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# The Chemistry of Perfluoroisobutene

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The literature data on the methods of synthesis and reactions of the highly electrophilic perfluoroisobutene with nucleophiles as well as electrophiles are surveyed. The possibilities of employing this fluoro-olefin in organofluorine synthesis are discussed. The advances in the study of the perfluoro-t-butyl anion, generated from perfluoroisobutene and the fluoride anion, are considered in a special section.
The bibliography includes 199 references.

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## I. INTRODUCTION

The ability of fluoro-olefins to react with nucleophiles, which distinguishes them radically from the hydrogen-containing analogues, is particularly pronounced in the case of perfluoroisobutene (PFIB), whose chemistry has developed vigorously since 1953. This fluoro-olefin is of special interest primarily because of its uniquely high electrophilic activity: PFIB reacts with almost all known nucleophiles and even the usual organic solvents, for example dimethylformamide or acetonitrile, are not sufficiently inert in relation to this compound. The properties of PFIB are close to those of activated olefins of the type of α,β-unsaturated carbonyl compounds or polycyano-olefins. At the same time the wide variety of the reactions of PFIB is determined by the lability of the fluorine atoms in the $CF_3$ group, characteristic of fluoro-olefins, and the possibility of further reactions of the addition products associated particularly with the high CH-acidity of the $(CF_3)_2CH$ group. All these factors, together with its ready availability, make it possible to employ PFIB widely in organofluorine synthesis.

The high electrophilicity of PFIB is due to the combination of the strong electron-accepting effects of the fluorine atoms and the $CF_3$ group on which is superimposed the capacity of the vinyl fluorine atoms for effective conjugation with the C=C bond. Indeed, the consecutive increase of the asymmetry of the molecule in the sequence $CF_2{=}CF_2 < CF_3CF{=}CF_2 < (CF_3)_2C{=}CF_2$ is accompanied by a gradual increase of the positive charge on the carbon atom of the $CF_2$ group, which has been confirmed by quantum-chemical calculations[1-3]. On the other hand, calculations for the molecules of PFIB and esters of perfluoromethylacrylic acid by the extended Hückel and CNDO methods[4] showed that their reactivity is determined by the dynamic properties of the distribution of electron density rather than the static distribution. The higher electrophilicity of perfluoromethylacrylate compared with PFIB can be explained by the greater ability of the alkoxycarbonyl group, compared with the $CF_3$ group, to stabilise the intermediate carbanions or carbanion-like transition states. From this point of view, the sharp increase of electrophilicity in the above sequence is caused in the first place by the growing stability of the carbanions: $NuCF_2\bar{C}F_2 < NuCF_2\bar{C}FCF_3 < NuCF_2\bar{C}(CF_3)_2$ (Nu is the nucleophile residue). Such variation of the state of the carbanion is evidently associated not only with the stabilising effect of the $CF_3$ group but also with the destabilisation of the carbanionic centre by the compact unshared electron pairs of the α-fluorine atoms.

The framework of the present review precludes a comparison of the electrophilic properties of PFIB and the lower fluoro-olefins in relation to specific examples. We shall only note that in all cases without exception PFIB is much more reactive in reactions with nucleophiles than, for example, hexafluoropropene. At the same time, the reactions of PFIB with electrophiles, if they occur at all, proceed with much difficulty. Nucleophilic catalysis therefore assumes special importance in such reactions, which reflects the change in the reaction mechanism from electrophilic in the case of non-fluorinated olefins and lower fluoro-olefins to nucleophilic for PFIB. Separate aspects of the chemistry of PFIB have already been discussed in a number of recent reviews[1-8]. However, the chemistry of this fluoro-olefin has not so far been fully considered.

## II. PHYSICAL PROPERTIES AND METHODS OF SYNTHESIS

PFIB is a colourless highly toxic† gas[9] with a boiling point of 6.5 °C, which can be readily identified from the infrared[10] and $^{19}F$ NMR [7] spectra. Its reduction potential at the platinum electrode is −2.65 V.[11]

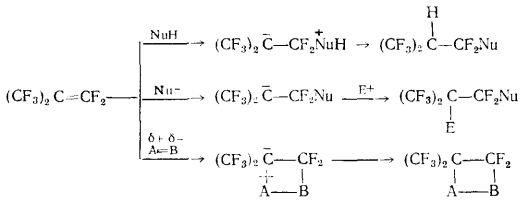
The main methods of synthesis of PFIB include thermolytic processes, which indicates a high thermal stability of this compound. PFIB is obtained by the pyrolysis of Teflon[12], tetrafluoroethylene[13], hexafluoropropene[14], and perfluorocyclobutane[10,15] at 700–750 °C (see also other communications [16-18]). It has been suggested that the synthesis of PFIB by pyrolysis involves the intermediate formation of difluorocarbene[13,19]. In addition, PFIB can be obtained by the dechlorination of 1,2-dichloro-octafluoroisobutane by zinc in dioxane or acetone[20], but this reaction is of limited practical interest, since the dichloride itself is obtained only on chlorination of PFIB.

## III. REACTIONS WITH NUCLEOPHILES

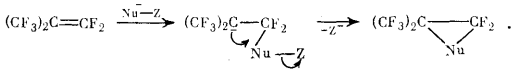
The chemistry of PFIB includes all the reactions with nucleophiles characteristic of fluoro-olefins. Addition to double bond of PFIB takes place when it interacts with

† PFIB is approximately 10 times more toxic than phosgene.

proton-donating nucleophiles. The conjugated nucleophilic addition reactions (the commonest instance is that of the reactions with participation of the $F^-$ anion) as well as ionic cycloaddition of 1,2- or 1,3-dipolar compounds belong to the same type:

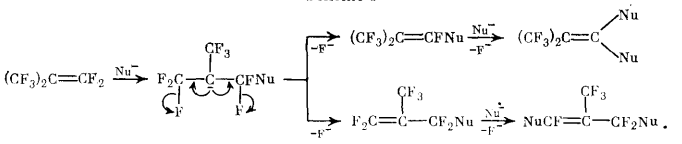


In those cases where the nucleophile is attached to a group Z capable of being split off in the form of an anion (or neutral molecule), the addition can be accompanied by intramolecular cyclisation [see Eqns.(3), (4), (6), and (7) below]:



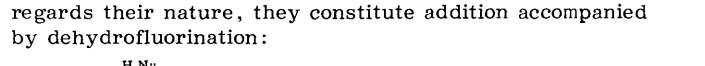
When PFIB interacts with conjugated nucleophiles, the vinyl fluorine atom is usually substituted. The same process is frequently accompanied by the addition of nucleophiles to PFIB, which distinguishes it sharply from the lower fluoroolefins for which addition is more typical. In many cases the products of the "allyl" substitution resulting from the elimination of an $F^-$ anion from the $CF_3$ group are formed. Both "vinyl" and "allyl" products are usually capable of further reactions with nucleophiles, which leads to geminal substitution of 1,3-disubstitution (Scheme 1):

Scheme 1



The relative contributions of the vinyl and allyl substitutions are determined by the nature of the entering nucleophile and also by the reaction conditions. The vinyl substitution is facilitated in the interaction with nucleophiles which ultimately give rise to a substituent with an unshared electron pair as a result of the reaction. In other cases allyl substitution competes with this process to some extent [see Eqn.(9) below].

