α-chlorofluoroketones for chlorine. When these reactions are carried out in donor solvents, organometallic compounds possessing perfluoroalkylating properties can be formed. For example, the reaction of perfluoroalkyl iodides with nickel tetracarbonyl in acetonitrile at 25–60 °C yields either dimeric products or unsaturated compounds.[392]



This reaction probably occurs *via* the intermediate formation of the nickel-containing compound **43**.

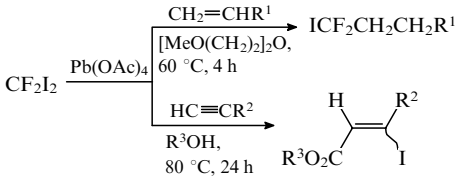
$$F(CF_2)_6I + Ni(CO)_4 \xrightarrow{MeCN} F(CF_2)_6NiI(MeCN)_2$$

43

The reaction of perfluoroallyl iodide with nickel tetracarbonyl is exotermic. The nickel compound formed reacts with the original substrate to give an isomeric mixture of perfluorohexa-2,4-diene. The reaction of perfluorohexyl iodide with nickel tetracarbonyl carried out at temperatures > 120 °C yields a mixture of two dodecenes, *viz*., *trans*-perfluorododec-6-ene and *trans*-perfluorododec-5-ene (1 : 1) and perfluorocyclohexene.

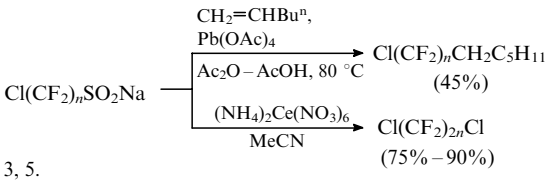
2. Reactions of perfluoroalkyl halides with unsaturated organic compounds in the presence of redox systems

Studies of reactions of perfluoroalkyl halides with unsaturated organic compounds in the presence of reducing and oxidising systems revealed many specific features in their behaviour which can be rationalised by generation of perfluoroalkyl radicals. These radicals can be formed in different ways, predominantly by the reduction of perfluoroalkyl iodide to the radical anion. Hence a question arises as to whether the radical $R_F^{\bullet}$ can be generated by an alternative route. According to some data, the reaction of perfluoroalkyl iodides with alkenes can be efficiently initiated by some oxidants, *e.g.*, $Pb(OAc)_4$, $(NH_4)_2S_2O_8-HCO_2Na$, $CrCl_3-Fe$. Thus lead tetraacetate initiates the reaction of diiododifluoromethane with alkenes and alkynes.[395]



R^1 = $(CH_2)_3Me$ (95%), CH_2OH (93%), $SiMe_3$ (95%), CH_2OEt (92%), $(CF_2)_4Cl$ (80%), $(CF_2)_4Br$ (78%);
R^2 = Bu^n: R^3 = Bu^n (72%), Et (78%); R^2 = C_5H_{11}, R^3 = Et (76%);
R^2 = CH_2OMe: R^3 = Bu^n (70%), Me (64%).

In addition to perfluoroalkyl iodides, these reactions occur with sodium perfluoroalkanesulfinates. For example, heating of $Cl(CF_2)_nSO_2Na$ with hex-1-ene in $Ac_2O-AcOH$ in the presence of $Pb(OAc)_4$ at 80 °C results in the formation of an addition product to the multiple bond, *viz*., $Cl(CF_2)_nCH_2C_5H_{11}$, in 45% yield.[396]



n = 3, 5.

Some peroxides are effective in reactions of perfluoroalkyl iodides with alkenes.[397]

$$Me(CH_2)_mCH{=}CH_2 + CF_3(CF_2)_nI \xrightarrow[2)\ Zn,\ EtOH]{1)\ n\text{-}C_6H_{13}C(O)OOBu^t,\ 85-100\ ^\circ C,\ 6\ h} CF_3(CF_2)_n(CH_2)_{m+2}Me$$

n = 1–21; m = 3–25.

Potassium permanganate can also initiate the reaction of perfluoroalkyl iodides with alkenes in aqueous MeCN at 80 °C.[398]

$$CH_2{=}CHR + R_FI \xrightarrow[MeCN-H_2O]{KMnO_4} R_FCH_2CHIR$$

R_F = $Cl(CF_2)_4$, $Cl(CF_2)_6$; R = Bu^n, CH_2OH, n-C_6H_{13}, n-$C_{10}H_{21}$, Me_3Si, $CH_2OCH_2CH{=}CH_2$, n-$C_{14}H_{29}$.

Some salts of Ce^{IV} efficiently induce perfluoroalkylation by perfluoroalkyl iodides. In the presence of $Ce(SO_4)_2\cdot 4H_2O$ or $(NH_4)_2Ce(NO_3)_6$, perfluoroalkyl halides R_FX [R_F = $Cl(CF_2)_n$ (n = 4, 6), $F_3C(CF_2)_5$, X = I; R_F = CF_2Br, X = Br] react smoothly with alkenes $RCH{=}CH_2$ (R = Bu^n, CH_2OH, n-C_8H_{17}, *etc*.) (Tables 20 and 21) and alkynes to give perfluoroalkylation products.[398,399]

Table 20. The effect of the solvent on the reaction of but-1-ene and hex-1-ene with $Cl(CF_2)_4I$ and $Cl(CF_2)_6I$ in the presence of $Ce(SO_4)_2\cdot 4H_2O$.[398]

Solvent	Conversion (%)		Yield (%)	
	A	B	C	D
DMF	100	100	81	82
MeOH	95	100	78	80
DMF–MeOH	50	60	31	38
DMSO	45	40	34	30
AcOH	0	0	0	0
$[MeO(CH_2)_2]_2O$	0	0	0	0

Note: A is $Cl(CF_2)_4I$, B is $Cl(CF_2)_6I$, C is $RCHICH_2(CF_2)_4Cl$, D is $RCHICH_2(CF_2)_6Cl$.