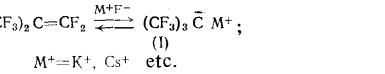
In certain reactions of PFIB both vinyl and fluorine atoms are substituted by an alkylidene residue, the imino-group, or a sulphur atom. However, these processes, which lead to the formation of cumulenes or heterocumulenes, can be classified only formally as substitution reactions, since, as regards their nature, they constitute addition accompanied by dehydrofluorination:



## 1. Reactions with Halide Ions

### *The Fluoride Ion*

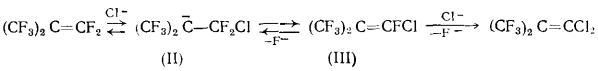
PFIB readily interacts with alkali metal fluorides (KF, CsF) in aprotic dipolar solvents with formation of the perfluoro-t-butyl anion (I). The reaction is reversible, so that the free fluoro-olefin is present in solution together with the anion (I).[7] The anion (I) is generated also in the reaction of PFIB with tetramethylformamidinium hydrogen fluoride[21] or hexamethylguanidinium fluoride[22] and in this case the equilibrium is displaced to a greater extent towards the anion (I), as shown by the $^{19}F$ NMR spectra:



In terms of their wide variety and importance for the chemistry of fluorocarbanions, the reactions of the anion (I) are of independent interest and will be considered in the concluding Section of this review. We shall only note that the anion (I) readily combines with a proton. Thus the interaction of PFIB with hydrogen fluoride in the presence of catalytic amounts of ammonium fluoride[23] or triethylamine[24] results in the formation of monohydroperfluoroisobutane $(CF_3)_3CH$. This reaction is important in the chemistry of PFIB because it accompanied the transformations of the latter in which the initial adducts are dehydrofluorinated.

### *The Chloride Ion*

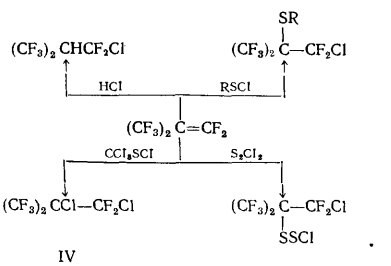
PFIB is also capable of combining with the $Cl^-$ anion via the double bond with formation of the anion (II). This might have led to the exchange of chlorine for fluorine but under the usual conditions this reaction does not occur, since the equilibrium in the exchange is largely displaced towards the initial reactants. The exchange reaction was achieved in the presence of compounds which irreversibly bind the $F^-$ anion. Thus fluorine is exchanged for chlorine in PFIB when the latter is treated with benzoyl chloride in the presence of pyridine; together with the monochloride (III), a certain amount of the *gem*-dichloride is formed under these conditions[25]:



(1)

The interaction of PFIB with phosphoryl chloride catalysed by triethylbenzylammonium chloride (TEBA) yielded the monochloride (III) and the dichloride $ClCF_2C(CF_3)=CFCl$.[25] Furthermore, TEBA or tertiary amines catalyse the hydrochlorination of PFIB [23] and the addition to the latter of aliphatic and aromatic sulphene chlorides[26] or sulphur monochloride[27]. It is of interest that the interaction of PFIB with sulphene chlorides containing electron-accepting groups, in the presence of the chloride ion, is of the halogenophilic type and leads to the chlorination of PFIB.[26] The dichloride (IV) has also been obtained on treatment of PFIB with chlorine under the conditions of nucleophilic catalysis[28] (Scheme 2):

Scheme 2



IV

In the absence of a catalyst, these reactions either do not occur at all or require very severe conditions [see Eqn.(13) below].

*The Bromide Ion*

Fluorine exchanges for bromine in PFIB on treatment of the latter with benzoyl bromide in the presence of pyridine. Together with the monobromide $(CF_3)_2C{=}CFBr$, disubstitution products are formed[25]. Under the conditions of nucleophilic catalysis, it has also been possible to achieve the hydrobromination of PFIB [23] and the addition of bromine to the latter[28] [see Eqn.(13)].

PFIB does not react with the iodide anion; hydriodic acid also does not add to PFIB under the conditions of nucleophilic reaction[23]. Iodoperfluoroisobutene has been obtained from the monochloride (III) by the exchange reaction with KI.[29]#

## 2. Reactions with *O*-Nucleophiles

*Water and Hydrogen Peroxide*

When PFIB reacts with water in acetone[30] or tetrahydrofuran (THF),[31] α-hydrohexafluoroisobutyric acid (V) is formed in a high yield. This is one of the most important reactions of PFIB in practice, particularly because the acid (V) is the starting compound for the synthesis of bis(trifluoromethyl)keten [32] and derivatives of perfluoromethacrylic acid[33]. Depending on the reactant ratio and the reaction conditions, the hydration of PFIB in the presence of triethylamine can yield the fluoride of the acid (VI), the acid (V), or its decarboxylation product—dihydroperfluoropropane[34]:

$$(CF_3)_2C{=}CF_2 \xrightarrow[-HF]{H_2O} \underset{(VI)}{(CF_3)_2CH{-}COF} \xrightarrow[-HF]{H_2O} \underset{(V)}{(CF_3)_2CH{-}COOH} \xrightarrow{-CO_2} (CF_3)_2CH_2 .$$

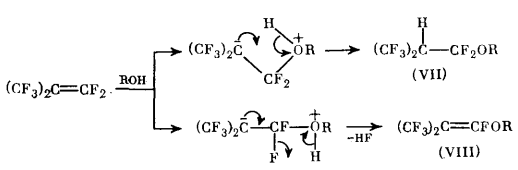
The alkaline epoxidation of PFIB leads to an epoxide[35-37] [see also Eqn.(4)], which has been suggested as a monomer[38,39]:

$$(CF_3)_2C{=}CF_2 \xrightarrow[NaOH]{H_2O_2} (CF_3)_2C(O{-}OH){-}CF_2 \xrightarrow{-OH^-} (CF_3)_2C(O){-}CF_2 . \qquad (3)$$

*Alcohols*

PFIB readily reacts with aliphatic alcohols[40-42] and cellulose[43]. The reaction results in the formation, apart from compound (VII), also of the vinyl ethers (VIII) (Scheme 3). It has been established that the saturated ethers (VII) are converted into the unsaturated ethers (VIII) under much more severe conditions than those in the reaction of PFIB with alcohols. On this basis, it is assumed that the ethers (VII) and (VIII) are formed independent of one another:

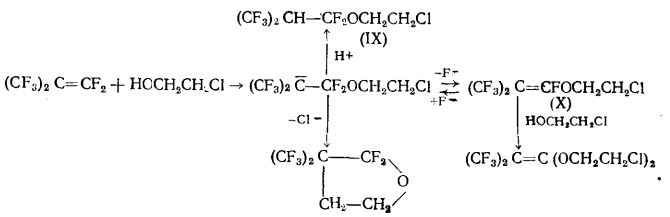
Scheme 3



# Perfluoroisobutenyl derivatives of lithium and magnesium, which can be used to synthesise compounds containing the $(CF_3)_2CF{=}CF$ group, were obtained from chloro- and iodoperfluoroisobutenes[29].

The intermediate dipolar ion is stabilised mainly as a result of the protonation of the anionic centre but enhancement of the electron-donating properties of the residue R promotes the elimination of the $F^-$ anion from the $CF_2$ group[40]. With increase of the acidity of the alcohols, their interaction with PFIB becomes more difficult. Thus $CF_3CH_2OH$, $HSCH_2CH_2OH$, and $ClCH_2CH_2OH$ react with PFIB under mild conditions only in the presence of basic catalysts[40], which tends to increase the fraction of the vinyl substitution products. For example, depending on the conditions, either the ethers (IX) and (X) or the acetal or bis(trifluoromethyl)keten can be obtained from PFIB and ethylene chlorohydrin[44,45]. The product of the intermolecular cyclisation of the intermediate carbanion is formed only under the conditions of thermodynamic control on interaction of the vinyl ether (X) with the $F^-$ anion[45] (Scheme 4):

Scheme 4

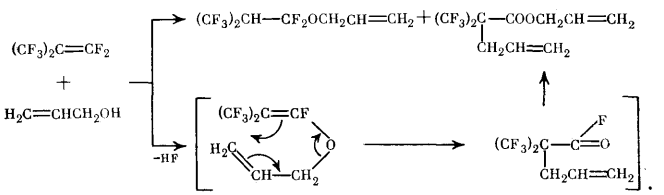


The addition of the enol of pentafluoroacetone to PFIB is catalysed by *N*-methylpyrrolidine or pyridine[46]:

$$(CF_3)_2C{=}CF_2 + CF_2{=}C(OH){-}CF_3 \rightarrow (CF_3)_2CHCF_2OC(CF_3){=}CF_2 .$$

The reactions of PFIB with allyl alcohols are of special interest. Together with the addition products, the products of the Claisen rearrangement of allyl vinyl ethers and not the ethers themselves are formed (Scheme 5):[47,48]

Scheme 5

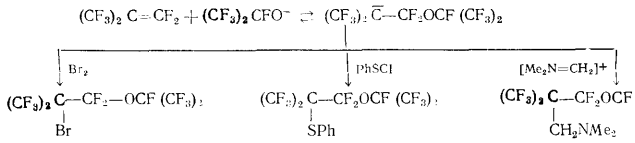


Propargyl alcohol and its homologues react analogously with PFIB and the migration of the propargyl group is accompanied by the acetylene–allene rearrangement[48]. It has been suggested that the products of all these reactions are formed as a result of the [3,3]-sigmatropic rearrangement of the intermediate fluorocarbanion[48].

The reactions of PFIB with sodium alkoxides in aprotic media lead to alkyl perfluoroisobutenyl ethers of bis(trifluoromethyl)keten acetals depending on the reactant ratio[49]. PFIB is apparently capable, in principle, of interacting also with alkali metal perfluoroalkoxides, but the reaction is reversible and the equilibrium is fully displaced towards the initial reactants (the perfluoroisopropoxide anion is a more effective leaving group than the fluoride anion). Indeed, in the presence of appropriate electrophiles it is possible to detect the formation of an intermediate carbanion and to obtain the products of the coupled perfluoroalkoxybromination or perfluoroalkoxysulphenylation of PFIB. The alteration of the nature of the counterion leads to an analogous result: the interaction of PFIB with the salt $[Me_2N{=}CH_2]^+\bar{O}CF(CF_3)_2$

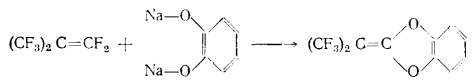
yields a fluorine-containing alkoxyamine as a result of the covalent binding of the intermediate carbanion to the methyleneimmonium cation (Scheme 6):[50]

Scheme 6



*Phenols*

On heating, PFIB reacts with phenol and resorcinol; only the addition products have been obtained as a result[51]. Like alkoxides, the phenoxides react in their turn with PFIB under mild conditions and give rise to the products of the vinyl monosubstitution[52,53] and disubstitution[54,55]. When PFIB reacts with the disodium salt of catechol, a cyclic keten acetal is formed[56]:

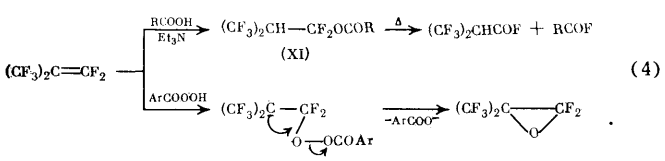


*Acids and Peracids*

In contrast to derivatives of perfluoromethacrylic acid[33], PFIB does not react with carboxylic acids in the absence of a catalyst. Acetic and benzoic acids add to PFIB only in the presence of triethylamine. The resulting adducts (XI) decompose into two acid fluorides on treatment with triethylamine[57] or on thermolysis[58].

Despite the fact that the introduction of electronegative substituents into the olefin molecule usually hinders the Prilezhaev epoxidation, PFIB readily interacts with aromatic peracids to form an epoxide (Scheme 7). The reaction mechanism is apparently inverted in this case and the peracid functions as a nucleophile[59]:

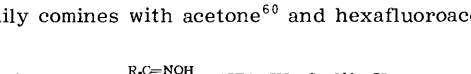
Scheme 7



(4)

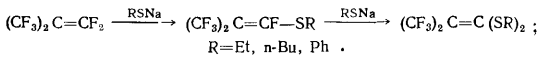
*Derivatives of Hydroxylamine*

PFIB readily comines with acetone[60] and hexafluoroacetone[61] oximes:



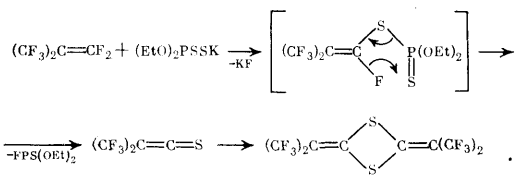
### 3. Reactions with *S*-Nucleophiles

The interactions of PFIB with benzylmercaptan[62], allylmercaptan[63], and thiophenol[26] lead mainly to addition products. Depending on the conditions, mono- or di-substitution products have been obtained in the reactions with mercaptides[64] and thiophenoxide[65]:

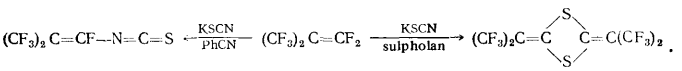


Disubstitution with formation of the bis(trifluoromethyl)-thioketen dimer takes place with PFIB reacts with potassium diethyl phosphorodithioate (Scheme 8):[66] the monosubstitution product could not be isolated owing to its spontaneous decomposition:

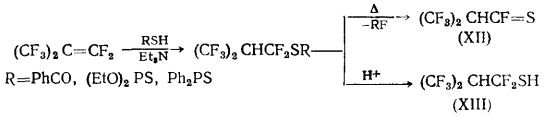
Scheme 8



This reaction is of preparative importance. The interaction of PFIB with the salts of other thiolo-acids leads to the same result[67-69]. It is of interest to note that, in the reaction of PFIB with KSCN, the thiocyanate ion exhibits the properties of an ambident nucleophile[70]:



Thiolo-acids add to PFIB in the presence of triethylamine as the catalyst. Like their oxygen analogues [see Eqn.(4)], the resulting adducts decompose on thermolysis with formation of the thioacid fluoride (XII). Acid hydrolysis of the adducts leads to the mercaptan (XIII) with two fluorine atoms in the α-position[58].

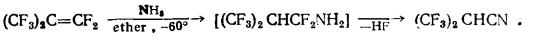


### 4. Reactions with *N*-Nucleophiles

PFIB readily reacts with ammonia and amines and the tendency towards the formation of unsaturated products is then enhanced.

*Ammonia*

PFIB vigorously combines with ammonia. Subsequent dehydrofluorination leads to hexafluoroisobutyronitrile, the low yield of which can be explained by its extreme instability in relation to ammonia[41]:

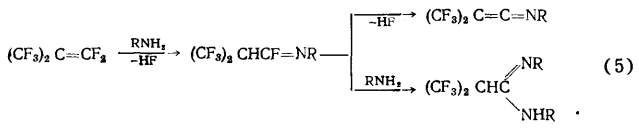


The much lower reactivity of hexafluoropropene in this reaction permits the employment of the latter for the elimination of PFIB from hexafluoropropene[71].

*Primary Amines*

The interaction of PFIB with primary amines leads to α-hydrohexafluoroisobutyroimidoyl fluorides, the amidines derived from this acid, or bis(trifluoromethyl)keten imines (Scheme 9):[72,73]

Scheme 9

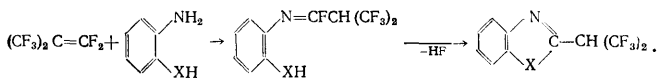


(5)

In the reaction of PFIB with an excess of *p*-toluidine, the corresponding amidines undergo further reactions: derivatives of azetidine and quinoline were obtained under these conditions[74].

Keten imines can be obtained either by the direct interaction of PFIB with primary amines catalysed by triethylamine (in this case the PFIB–$Et_3N$ system behaves simultaneously as the acceptor of the HF evolved) or with preliminary isolation of imidoyl fluorides and subsequent dehydrofluorination with powdered KOH in ether or with the adduct $BF_3.Et_3N$§. The interaction of PFIB with primary amines in the presence of CaF does not stop at the stage involving the formation of ketene imines but leads to their cyclic adducts with PFIB [see Eqn.(12) below].