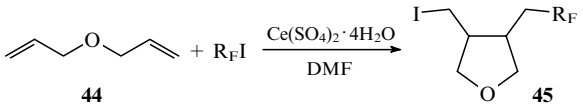
Table 21. The reaction of alkenes $RCH{=}CH_2$ with perfluoroalkyl halides R_FX in the presence of $Ce(SO_4)_2\cdot 4H_2O$ in DMF.[398]

R	Yields for different R_FX (%)			
	$Cl(CF_2)_4I$	$Cl(CF_2)_6I$	$CF_3(CF_2)_5I$	CF_2Br_2
Bu^n	81	73	84	83
CH_2OH	73	74	56	–
n-C_6H_{13}	82	85	82	86
n-C_8H_{17}	84	78	84	–
n-C_9H_{19}	84	81	–	86
n-$C_{10}H_{21}$	80	83	–	79
Me_3Si	68	–	–	–
$CH_2OCH{=}CH_2$	65	81	–	83
n-$C_{14}H_{29}$	78	–	–	–

Note. The reaction was carried out at 80 °C for 8 h (100% conversion).

In the presence of $Mn(OAc)_3 \cdot 2\ H_2O$ or $Ce(SO_4)_2$, sodium polyfluoroalkanesulfinates can be used in these reactions instead of perfluoroalkyl iodides. In this case, the perfluoroalkyl radical formed reacts with aromatic compounds [400] and alkenes,[250] which results in the formation of either substitution products of the hydrogen atom in the benzene ring or in the formation of adducts to the multiple bond. This approach was used for introducing perfluoroalkyl groups into the benzene rings of benzocrown ethers under the action of sodium perfluorosulfinates.[401]

Tetrahydrofuran **45** derivatives (see Table 21) were prepared using diallyl ether (**44**) as a substrate; this reaction resulted in the formation of a free radical intermediate as could be evidenced from the EPR spectra.[234]



44 **45**

Reactions of perfluoroalkyl iodides with alkynes in the presence of Ce^{IV} salts (Table 22) proceed at a higher temperature (120 °C) and are slower (the reaction time varies from 18 to 20 h) than the corresponding reactions with alkenes.[398, 399]

$$HC{\equiv}CR + R_FI \xrightarrow[DMF]{Ce(SO_4)_2 \cdot 4H_2O} R_FCH{=}CRI$$

R_F = $Cl(CF_2)_4$, $Cl(CF_2)_6$, $CF_3(CF_2)_5$;
R = Bu^n, Ph, n-C_6H_{13}, n-C_7H_{15}, CH_2OH, $MeOCH_2$.

Table 22. The reaction of acetylene derivatives $HC{\equiv}CR$ with $Cl(CF_2)_4I$ and $Cl(CF_2)_6I$ in the presence of Ce^{IV} salts in DMF.[398]

R	Inducer	Yield of RFCH=CRI (%) (E:Z)	
		$Cl(CF_2)_4$	$Cl(CF_2)_6$
Bu^n	$Ce(SO_4)_2 \cdot 4H_2O$	73 (3:1)	71 (1:1)
Ph	$Ce(SO_4)_2 \cdot 4H_2O$	55 (3:1)	74 (11:1)
	$(NH_4)_2Ce(NO_3)_6$	53 (6:1)	78 (5:1)
n-C_6H_{13}	$Ce(SO_4)_2 \cdot 4H_2O$	68 (3:1)	–
	$(NH_4)_2Ce(NO_3)_6$	52 (4:1)	–
	$Ce(SO_4)_2 \cdot 4H_2O$	59 (4:1)	76 (3:1)
n-C_7H_{15}	$(NH_4)_2Ce(NO_3)_6$	61 (6:1)	71 (5:1)
CH_2OH	$Ce(SO_4)_2 \cdot 4H_2O$	48 (10:1)	65 (65:0)
	$(NH_4)_2Ce(NO_3)_6$	–	67 (9:1)
CH_2OMe	$Ce(SO_4)_2 \cdot 4H_2O$	48 (2:5)	–

Note. The reaction was carried out at 120 °C for 18–20 h.

Butadiene undergoes perfluoroalkylation under the action of perfluoroalkanesulfonyl bromide R_FSO_2Br in the presence of dibenzoyl peroxide to give a mixture of isomeric unsaturated addition products.[402]

$$CH_2{=}CHCH{=}CH_2 + R_FSO_2Br \xrightarrow{(PhCOO)_2} R_FCH_2CHBrCH{=}CHR'_F + R_FCH_2CH{=}CHCHBrR'_F$$

R_F, R'_F = $Cl(CF_2)_4$, $Cl(CF_2)_5$, $F(CF_2)_5$.

Dibenzoyl peroxide can also be used for perfluoroalkylation of aromatic compounds.[268]

The use of hydrogen peroxide, di-*tert*-butyl peroxide and dibenzoyl peroxide as inducers gave encouraging results. Thus the reaction of trimethylsilylacetylene with 1,6-diiodoperfluorohexane in the presence of di-*tert*-butyl peroxide results in 1,10-diiodo-1,10-bis(trimethylsilyl)dodecafluorodeca-1,9-diene in 92% yield.[70]

$$HC{\equiv}CSiMe_3 \xrightarrow[120\ ^\circ C,\ 85\ h]{I(CF_2)_nI,\ (Bu^tO)_2} Me_3SiCI{=}CH(CF_2)_nCH{=}CISiMe_3$$

n = 6, 8, 10, 12.

Treatment of phenylacetylene with perfluoroheptyl iodide in the presence of di-*tert*-butyl peroxide results in (*E*)-1-iodo-1-phenylpentanedecafluorononon-1-ene.[70]

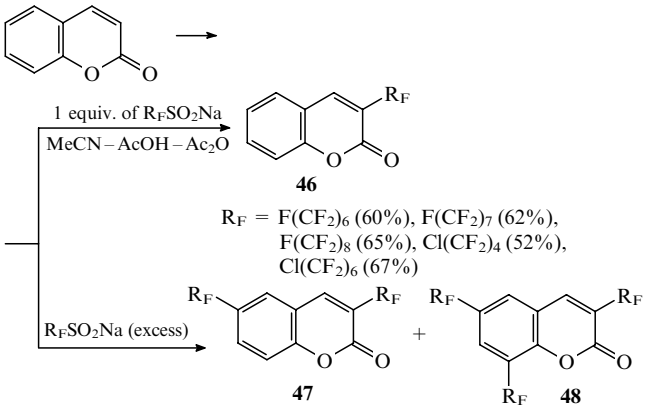
$$PhC{\equiv}CH + CF_3(CF_2)_6I \xrightarrow[120\ ^\circ C,\ 48\ h]{(Bu^tO)_2} PhIC{=}CH(CF_2)_6CF_3\ (89\%)$$