When PFIB was allowed to react with *ortho*-substituted anilines, the products of the cyclisation of the intermediate imidoyl fluorides were obtained[56] (see also Nakai et al.[75]):

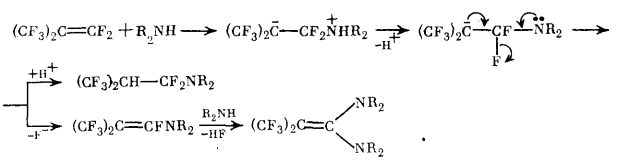


X=O, S, NH

*Secondary Amines*

The interaction of PFIB with secondary amines leads to both addition products and unsaturated products (Scheme 10) and the available data do not permit a rigorous distinction to be made (as in the reaction with alcohols) between situations where the unsaturated products are formed as a result of direct vinyl substitution or as a result of the dehydrofluorination of the adducts formed initially[76–78]:

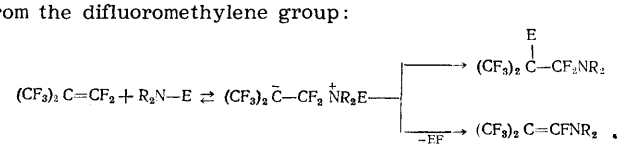
Scheme 10



It has been suggested[76] that the presence of electron-donating substituents at the nitrogen atom increases the ability of its electron pair to "expel" the fluoride ion from the intermediate carbanion. The reactions of PFIB with highly basic secondary amines therefore lead to unsaturated products, while the reactions with weakly basic amines lead to the formation of addition products. The interaction of PFIB with dimethylamine or piperidine in the presence of an excess of the base leads to bis(trifluoromethyl)keten aminals. The corresponding aminal could not be obtained by the reaction with diethylamine, apparently owing to the influence of steric factors in this reaction[79].

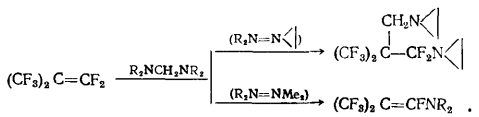
*Tertiary Amines*

The interaction of PFIB with tertiary amines leads to the formation of a dipole ion. When a group capable of cationoid abstraction is present at the nitrogen atom, the ion is stabilised either via the migration of this group to the carbanionic centre or via its elimination with a fluorine atom from the difluoromethylene group:



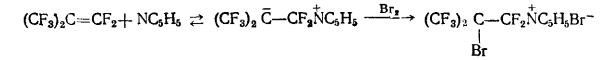
Thus, depending on the character of the substituents at the nitrogen atom, the insertion products or the products of the substitution of a fluorine atom by a dialkylamino-group have been obtained by the reaction of PFIB with tetra-alkyldiaminomethanes (Scheme 11):[80]

Scheme 11



The latter case evidently obtains also in the interaction of PFIB with *N*-trimethylsilylpiperidine[79].

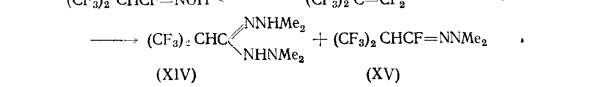
The formation of a dipolar ion from PFIB and $R_3N$ has been confirmed in the study of the reaction of PFIB with pyridine in the presence of bromine; this yielded a coupled addition product[28]:



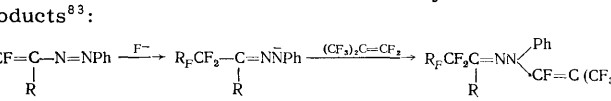
There exist many indirect data indicating the reversible addition of $R_3N$ to PFIB. Thus the dimerisation of bis(trifluoromethyl)keten imines by tertiary amines is retarded in the presence of PFIB by a factor greater than 100.[72]

*Hydroxylamine, Organic Derivatives of Hydrazine, and Hydrazoic Acid*

When PFIB reacts with free hydroxylamine, the fluoride of α-hydrohexafluoroisobutyrohydroxamic acid is formed[81]. The reaction of PFIB with 1,1,-dimethylhydrazine gives rise to the hydrazine derivatives (XIV) or (XV), depending on the reactant ratio[82]:



The interaction of PFIB with phenylazo-olefins in the presence of CsF results in the formation of vinyl substitution products[83]:

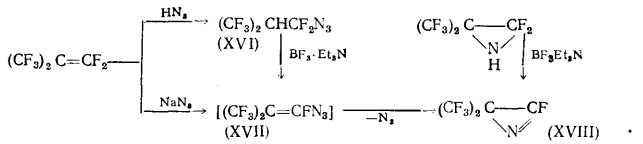


PFIB combines with 3,3-dimethylaziridine[84]. An addition product has been obtained from PFIB and hydrazoic acid, generated *in situ* from $NaN_3$ and sulphuric acid in dimethylformamide[85]. PFIB reacts even more readily with sodium azide[85,86]. The azirine (XVIII), formed as a result of the spontaneous decomposition of the unsaturated azide (XVII),

§ This reagent is particularly convenient in the synthesis of keten imines which readily dimerise in the presence of traces of bases.

then polymerises under the influence of the nucleophiles present in the reaction mixture. However, it was obtained under neutral conditions by the dehydrofluorination of the saturated azide (XVI) or 3,3-difluoro-2,2-bis(trifluoromethyl)aziridine by the complex $BF_3.Et_3N$ (Scheme 12):

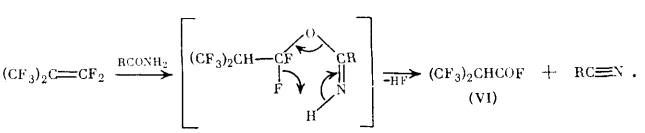
Scheme 12



*Amides and Sulphonamides*

The electrophilic properties of PFIB are sufficiently strong for it to react with carboxylic acid amides in the absence of bases[87]. When PFIB was allowed to react with acetamide or benzamide in diglyme, the acid fluoride (VI) and the corresponding nitriles were obtained (Scheme 13). Evidently in this case the amides undergo *O*-alkylation with formation of unstable iminoesters, which decompose subsequently like the acyl derivatives of α,α-difluoroalcohols [see Eqn.(4)]:

Scheme 13



The much less basic benzenesulphonamide and urethane react with PFIB only in the presence of bases. PFIB readily reacts with the potassium salt of benzenesulphonamide to form the adduct (XIX) of *N*-phenylsulphonylketen imine with KF:[87]

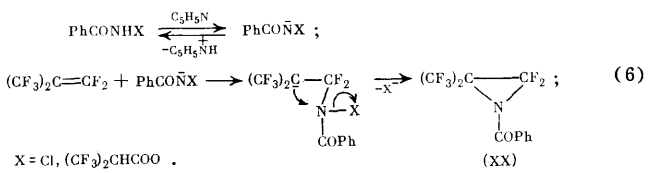
$$(CF_3)_2C{=}CF_2 + PhSO_2\bar{N}H\ K^+ \xrightarrow{-HF} (CF_3)_2C{=}CF\bar{N}SO_2Ph\ K^+ \quad (XIX)$$

The reaction of PFIB with urethane takes place in the presence of KF as the catalyst and leads to the adduct of the corresponding keten imine with PFIB [see Eqn.(12) below]

*N-Nucleophiles Containing Leaving Groups*

When PFIB interacts with *N*-chloro- or *N*-acyloxy-benzamide in the presence of bases, *N*-benzoylaziridine (XX) is formed in a satisfactory yield (Scheme 14). This reaction, which constitutes nucleophilic cyclisation of PFIB, is an example of the fixation of the amide anion formed as an intermediate in the Hofmann and Lossen rearrangements by the interaction with the electrophilic C=C bond[88]:

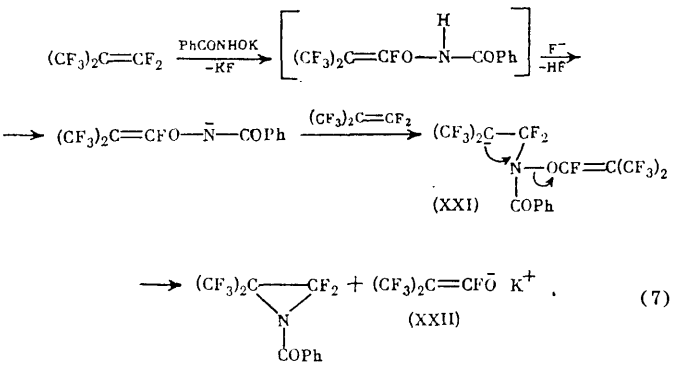
Scheme 14



(6)

The reaction of PFIB with the potassium salt of benzohydroxamic acid proceeds via an analogous route (Scheme 15). In this case the carbanion (XXI) cyclises and the mesomeric anion (XXII) plays the role of the leaving group[88]:

Scheme 15

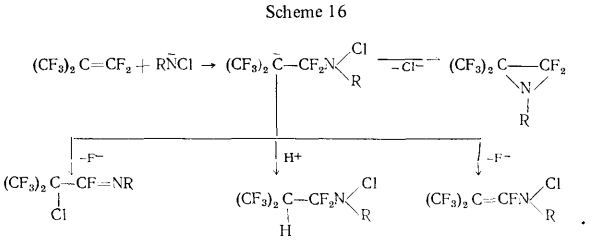


(7)

The formation of the aziridine (XX) was also detected in the reaction of PFIB with $Me_3\dot{N}-\bar{N}COPh$.[88]

When various *N*-chloroamides were involved in the nucleophilic cyclisation reaction, it was observed that products other than aziridines are also formed; this is associated with the low effectiveness of the $Cl^-$ anion as the leaving group and also with the tendency of the chlorine in the *N*-chlorocompounds to undergo cationoid abstraction (Scheme 16):[89]

Scheme 16



The cyclisation of PFIB with the aid of *N*-(*p*-nitrobenzenesulphonyloxy)amides takes place much more unambiguously[89]:

$$(CF_3)_2C{=}CF_2 + O_2NC_6H_4SO_2ONHR \xrightarrow[-O_2NC_6H_4SO_3\bar{E}t_3\dot{N}H]{Et_3N} (CF_3)_2C\!-\!CF_2 \quad (N,R);$$

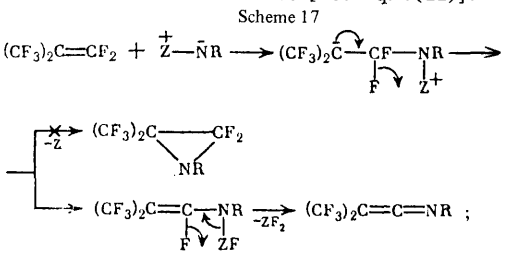
R=COOEt, $PhSO_2$.

These reagents have been used successfully for the cyclisation of other highly electrophilic unsaturated fluorine compounds[89].

It has been established that PFIB does not form cyclic adducts with acylnitrenes generated by the photolysis of benzoyl[88] or alkoxycarbonyl azides[89]; this confirms the nucleophilic mechanism of the formation of the fluorine-containing aziridines.

In the interaction of PFIB with iminophosphoranes[90] or iminosulphuranes[91], rings are not formed either. The only pathway in these reactions involves vinyl substitution in accordance with Scheme 17 accompanied by the β-decomposition of the intermediate fluorides [see Eqn.(11)]:

Scheme 17



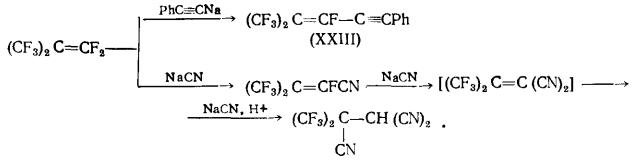
(8)

Z = $Ph_3P$, R = Ph; Z = $Me_2S$, R = COOEt.

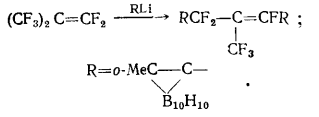
## 5. Reactions with *C*-Nucleophiles

*Organometallic Compounds*

The replacement of the vinyl fluorine atom by the CN group is readily achieved by the reaction of PFIB with NaCN and the resulting nitrile is capable of further reaction with the cyanide[92]. The reaction of PFIB with sodium phenylacetylide in ether results in the formation of the enyne (XXIII):[93]

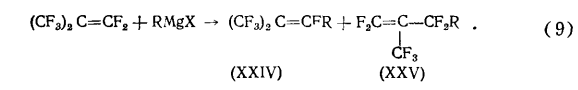


When PFIB was allowed to react with aryl-lithium compounds, a series of vinyl mono- and di-substitution products were obtained; the latter exhibit a high contraceptive activity[94,95]. PFIB reacts with 2-lithio-1-methyl-*o*-carbaborane to form a 1,3-disubstitution product[96]:



The corresponding derivative of *m*-carbaborane gives rise to the product of the usual vinyl substitution[97].

PFIB reacts readily with alkyl- and benzyl-magnesium halides with formation of vinyl and allyl substitution products[98–100]:



(9)

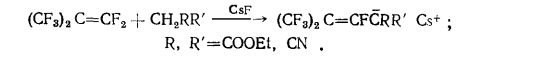
The terminal olefins (XXV) are readily converted into the inner olefins (XXIV) by Lewis bases¶ or acids. This apparently explains the finding that, when PFIB interacts with arylmagnesium halides, it is possible to identify only the inner olefins (XXIV). The corresponding terminal olefins should contain the highly mobile "benzyl" fluorine atom, as a result of which they are converted into the olefins (XXIV) under the reaction conditions.

*Compounds with Active Methylene and Methyl Groups*

PFIB does not react with malonic ester in the absence of bases but, with catalysis by triethylamine, it gives rise to a mixture of products containing the alkylidenemalonic ester (XXVI), the allene (XVII), and the pyran (XXVIII).[101] The reaction of PFIB with sodiomalonic ester leads to the same result†. The allene and pyram are formed as a result of the dehydrofluorination of the alkylidenemalonic ester (XXVI) via two pathways: with elimination of the vinyl fluorine atom or the fluorine atom from the $CF_3$ group; in the latter case the 1,3-diene cyclises to a pyran (Scheme 18):[100]

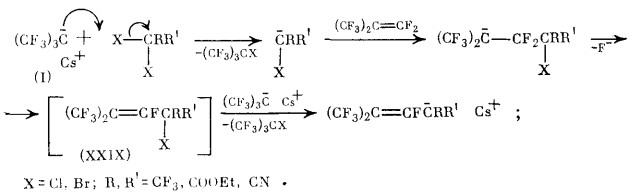
The use of the complex $BF_3.Et_3N$ in the reaction of PFIB with malonic esters made it possible to achieve the preparative synthesis of the allenes (XXVII).[101] This complex not only activates the methylene group but at the same time it plays the role of the dehydrofluorinating agent.

The condensation of PFIB with active methylene groups in the presence of CsF has also been investigated. 3-Ethoxycarbonyl-3-phenyl-1,1-bis(trifluoromethyl)allene was obtained in this way from phenylacetic ester[103]. More reactive allenes, obtained from malonic acid derivatives, have been isolated in the form of stable adducts with CsF:[103]

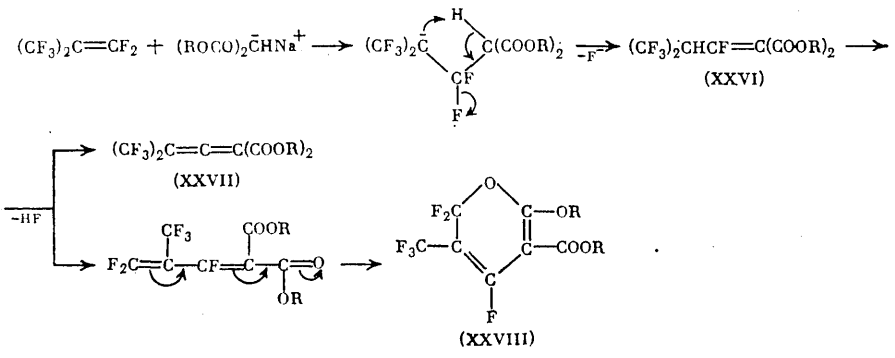


Analogous adducts have been obtained also in the reaction of PFIB with certain compounds containing dihalogenomethylene groups[104]. In this case the attacking species is the α-halogenocarbanion, which is generated as a result of the halogenophilic reaction of the perfluoro-t-butyl anion with a *gem*-dihalide [see Eqn.(14)]. This carbanion substitutes the vinyl fluorine atom in PFIB with formation of the intermediate (XXIX), which is also dehalogenated by the anion (I) (Scheme 19):

Scheme 19



Scheme 18



¶ This rules out the possibility of obtaining the allyl substitution products in aprotic dipolar solvents containing the $F^-$ anion (see the discussion in the communication of Zeifman et al.[87]).