The reaction of alkenes with perfluoroalkyl iodides in the presence of hydrogen peroxide in acetone, acetonitrile or ethanol gives addition products to the multiple bond in good yields.[403]

Potassium superoxide (KO_2) reacts with 1,4-diiodoperfluorobutane in benzene containing dicyclohexano-18-crown-6 (its role in this reaction is ambiguous) to give $I(CF_2)_3CO_2H$.[404, 405]

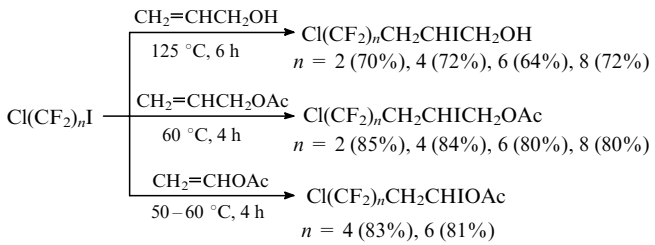
Sodium perfluoroalkanesulfinates of the type $Cl(CF_2)_nSO_2Na$ (n = 4, 6, 8) the reduction potentials of which are equal to 0.95–1.00 V generate perfluoroalkyl radicals in the presence of oxidants, *e.g.*, $Mn(OAc)_3 \cdot 2\ H_2O$, $Ce(SO_4)_2$, $HgSO_4$ and Co_2O_3.[250–256] The radicals formed react with aromatic compounds to give monoperfluoroalkylation products. For example, the reaction of 1,4-dimethoxybenzene with $Cl(CF_2)_4SO_2Na$ in the presence of $Mn(OAc)_3$ in H_2O, MeCN or AcOH at 80 °C gave the adduct 1,4-$(MeO)_2C_6H_3(CF_2)_4Cl$-2 in 50% yield.[406]

The reaction of sodium perfluoroalkanesulfinates with coumarin gives the 3-perfuoroalkyl derivatives **46**.[257] 3,6-Bis(perfluoroalkyl)- (**47**) and 3,6,8-tris(perfluoroalkyl) derivatives (**48**) are formed when the perfluoroalkylating reagent is used in excess. These compounds have found applications as fluorescent dyes and for laser systems.



The reaction of perfluoroalkyl iodides R_FI [R_F = $CF_3(CF_2)_5$, $H(CF_2)_4$, $Cl(CF_2)_n$ (n = 4, 6, 8), $I(CF_2)_m$ (m = 4, 6), $NaO_3S.(CF_2)_2O(CF_2)_m$ (m = 2, 4)] with $NaHSO_3$ in the presence of $(NH_4)_2Ce(NO_3)_6$ in aqueous acetonitrile at 70 °C results in the salts R_FSO_2Na in 70% to 88% yields.[156]

The $Ce^{IV}-NaHCO_3$ and $Fe^{III}-NaHSO_3$ systems efficiently catalyse the reactions of perfluoroalkyl iodides with alkenes. These reactions give high yields of addition products to the double bond.[353, 407] $K_2[Fe(CN)_6]$ was found to be an excellent inducer of reactions of addition of perfluoroalkyl iodides to alkenes and their derivatives.[244]



Let us now discuss the tentative reaction mechanisms underlying reactions of perfluoroalkyl halides and sodium perfluoroalkanesulfinates with unsaturated compounds in the presence of redox systems. These reactions were surveyed by Hu *et al.*[30]

Two schemes are probable. According to the first of them, a radical cation is generated from perfluoroalkyl iodide under the action of an oxidant and is transformed to a perfluoroalkyl radical. The second route includes initial oxidation of the unsaturated substrate to the radical cation, which then reacts with perfluoroalkyl iodide to produce the perfluoroalkyl radical.

The latter was proposed by Huang and Xie[400] for the reaction with styrene in the presence of lead tetraacetate.

$$CH_2{=}CHR \xrightarrow{Ox} [CH_2{=}CHR]^{+\bullet} \xrightarrow{R_FI} \overset{+}{R}CHCH_2I + R_F^{\bullet} \longrightarrow$$

$$\longrightarrow R_FCH_2\dot{C}HR \xrightarrow{R_FI} R_FCH_2CHIR + R_F^{\bullet}$$

Ox, oxidant.

However, standard oxidation potentials (E°_{ox}) of the alkenes used are too high to ensure their oxidation to the corresponding radical cations. For instance, E°_{ox} of oct-1-ene is 2.70 V relative to $Ag^+/AgNO_3$,[408] although polar effects can to certain degree compensate for this stability.

An alternative intermediate, *viz.*, the radical cation of perfluoroalkyl iodide $[R_FI]^{+\bullet}$, can be formed under the action of a strong oxidant. Indeed, the same radical cation is formed in the electrochemical[409] oxidation of perfluoroalkyl iodide in the presence of perfluoroalkanesulfinic acid.

Efficient catalysis of the reaction of perfluoroalkyl iodide with alkenes [*e.g.*, E°_{ox} of $MeOC_6H_4C(Me){=}CH_2$ is 1.49 V (see Ref. 410), E°_{ox} of α-phenylstyrene is 1.22 V relative to SCE[411]] requires an oxidant with a reduction potential, E°_{ox}, of > 1.6 V (rel. SCE). In this case, the radical cation $[R_FI]^{+\bullet}$ can be formed. The radical cation $[R_FI]^{+\bullet}$ is rapidly decomposed into $R_F^{\bullet}$ and the iodonium cation. The radical $R_F^{\bullet}$ was detected in its reaction with alkene, which resulted in the generation of a new radical. The latter detached iodine from R_FI to yield the reaction product and the radical $R_F^{\bullet}$.

The reduction potentials of some oxidants are listed in Table 23.[412,413] If the reduction potential of an oxidant is ⩾ 1.60 V (rel. SCE), this can efficiently initiate the reaction with alkenes.

Table 23. Standard reduction potentials (E°_{red}) of different oxidants.

Oxidant	Ion	E°_{red} /V	Ref.
$Na_2S_2O_8$, $(NH_4)_2S_2O_8$	$S_2O_8^{2-}$	2.01	412
$KMnO_4$	MnO_4^-	1.695	412
$Pb(OAc)_4$, PbO_2	Pb^{4+}	1.69	412
$Ce(SO_4)_2$, $(NH_4)_2Ce(NO_3)_6$	Ce^{4+}	1.61	412
$Mn_2(OAc)_3$	Mn^{3+}	1.51	412
$K_2Cr_2O_7$	$Cr_2O_7^{2-}$	1.33	412
$FeCl_3$	Fe^{3+}	0.771	412
Chloranil		0.02	413
$[N(C_6H_3Br\text{-}2,4)_3]^+$		1.14	413
$[N(C_6H_4Br\text{-}3)_3]^+$		0.70	413
$[C_6H_4Br\text{-}4]_3N^+$		1.06	414

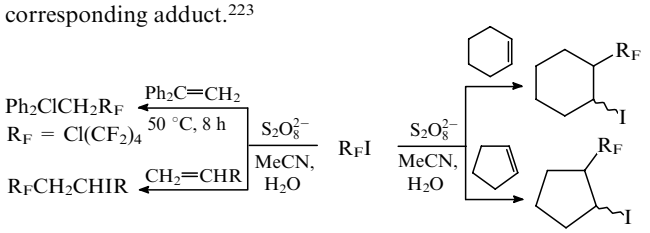
Thus, the reactions of perfluoroalkyl halides with alkenes or alkynes in the presence of oxidants appear to be a convenient method for fluoroalkylation of alkenes or alkynes.

Perfluoroalkyl iodides successfully react with alkenes in aqueous MeCN (6–8 h, 60 °C) in the presence of $Na_2S_2O_8$ or $(NH_4)_2S_2O_8$ (Table 24).[398] Cyclohexene and cyclopentene also react with R_FI to produce the 1 : 1 adducts in good yields. The reaction of α-chloro-ω-iodoperfluoroalkanes with alkenes in the presence of the $(NH_4)_2S_2O_8-HCO_2Na$ system gives addition products at the expense of the C–I bond without involving the C–Cl bond.[415,416] The reaction of perfluoroalkyl iodides with α-phenylstyrene carried out under identical conditions gives the corresponding adduct.[223]

Table 24. Reactions of R_FI with alkenes $RCH{=}CH_2$ in the presence of $Na_2S_2O_8$ in $MeCN-H_2O$.[398]

R	Yield of $RCHICH_2R_F$ for different R_FI (%)		
	$Cl(CF_2)_4I$	$Cl(CF_2)_6I$	$CF_3(CF_2)_5I$
Bu^n	81	84	81
CH_2OH	73	83	61
C_6H_{13}	85	83	83
C_8H_{17}	83	85	85
C_9H_{19}	85	87	88
$C_{10}H_{21}$	83	84	–
$C_{14}H_{29}$	78	–	–

Note. Reactions were carried out at 60 °C for 6–8 h.



$R_F = Cl(CF_2)_4$, $Cl(CF_2)_6$, $CF_3(CF_2)_5$;
R = Bu^n, CH_2OH, n-C_6H_{13}, n-C_8H_{17}, n-C_9H_{19}, n-$C_{10}H_{21}$, Me_3Si, $CH_2OCH_2CH{=}CH_2$.

Reactions of sodium perfluoroalkanesulfinates $R_FCF_2SO_2Na$ with allyl halide and propargyl halide in the presence of $(NH_4)_2S_2O_8$ result in good yields of 3-(perfluoroalkyl)prop-1-ene and 3-(perfluoroalkyl)allene, respectively.[326]

An interesting transformation of perfluoroalkyl iodides and -bromides as well as of compounds containing a CCl_3 group at the end of the perfluorinated carbon chain into the corresponding perfluorocarboxylic acids was observed in the presence of a redox system.[132–144,159,193,401,417,418]

$$CF_3CCl_3 \xrightarrow[DMF,\ 40\ ^{\circ}C]{Ox} CF_3CO_2H$$

Ox = $(NH_4)_2S_2O_8-HCO_2Na\cdot 2H_2O$, $(NH_4)_2S_2O_8$–oxalate, $H_2O_2-FeSO_4\cdot 7H_2O$, $(NH_4)_2S_2O_8-Na_2S_2O_4$, $H_2O_2-Na_2S_2O_4$, $KBrO_3-Na_2S_2O_4$, $(PhCO)_2O_2-PhNMe_2$.

$CF_3CCl{=}CHCH_2Cl$ is the reaction product of CF_3CCl_3 with ethylene in the presence of Cr_2O_3.[419] Perfluoroalkylation by perfluoroalkyl iodides and sodium perfluoroalkanesulfinates was performed using a variety of redox reagents and systems, *e.g.*, $Ce(SO_4)_2$, $H_2O_2-FeSO_4$, $(NH_4)_2Ce(NO_3)_6$, $Pb(OAc)_4-HOAc-Ac_2O$, $Mn(OAc)_3\cdot H_2O$, *etc.* This reaction occurs *via* the intermediate formation of the perfluoroalkyl radical, since the introduction of compounds containing labile (C–Hal) bonds yields products of substitution of the R_FCF_2 group for the halogen atom.[420]

$$R_FCF_2SO_2Na \xrightarrow[DMF,\ 40\ ^{\circ}C]{(NH_4)_2S_2O_8}$$

$$\xrightarrow{CH_2=CHCH_2X} R_FCF_2CH_2CH{=}CH_2 + R_FCO_2H + R_FCF_2X$$

$$\xrightarrow{HC\equiv CCH_2X} R_FCF_2CH{=}C{=}CH_2 + R_FCO_2H + R_FCF_2X$$

X = Cl, Br; $R_F = Cl(CF_2)_n$ (n = 2, 4, 6), $CF_3(CF_2)_n$ (n = 3, 5, 7).

The optimum conditions for this reaction are as follows: temperature below 40 °C and DMF as a solvent.