† The condensation of PFIB with sodiomalonodinitrile afforded $(CF_3)_2CHCF=C(CN)_2$.[102]

In the presence of CsF and under comparatively mild conditions, PFIB condenses with acetonitrile to form the salt (XXX):[105]

$$(CF_3)_3\bar{C} \underset{}{\overset{MeCN}{\rightleftharpoons}} (CF_3)_3CH + \bar{C}H_2CN$$

$$(CF_3)_2C{=}CF_2 \xrightarrow[-F^-]{\bar{C}H_2CN} (CF_3)_2C{=}CFCH_2CN \xrightarrow[-(CF_3)_3\bar{C}]{(CF_3)_3\bar{C}}$$

$$\rightarrow (CF_3)_2C{=}CF\bar{C}H{-}CN \xrightarrow[-(CF_3)_3CH]{(CF_3)_2C=CF_2} [(CF_3)_2C{-}CF]_2\bar{C}{-}CN\ Cs^+ \quad .$$

(XXX)

PFIB reacts analogously with acetyl bromide in the presence of CsF.[7]

Vinyl substitution products have been obtained also in the condensation of PFIB with a number of other *C*-nucleophiles [100,106,107] catalysed by the $F^-$ anion or tertiary amines:

$$(CF_3)_2C{=}CF_2 \xrightarrow{Me_2CHCOF} Me_2C\begin{matrix}CF{=}C(CF_3)_2\\ COF\end{matrix}$$

$$(CF_3)_2C{=}CF_2 \xrightarrow{(CF_3)_2CHCOOEt} (CF_3)_2C\begin{matrix}CF{=}C(CF_3)_2\\ COOEt\end{matrix} \qquad (10)$$

$$(CF_3)_2C{=}CF_2 \xrightarrow{NaC(COOMe)_2} (CF_3)_2C{=}C\begin{matrix}Me\\ |\\ F\end{matrix}\begin{matrix}Me\\ |\\ C(COOMe)_2\end{matrix} \quad .$$

A similar product obtained from PFIB and chloroform is dehalogenated under the reaction conditions with formation of dichlorobis(trifluoromethyl)allene (isolated in the form of an adduct with furan):[108,109]

$$(CF_3)_3\bar{C} + H{-}CCl_3 \rightleftharpoons (CF_3)_3CH + \bar{C}Cl_3 \ ;$$

$$(CF_3)_2C{=}CF_2 \xrightarrow[-F^-]{\bar{C}Cl_3} (CF_3)_2C{=}\underset{F}{C}{-}\underset{Cl}{CCl_2} \xrightarrow{-[FCl]} (CF_3)_2C{=}C{=}CCl_2 \quad .$$

The reactions of PFIB with fluorocarbanions are described below in Section VI.

### *Nitroalkanes*

The ambident anions of the salts of nitroalkanes attack the double bond in PFIB via the oxygen atom. The subsequent reactions according to Scheme 20 lead to the formation of the dioxazoles (XXXI).[110,111] The key stage of the reaction is apparently the migration of the perfluoroisobutenoxide anion [cf.Eqn.(7)] from the nitrogen atom to the carbon atom in the intermediate *O*-perfluoroisobutenylnitrone ether:

Scheme 20

$$(CF_3)_2C{=}CF_2 + RCH{=}N\overset{O}{\underset{O^-}{}} \rightarrow \left[(CF_3)_2C{=}CFO{-}N{=}CHR\right] \rightarrow$$

$$\rightarrow \left[(CF_3)_2C{=}CF\bar{O}\underset{R}{\underset{|}{CH}}{-}N{=}O\right] \rightarrow \left[(CF_3)_2C{=}CFO\underset{R}{\underset{|}{CH}}{-}N{=}O\right] \rightarrow$$

$$\rightarrow \left[(CF_3)_2C{=}CFOC(R){=}NOH\right] \xrightarrow{-HF} (CF_3)_2C{-}C\begin{matrix}O{-}N\\ \|\\ O{-}C{-}R\end{matrix} \quad .$$

(XXXI)

### *Phosphorus and Sulphur Ylides*

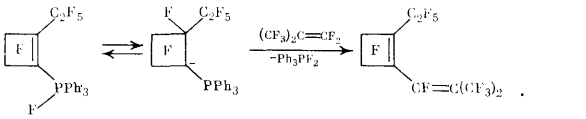
The reaction of PFIB with the ylide (XXXII), leading to the cross-conjugated perfluorotriene (XXXIII),[112,113] has been investigated (for the mechanism, see the review of Tyuleneva et al.[114]):

$$(CF_3)_2C{=}CF_2 + (CF_3)_2C{=}C{=}PPh_3 \xrightarrow{-Ph_3PF_2} (CF_3)_2C{=}C\begin{matrix}CF{=}C(CF_3)_2\\ CF{=}C(CF_3)_2\end{matrix} \quad .$$

(XXXII) (XXXIII)

When PFIB was allowed to interact with the fluorophosphorane (XXIV), the fluorodiene (XXXVI) was obtained; the preliminary isomerisation of the phosphorane to the phosphorus ylide (XXXV) has been postulated (Scheme 21):[115]

Scheme 21



(XXXIV) (XXXV) (XXXVI)

In the reaction of PFIB with the S-ylide (XXXVII), the intermediate fluorosulphurane is dehydrofluorinated to the fluorine-containing ylide (XXXVIII).[91] As in the reaction of PFIB with α-halogenocarbanions discussed above, in this reaction the only pathway leading to the stabilisation of the intermediate fluorocarbanion involves the elimination of the $F^-$ anion from the $CF_2$ group and not intramolecular cyclisation (Scheme 22). In this case vinyl substitution is specially preferred owing to the presence of the onium fragment [see Eqn.(8)]:

Scheme 22

$$(CF_3)_2C{=}CF_2 + \underset{(XXXVII)}{Me_2\overset{+}{S}{-}\bar{C}HCOOEt} \rightarrow (CF_3)_2\bar{C}{-}\underset{F}{CF}{-}\underset{S^+Me_2}{CH}COOEt \rightarrow$$

$$\rightarrow \left[(CF_3)_2C{=}\underset{F{-}SMe_2}{CF}CHCOOEt\right] \xrightarrow{-HF} (CF_3)_2C{=}CF{-}\underset{S^+Me_2}{\bar{C}}{-}COOEt \qquad (11)$$

(XXXVIII)

## 6. Reactions with *P*-Nucleophiles

PFIB readily reacts with trialkyl phosphites, forming trialkoxyfluoroperfluoroisobutenylphosphoranes (XXXIX).[115-117] The synthesis of the adducts (XXXIX) constitutes a rare instance of the isolation of pentacovalent (and not tetracovalent quasi-phosphonium) intermediates of the Arbuzov rearrangement. On heating, the adducts (XXXIX) decompose via two pathways:

$$(CF_3)_2C{=}CF_2 + P(OR)_3 \rightarrow (CF_3)_2C{=}CF{-}PF(OR)_3 \begin{cases} \xrightarrow{-R_2O} (CF_3)_2C{=}CF{-}\underset{O}{\overset{F}{P}}{-}OR \\ \xrightarrow{-RF} (CF_3)_2C{=}CF{-}\underset{O}{P}(OR)_2 \end{cases} .$$

(XXXIX)

The interaction of PFIB with bis(dialkylamino)chlorophosphines is complicated by the exchange of the substituents at the carbon and phosphorus atoms[118]:

$$(CF_3)_2C{=}CF_2 + ClP(NR_2)_2 \rightarrow (CF_3)_2C{=}\underset{Cl}{\overset{F}{C}}{-}PF(NR_2)_2 \rightarrow$$

$$(CF_3)_2C{=}\underset{Cl}{C}{-}PF_2(NR_2)_2 \quad .$$

PFIB reacts with di-isopropylphosphine to form a vinyl substitution product[119].