The use of redox systems allows for selective transformation of perfluoroalkyl iodides, α,ω-diiodoperfluoroalkanes and com-

Table 25. Conversion of polyfluoroalkyl halides into the corresponding acids under the action of the $(NH_4)_2S_2O_8-HCO_2Na\cdot 2H_2O$ system in DMF.[421]

Substrate	T /°C	t /h	Acid	Conversion (%)	Yield (%)
$C_6F_{13}I$	55	12	$C_5F_{11}CO_2H$	75	83.9
$Cl(CF_2)_4I$	50	14	$Cl(CF_2)_3CO_2H$	69	78.7
$Cl(CF_2)_6I$	50	14	$Cl(CF_2)_5CO_2H$	70	81.2
$I(CF_2)_6I$	50	12	$(CF_2)_4(CO_2H)_2$	50	92.0
$I(CF_2)_8I$	50	12	$(CF_2)_6(CO_2H)_2$	62	89.0
CF_3CCl_3	25	10	CF_3CO_2H	100	72.5
CF_3CBr_2Cl	50	4	CF_3CO_2H	100	71.8
$CCl_3CF_2CFClBr$	30	5	$CF_2(CO_2H)_2$	100	74.6
$CF_2(CCl_3)_2$	30	5	$CF_2(CO_2H)_2$	100	69.8
$CF_2ClCFCl_2$	20	10	$ClCF_2CO_2H$	100	55.6
$CF_2BrCFClBr$	15	20	$BrCF_2CO_2H$	100	63.4
$CF_2ClCFClCF_2CFCl_2$	30	5	$CF_2ClCFClCF_2CO_2H$	100	78.6

pounds of the type R_FCCl_3, $R_FCFBrCl$, R_FCBr_2Cl, R_FCFCl_2, *etc*., into the corresponding acids (Table 25).[421–423]

$$(NH_4)_2S_2O_8-HCO_2Na\cdot 2H_2O \xrightarrow{X(CF_2)_nCF_2I} X(CF_2)_nCO_2H \quad (X = F,\ n = 5;\ X = Cl,\ n = 4, 6)$$
$$(NH_4)_2S_2O_8-HCO_2Na\cdot 2H_2O \xrightarrow{ICF_2(CF_2)_nCF_2I} HO_2C(CF_2)_nCO_2H \quad (n = 4, 6)$$

Oxidising systems based on sulfur-containing acids have been studied by physicochemical methods.[424,425]

Perfluorocarboxylic acids can also be prepared from sodium perfluoroalkanesulfinates in the presence of a redox reagent.[159]

$$R_FCF_2SO_2Na \xrightarrow[60\ ^\circ C]{(NH_4)_2S_2O_8,\ H_2O} R_FCO_2H + R_FCHF_2 \quad (68\%)$$

The $AgNO_3-HCO_2Na$ system in aqueous acetonitrile catalyses the reaction in a similar way.[426]

$$R_FCF_2I \xrightarrow[MeCN-H_2O,\ 20\ ^\circ C,\ 24\ h]{AgNO_3-HCO_2Na} R_FCO_2H$$

R_F = $ClCF_2$ (50%), $Cl(CF_2)_3$ (65%), $Cl(CF_2)_5$ (72%), $F(CF_2)_7$ (85%), $F(CF_2)_5$ (89%).

1,1,1-Trichlorotrifluoroethane can be converted into trifluoroacetic acid in the presence of various oxidants (Table 26).[421] The reaction induced by $(NH_4)_2S_2O_8-HCO_2Na$ presumably occurs in accordance with the following scheme:[421]

$$S_2O_8^{2-} \rightleftharpoons 2SO_4^{-\bullet},$$
$$SO_4^{-\bullet} + HCO_2^- \longrightarrow HSO_4^- + CO_2^{-\bullet},$$
$$R_FCCl_3 + CO_2^{-\bullet} \longrightarrow R_F\dot{C}Cl_2 + CO_2 + Cl^-,$$
$$R_F\dot{C}Cl_2 \xrightarrow{H^\bullet} R_FCHCl_2$$
$$R_F\dot{C}Cl_2 \xrightarrow{O_2} R_FCCl_2OOH \xrightarrow[-HOCl]{} R_FCOCl \xrightarrow{H_2O} R_FCO_2H$$

In this case, the generation of the polyfluoroalkyl radical by the radical anion $CO_2^{-\bullet}$ is the key step of this reaction. In the presence of alkenes and alkynes, the acids are not formed, the addition to multiple bonds occurs instead.

$$CF_2ClCFCl_2 + CH_2{=}CHR \xrightarrow{(NH_4)_2S_2O_8-HCO_2Na} CF_2ClCFCl(CH_2)_2R$$

R = Bu^n, n-C_5H_{11}, CH_2Br, CH_2OH, OAc, $(CH_2)_4CH{=}CH_2$.

It is known that other radical anions can initiate such transformations. Thus in the presence of an electrochemically generated radical anion of molecular oxygen $O_2^{-\bullet}$, perfluorobutyl iodide, perfluorooctyl iodide and α,ω-diiodoperfluorobutane produce the corresponding acids in up to 50% yields.[417]

$$CF_3(CF_2)_2CF_2I + 4e^- + O_2 \xrightarrow{DMF} CF_3(CF_2)_2CO_2^- + I^- + 2F^-$$

This reaction occurs according to the following scheme:

$$O_2 + e^- \rightleftharpoons O_2^{-\bullet},$$
$$R_FI + O_2^{-\bullet} \longrightarrow R_FOO^\bullet + I^-,$$
$$R_FOO^\bullet \xrightarrow{O_2^{-\bullet}} R_FOO^- + O_2 \longrightarrow R'_FCO_2H$$
$$R_FOO^\bullet \xrightarrow{\text{dimerisation}} R_FO_4R_F \longrightarrow R'_FCO_2H.$$

This system can also be used for the activation of inert Freon-113.[422,423]

The redox system $(NH_4)_2S_2O_8-HCO_2Na\cdot 2H_2O$ manifests high selectivity.[421,426]