The reaction of PFIB with tertiary phosphines is unusual. It does not stop at the stage involving the formation of the vinyl substitution products—fluorophosphoranes $(CF_3)_2C{=}CF{-}PR_3F$; subsequent reactions yielded the perfluorodiene (XL) and the cross-conjugated perfluorotriene (XXXIII) [112,113] (for the reaction mechanism, see Tyuleneva et al.[114]):

$$(CF_3)_2C{=}CF_2 \xrightarrow[-R_3PF_2]{PR_3} (CF_3)_2C{=}CFCF{=}C(CF_3)_2 + (CF_3)_2C{=}C\begin{matrix}CF{=}C(CF_3)_2\\ CF{=}C(CF_3)_2\end{matrix} \quad .$$

(XL) (XXXIII)

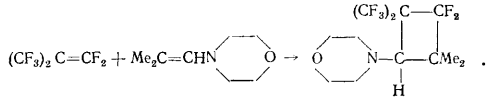
The rate and direction of the reaction depend greatly on the nature of the phosphine and the polarity of the solvent. Thus PFIB reacts with tributylphosphine in ether to form only products of the exchange of the ligands in the intermediate $(CF_3)_2C{=}CFPFBu_3$, namely the phosphoranes $(CF_3)_2C{=}CBuPF_2Bu_2$ and $(CF_3)_2C{=}CFPF_2Bu_2$, while in acetonitrile and diglyme the defluorodimerisation and defluorotrimerisation products are formed[113].

The observed characteristic features made it possible to extend the reaction of tertiary phosphines with PFIB to other fluoro-olefins and to establish it as a method of synthesis of fluorine-containing dienes[120].

## 7. Cycloaddition

PFIB enters into [2 + 2]-, [2 + 3]-, and [2 + 4]-cycloaddition reactions with various unsaturated compounds to form products with four-, five-, and six-membered rings, the first two types of cycloaddition being most characteristic of this fluoro-alkene. PFIB undergoes the Diels–Alder reaction only under very severe conditions (with cyclopentadiene at 150 °C and with butadiene at 200 °C) and produces a low yield of cyclic 1,4-adducts[121]. On the other hand, a cyclic analogue of PFIB, namely perfluoromethylenecyclopropane, is an active dienophile and forms an adduct with cyclopentadiene at a temperature as low as 0 °C.[122]

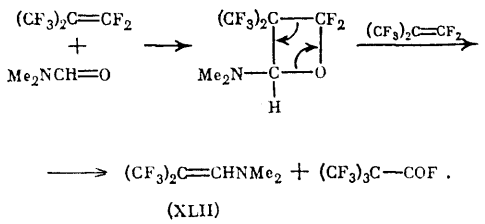
At the same time, PFIB readily undergoes cycloaddition reactions with multiple bonds enhanced nucleophilic properties. Such reactions include the formation of a derivative of cyclobutane when PFIB interacts with isobutenyl-morpholine[123]:



This reaction is accelerated with increase of the polarity of the solvent, which supports an ionic mechanism of the cycloaddition. Perfluoroalkenylation products have been obtained by the interaction of PFIB with the enamine (XLI)[123] or the keten acetal[100] (Scheme 23). Evidently the intermediate dipolar ions are stabilised not only by cyclisation but also by the elimination of the $F^-$ anion and a proton:

PFIB probably reacts with dimethylformamide via the [2 + 2]-cycloaddition mechanism[124], but the unstable cyclic adduct decomposes with elimination of carbonyl fluoride, which leads to the fluoride of perfluoropivalic acid and the enamine (XLII) (Scheme 24):

Scheme 24

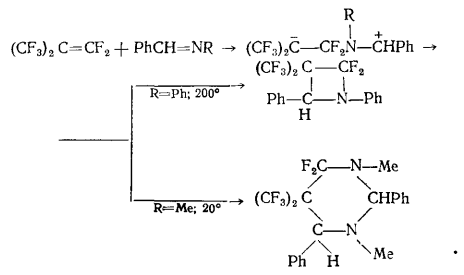


(XLII)

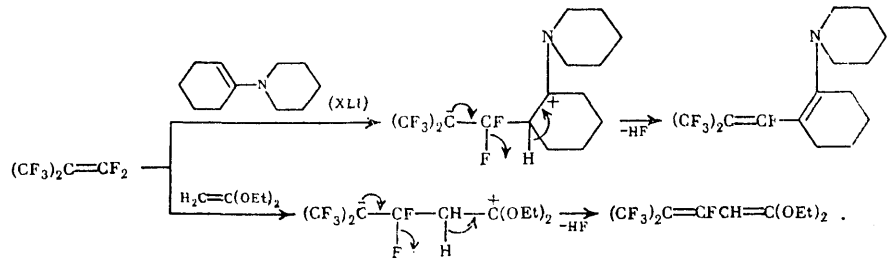
PFIB reacts in the same way with dimethylaminobenzaldehyde#[125], nitrosobenzene[61], and sodium nitrite[61], which lead to the olefin $(CF_3)_2C{=}CHC_6H_4NMe_2$ and the anil and oxime of hexafluoroacetone respectively.

A stable cyclic adduct has been obtained from PFIB and benzylideneaniline under severe conditions. The more nucleophilic benzylidenemethylamine reacts with PFIB much more readily; however, this involves the formation of a six-membered cyclic adduct incorporating two molecules of the imine (Scheme 25)[126]:

Scheme 25



Scheme 23

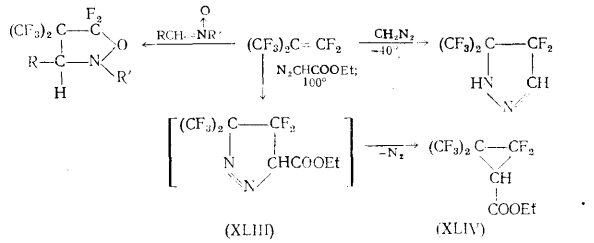


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# In the absence of the activating dimethylamino-group, aromatic aldehydes react with PFIB only under the conditions of nucleophilic catalysis[125].

PFIB readily gives rise to 1,3-cycloaddition products on reaction with diazomethane[93] and nitrones[127,128]. Pyrazoline (XLIII) obtained from PFIB and diazoacetic ester eliminates nitrogen, which leads to the cyclopropane (XLIV) (Scheme 26):[91]

Scheme 26



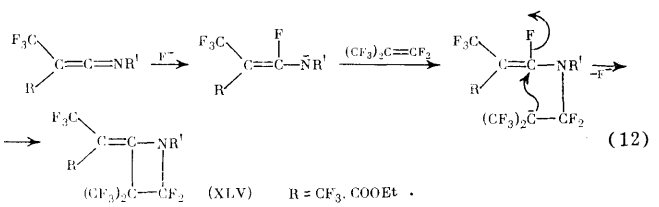
(XLIII) (XLIV)

The range of cycloaddition reactions with participation of PFIB has been expanded by employing nucleophilic catalysts. This approach made it possible to involve in the cycloaddition to PFIB compounds containing electrophilic multiple bonds.

We may note that the application of nucleophilic catalysis is of general importance in the chemistry of compounds with electrophilic multiple bonds and in particular such catalysis is used widely for the dimerisation and trimerisation of isocyanates[129], ketens[130], keten imines[72], and activated olefins[131]. The application of nucleophilic catalysts makes it possible to achieve also mixed cyclodimerisation, for example, in the case of hexafluoroacetone and ketens[132] or isocyanates[133].

In the presence of alkali metal fluorides or tertiary amines, PFIB reacts with fluorine-containing keten imines under mild conditions in accordance with Scheme 27 to form cyclic adducts—the azetidines (XLV).[134] The role of the catalyst evidently consists in converting the electrophilic keten imine into a nucleophilic mesomeric anion capable of adding to the double bond of PFIB. Such addition is accompanied by cyclisation and regeneration of the catalyst:

Scheme 27



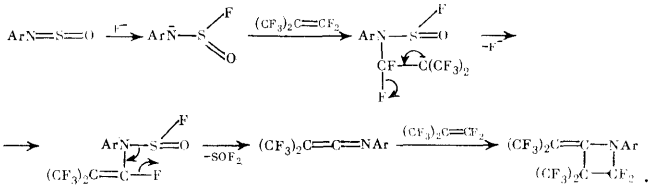
(12)

(XLV) R = $CF_3$, COOEt .