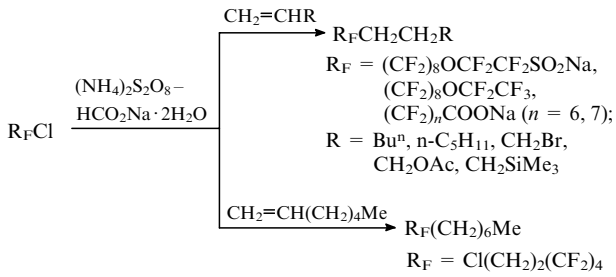
Selective reduction of perfluorochloroalkanes by the $(NH_4)_2S_2O_8-HCO_2NH_4$ or the $(NH_4)_2S_2O_8-NaH_2PO_4\cdot H_2O$ system is of considerable practical importance because it yields products which can further be used as inhalation anesthetics similar to the widely employed ethers CHF_2OCF_2CHClF (influrane) and $CHF_2OCHClCF_3$ (isoflurane).[421–423]

$$CF_2ClCFClCF_2CFCl_2 \xrightarrow{(NH_4)_2S_2O_8-HCO_2NH_4} CF_2ClCFClCF_2CHClF + CF_2ClCHFCF_2CFCl_2 + CF_2ClCHFCF_2CHClF$$
(44%; 14%; 16%)

In contrast with perfluoroalkyl iodides which are oxidised at the CF_2I fragment to yield carboxylic acids, perfluoroalkyl chlorides smoothly yield addition products to the multiple bond under identical conditions.

Table 26. Conversion of CF_3CCl_3 into trifluoroacetic acid in the presence of various redox systems.[421]

System	Reaction conditions			Conversion (%)	Yield (%)
	solvent	T /°C	t /h		
$(NH_4)_2S_2O_8-HCO_2Na$	DMF	25	10	100	95
$H_2O_2-FeSO_4$	DMF–H_2O	40	0.5	100	100
$(NH_4)_2S_2O_8-Na_2S_2O_4$	DMF–H_2O	35	5	100	100
$H_2O_2-Na_2S_2O_4$	DMF–H_2O	40	1	100	100
$KBrO_3-Na_2S_2O_4$	DMF–H_2O	45	3	85	100
$(PhCO_2)_2-PhNMe_2$	DMF	30	16	25	100



The intermediate perfluoroalkyl radical not only reacts with alkenes, but can undergo other transformations depending on the reaction conditions and the oxidant type. For example, reactions of sodium chloropolyfluoroalkanesulfinates yield dimerisation products, carboxylic acids and adducts to the multiple bond.[396]

Perfluoroalkylated alkenes are the main products in the reaction of sodium perfluoroalkanesulfinates with conjugated dienes in the presence of $M_2S_2O_8$.[159, 427, 428]

The nature of other functional groups in the molecule can influence the lability of the C–Cl bond. For example, the activity of compounds of the type $Cl(CF_2)_7X$ (X = CO_2Na, CO_2Me, CO_2H) in the reaction with hept-1-ene decreases in the following order: $Cl(CF_2)_7CO_2Na > Cl(CF_2)_7CO_2Me > Cl(CF_2)_7CO_2H$.

In polyhalogenopolyfluoroalkanes containing I and Cl atoms, the latter is much less active than iodine. The chlorine atom reacts with hept-1-ene only after substitution of the SO_3Na group for iodine.

The perfluoroalkylation reaction can occur with different redox reagents and systems, *e.g.*, $(NH_4)_2Ce(NO_3)_6$, H_2O_2–$FeSO_4$, $Ce(SO_4)_2$, $Pb(OAc)_4$–HOAc–Ac_2O, $Mn(OAc)_3 \cdot H_2O$, *etc*. This reaction proceeds through the generation of the perfluoroalkyl radical and results in the products of substitution of the R_FCF_2 group for the halogen atom (Table 27).[325, 326]

$$CF_2ClCFCl_2 + CH_2{=}CHR \xrightarrow{(NH_4)_2S_2O_8 - HCO_2Na} CF_2ClCFCl(CH_2)_2R$$

R = Bu^n, n-C_5H_{11}, CH_2Br, CH_2OH, $MeCO_2$, $(CH_2)_4CH{=}CH_2$.

Table 27. Synthesis of 3-(perfluoroalkyl)prop-1-enes and 3-(perfluoroalkyl)allenes.[326]

Substrate	R_FCF_2X	Yield (%)	
		A	B
$CH_2{=}CHCH_2X$	$Cl(CF_2)_8CF_2CF_2Br$	75	10
	$Cl(CF_2)_8OCF_2CF_2Cl$	34	16
	CF_3CCl_2Br	46	33
	$Cl(CF_2)_2Br$	53	14
	$Cl(CF_2)_4Br$	62	10
	$Cl(CF_2)_6Br$	65	18
	$Cl(CF_2)_4Cl$	28	15
	$Cl(CF_2)_6Cl$	40	16
	$CF_3(CF_2)_3Br$	72	10
	$CF_3(CF_2)_5Br$	67	12
	$CF_3(CF_2)_7Br$	74	15
	$CF_3(CF_2)_7Cl$	32	17
$HC{\equiv}CCH_2X$	$Cl(CF_2)_2Br$	32	12
	$Cl(CF_2)_4Br$	46	20
	$Cl(CF_2)_4Cl$	27	30
	$Cl(CF_2)_6Br$	47	15
	$CF_3(CF_2)_3Br$	42	10
	$CF_3(CF_2)_5Br$	54	17
	$CF_3(CF_2)_7Br$	50	25

Note: A is $R_FCF_2CH{=}CH_2$, B is $R_FCF_2CH{=}C{=}CH_2$.

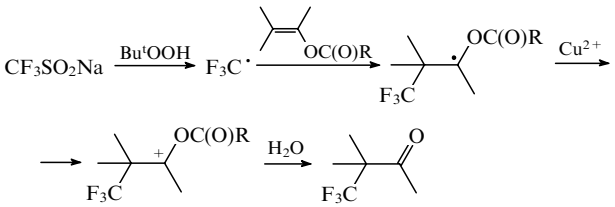
The reaction of perfluoroalkyl iodides with alkenes in the presence of H_2O_2 in acetone, MeCN or EtOH gives an addition product to the multiple bond in high yield.[403]

The reagent $R_F(CF_2)_nSO_2Na - MoO_2(acac)_2$ is effective in perfluoroalkylation, *e.g.*, of disulfides, which occurs in the presence of $M_2S_2O_8$ (M = K, Na, NH_4) or Bu^{t}OOH in a mixture of water and a polar aprotic solvent, such as MeCN, DMF, dimethylacetamide, sulfolan, glymes, HMPT, *etc*.[429–431]

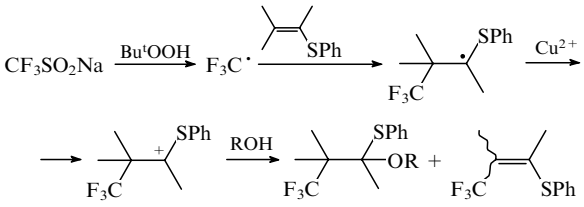
$$RSSR + CF_3SO_2Na \xrightarrow[MeCN,\ 20^\circ C]{Bu^tOOH} RSCF_3 + RSO_2SR$$

R	Yield of $RSCF_3$ (%)
$Me(CH_2)_6CH_2$	95
$(CH_2)_2CO_2Et$	75
$(CH_2)_2CO_2Et$	100
CH_2CO_2Et	60
$CH_2CH(\overset{+}{N}H_3)CO_2Me$	47
$(CH_2)_2CH(\overset{+}{N}H_3)CO_2Me$	55

Trifluoroalkylation of vinyl esters in the presence of Bu^{t}OOH results in α-trifluoromethyl ketones.[432]



Trifluoromethyl derivatives are formed in reactions of CF_3SO_2Na with vinyl sulfides. The sulfur atom effectively stabilises the carbocation, which can be trapped by the reaction with a nucleophile, particularly, with an alcohol. α-Trifluoromethyl thioketals are the end products in this reaction.

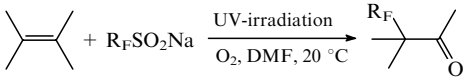


Aromatic compounds also undergo perfluoroalkylation in the presence of Bu^{t}OOH.[433]

The trifluoromethyl radical can also be generated in the oxidation of the sodium trifluoromethanesulfinate by aqueous *tert*-butyl hydroxyperoxide in the presence of Cu^{2+} (Refs 326, 432) and $M_2S_2O_8$ (M = K, Na, NH_4).[430, 432–435] Some of these reactions are depicted in Scheme 2.

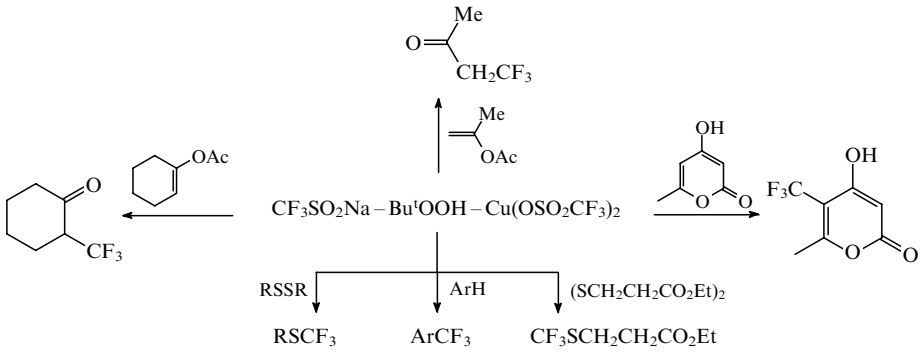
The $CF_3SO_2Na - Bu^tOOH - Cu^{2+}$ system can be used as a formal 'cationoid' reagent in the trifluoromethylation of arenes (Table 28).[250, 253, 430, 432]

Perfluoroalkanesulfinates react with mono- and disubstituted alkenes in air or in oxygen with UV irradiation resulting in α-perfluoroalkyl ketones.[253]



$R_F = X(CF_2)_n$, n = 4, 6, 8; X = F, Cl.

Scheme 2



The reactions of terminal alkenes with sodium perfluoroalkanesulfinates in the presence of $(NH_4)_2S_2O_8$ or the Fenton reagent ($H_2O_2-FeSO_4\cdot 7H_2O$) proceed rather vigorously. In the presence of additional nucleophiles, side reactions of the intermediate carbocations are possible, which has been used for the synthesis of secondary amines.[436]

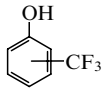
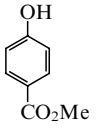
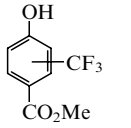
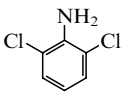
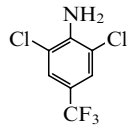
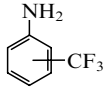
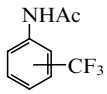
$$CH_2{=}CHR + R_FSO_2Na \xrightarrow[NaN_3]{H_2O_2-FeSO_4\cdot 7H_2O} R_FCH_2CHRN_3 \xrightarrow{[H]} R_FCH_2CHRNH_2 \quad (50\%-70\%)$$

$R_F = Cl(CF_2)_n$ (n = 4, 6), $CF_3(CF_2)_5$; R = Bu^n, n-C_7H_{15}, n-C_8H_{17}, AcO, CH_2OAc, $(CH_2)_8CO_2Et$.

Pyrrole and its derivatives undergo perfluoroalkylation under the action of perfluoroalkyl iodides in the presence of the $H_2O_2-FeSO_4$ system in DMSO (Table 29).[437]

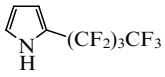
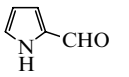
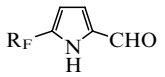
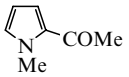
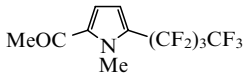
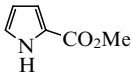
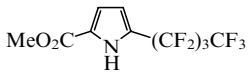
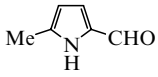
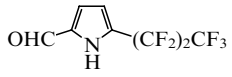
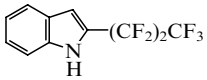
Table 28. Synthesis of trifluoromethylarenes.[253]

$$ArH \xrightarrow{CF_3SO_2Na - Bu^tOOH - Cu^{2+}} ArCF_3$$

Substrate	Product	Yield (%)
PhOH		45 [a]
		21
		20
$PhNH_2$		13
PhNHAc		52 [b]

[a] The ratio of *ortho*:*meta*:*para* isomers is 4:1:6. [b] The ratio of *ortho*:*meta*:*para* isomers is 4:1:2.

Table 29. Homolytic perfluoroalkylation of pyrrole by perfluoroalkyl iodides in the presence of hydrogen peroxide and $FeSO_4$.[437]

Substrate	R_FI	Product	Yield (%)
	$I(CF_2)_3CF_3$		78
	$I(CF_2)_3CF_3$ $ICF(CF_3)_2$ $I(CF_2)_2CF_3$		55 73 64
	$I(CF_2)_3CF_3$		71
	$I(CF_2)_3CF_3$		73
	$I(CF_2)_2CF_3$		36
	$I(CF_2)_2CF_3$		30

3. Activation of perfluoroalkyl iodides by radicals

The above data suggest that under different reaction conditions perfluoroalkyl iodides can generate perfluoroalkyl radicals which further react with alkenes and aromatic compounds by a free-radical mechanism. Bravo *et al.*[438] found that the radical $Ph^{\bullet}$ can rapidly detach the iodine atom from secondary perfluoroalkyl iodides. This can be explained by the fact that the Ph–I bond is stronger than the R_F–I bond. The kinetics of the reaction of perfluoroalkyl iodides with the phenyl radical was studied by Kryger *et al.*[439]

$$R_FI + Ph^{\bullet} \longrightarrow R_F^{\bullet} + PhI,$$

$$\text{sec-RI} + Ph^{\bullet} \longrightarrow \text{sec-R}^{\bullet} + PhI \quad (k = 10^9 \text{ litre mol}^{-1} \text{ s}^{-1})$$

sec-R is secondary alkyl.

In other words, it is the iodide ion that is responsible for the electron transfer. It was thus suggested that perfluoroalkyl iodides can be activated by radicals generated from other substrates. For example, the methyl radical can activate the C–I bond.

In turn, the methyl radical is formed in the reaction of acetone or DMSO with hydrogen peroxide in trifluoroacetic acid or in the presence of Fe^{2+} salts, respectively. The methyl radical reacts with perfluoroalkyl iodide to produce a perfluoroalkyl radical. The

latter initiates further perfluoroalkylation of unsaturated or aromatic compounds.

$$R_FI + \dot{C}H_3 \longrightarrow R_F^{\bullet} + MeI,$$

$$ArH + C_4F_9I \xrightarrow[CF_3CO_2H]{H_2O_2,\ Me_2CO} ArC_4F_9 + MeI + MeCO_2H + H_2O.$$

Perfluoroalkyl radicals were generated by the following systems: $Bu^tOOH - Fe(OAc)_2OH$, $Me_2CO - H_2O_2$, $Me_2SO - H_2O_2 - Fe^{2+}$.[440] These systems effect smooth perfluoroalkylation of aromatic compounds and alkenes (*e.g.*, oct-1-ene, cyclohexene).

$$CH_2{=}CHCH_2R + C_4F_9I \longrightarrow$$

$$\xrightarrow{(PhCOO)_2} C_4F_9CH_2CH{=}CHR + PhI + PhCO_2H + CO_2$$

$$\xrightarrow{Bu^tOOH} C_4F_9CH_2CH{=}CHR + MeI + Me_2CO + H_2O$$

$$ArH + C_4F_9I \xrightarrow[Fe^{III}]{Bu^tOOH} ArC_4F_9$$

$$ArH + C_4F_9I \xrightarrow[Fe^{II}]{H_2O_2,\ Me_2SO} ArC_4F_9 + MeI + MeSO_2H + H_2O$$

The ratio of isomers formed in perfluoroalkylation of aromatic compounds and the relative rates of these reactions suggest the radical mechanism of this reaction.[438]

Reductive perfluoroalkylation of alkenes with perfluoroalkyl iodides can be carried out in the presence of *tert*-butyl hydroperoxide in acetic acid (Table 30).[441]

Table 30. Reductive perfluoroalkylation of alkenes by perfluoroalkyl iodides R_FI in the presence of Bu^tOOH.[441]

Alkene	R_F	Yield (%)
Hex-1-ene	C_4F_9	77
	C_8F_{17}	72
Oct-1-ene	C_4F_9	73
	C_8F_{17}	71
3,3-Dimethylbut-1-ene	C_4F_9	83
	C_8F_{17}	86
Cyclohexene	C_4F_9	85
	C_8F_{17}	73

It should be noted that this approach was first used in reactions of some aromatic compounds with perfluoroalkyl iodides and equimolar amounts of the peroxide.[442] It may be expected that after optimal conditions for such reactions are found, their role in perfluoroalkylation will increase.

IV. Conclusion

The data presented above testify to the increasing interest of investigators in the development of new approaches to the introduction of perfluorinated fragments into organic molecules and the transformation of simple substituents into complex functional groups. The novel perfluoroalkylating reagents considered above can be regarded as an alternative to classical and popular reagents. In particular, perfluoroalkyl iodides are widely used in perfluorination of unsaturated and aromatic organic substrates in the presence of initiators and catalysts. Radical perfluoroalkylation, syntheses of perfluoroalkanesulfinic and perfluorocarboxylic acids and polyfluorinated aldehydes as well as electrochemical synthesis of perfluoroalkyl derivatives offer obvious advantages because of simplicity and possibility to be used on an industrial scale. It remains to be hoped that further investigations will culminate in the discovery of other approaches to the synthesis of fluorine-containing compounds.

In this review, we made an attempt to demonstrate the most recent approaches and synthetic potentialities of novel reagents and to outline the main trends in the synthesis of perfluoroorganic compounds containing various molecular backbones and functional groups. This form of presentation of the experimental material makes it possible to contemplate the problem from the unusual for traditional chemistry standpoint and to propose certain original solutions based on the use of novel approaches to the generation of perfluoroalkyl radicals and their involvement in reactions with various compounds.

Needless to say, the practical implementation of the above-mentioned ideas and processes occurring by a single-electron transfer mechanism presents special interest not only for practitioners in fluoroorganic chemistry but also for specialists in organic synthesis and investigators elaborating radically new approaches to directed synthesis of organic molecules with the ultimate goal to develop new technologies. It should be noted that perfluoroorganic compounds often represent convenient, even unique models for the formulation and solution of fundamental problems of theoretical organic chemistry. In this context, the role of perfluorinated organic materials is steadily increasing, although the number of perfluoroalkylating agents which are suitable for large-scale production is still too small. A breakthrough in this area can be expected in the nearest future. The advent of advanced methodologies for transformation of organic compounds into valuable fluorine-containing products will speed up further progress in organic synthesis.

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