The azetidines (XLV, R=$CF_3$) are also formed in the reaction of PFIB with primary amines in the presence of the same catalyst[134], since the keten imines themselves are obtained from PFIB and primary amines [see Eqn.(5)]. It is striking that the rate of addition of $RNH_2$ to PFIB is higher than the rate of the subsequent reactions, including the formation of imidoyl fluorides and keten imines. By selecting the appropriate reactant ratio and the catalyst, this makes it possible to control the reaction by arresting it at any stage. Such control cannot be achieved in the reaction of PFIB with the weakly basic urethane. In this case the first stage is the slowest and the only product isolated is therefore the corresponding *N*-epoxycarbonylazetidine[134].

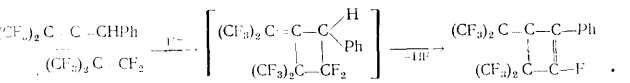
The azetidines (XLV, R=$CF_3$) are also formed in the reaction of PFIB with *N*-sulphinylamines in the presence of CsF (Scheme 28).[135] Evidently vinyl substitution and β-elimination of $SOF_2$ and not cycloaddition take place initially in this reaction; the keten imines thus formed combine with a further PFIB molecule:

Scheme 28



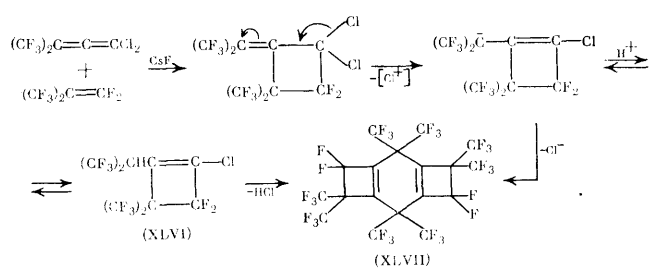
This Scheme confirms that the reaction of PFIB with *N*-sulphenylbenzenesulphonamide leads to *N*-benzenesulphonyl-bis(trifluoromethyl)keten imine, which gives rise to a stable adduct with CsF, analogous to the adduct (XIX).[87]

The application of nucleophilic catalysis also made it possible to achieve the cycloaddition of PFIB to allenes[10]:



PFIB apparently interacts via the analogous Scheme 29 with dichlorobis(trifluoromethyl)allene. The reduction of the intermediate cyclic adduct by the $(CF_3)_3C^-$ anion results in the formation of the cyclobutene derivative (XLVI), whose dehydrochlorination leads to the tricyclic compounds (XLVII):[108,109,136]

Scheme 29



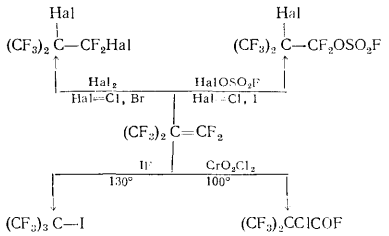
(XLVI) (XLVII)

## IV. REACTIONS WITH ELECTROPHILES

As already mentioned above, in reactions with electrophiles PFIB is much less reactive than lower fluoro-olefins and these reactions require as a rule extremely severe conditions.

The addition of halogens to PFIB via a radical mechanism can be achieved photochemically or thermally in the presence of catalysts. Thus PFIB is chlorinated in the gas phase at 128 °C over $FeCl_3$ on activated charcoal (AC).[137] The heat of chlorination of PFIB is $\Delta H$ = 42.2 kcal mole$^{-1}$, while for tetrafluoroethylene $\Delta H$ = 57 kcal mole$^{-1}$. PFIB is not brominated under illumination; the method of elimination of unsaturated impurities from PFIB is based on this property of the latter. However, in the presence of catalytic amounts of acetamide, PFIB combines with bromine under ultraviolet irradiation[10]. The addition of iodine fluoride to PFIB [14] and its reaction with chromyl chloride[138] on heating have also been described.

Highly reactive chlorine and iodine fluorosulphates add to PFIB at a temperature as low as 20 °C:[139]



(13)

PFIB exchanges fluorine for chlorine under severe conditions on treatment with $AlCl_3$ and, in contrast to the exchange reaction with the $Cl^-$ anion [Eqn.(1)], the polysubstitution products $ClCF_2C(CF_3)=CCl_2$ and $Cl_2FC(CF_3)=CCl_2$ are formed in this case together with monochlorides and dichlorides[25].

The addition of hydrogen halides to PFIB in the gas phase takes place only on heating, in contrast to nucleophilic hydrohalogenation [Eqn.(2)]:[140]

$$(CF_3)_3CH \xleftarrow{HF,\ 200^\circ} (CF_3)_2C{=}CF_2 \xrightarrow[CaSO_4/Al_2O_3,\ \Delta]{HX} (CF_3)_2CHCF_2X;\quad X=Cl,\ Br.$$

Mercuration of PFIB in anhydrous HF or $AsF_3$ yields bis-(perfluoro-t-butyl)mercury:

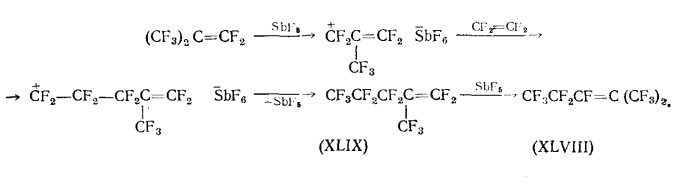
$$(CF_3)_2C{=}CF_2 \xrightarrow[200^\circ]{HgF_2} (CF_3)_2\overset{+}{C}-CF_2 \xrightarrow{HF} (CF_3)_3CHgF \xrightarrow{(CF_3)_2C=CF_2} (CF_3)_3C-Hg-C(CF_3)_3.$$

It has been suggested that the reaction proceeds as a result of the attack by the metal cation on the double bond of PFIB or via a four-centre cyclic transition state[141]. The nucleophilic mercuration of PFIB takes place under much milder conditions[7].

In the presence of $SbF_5$, it is impossible to achieve the interaction of PFIB with elemental sulphur. The attacking agent is apparently the doubly charged sulphur cation formed when sulphur is oxidised by $SbF_5$.[142] The reaction of PFIB with bis(pentafluorophenyl) disulphide has also been studied[143]:

$$(CF_3)_3C-SS-C(CF_3)_3 \xleftarrow[100^\circ]{S;\ SbF_5} (CF_3)_2C{=}CF_2 \xrightarrow{(C_6F_5S)_2;\ SbF_5} (CF_3)_3C-SC_6F_5.$$

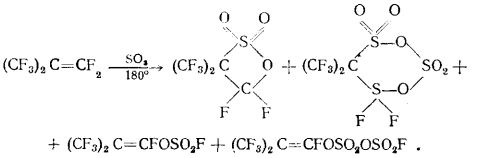
The condensation of PFIB with fluorinated ethylenes has also been achieved in the presence of $SbF_5$ under extremely mild conditions[144,145]. The primary step in these reactions is the formation of the perfluoromethylallyl cation (detected by $^{19}F$ NMR):



Together with the 1 : 1 adduct (XLVIII), the 1 : 2 adduct $C_3F_7C(CF_3)=CFC_2F_5$ is formed in the reaction via the intermediate isohexene (XLIX).

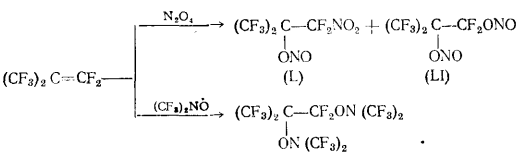
PFIB reacts via an analogous mechanism with perfluoroazapropene, giving rise to a high yield of the perfluoroenamine $(CF_3)_2NCF=C(CF_3)_2$.[146]

The electrophilic addition of sulphur trioxide to PFIB at 180 °C leads to the corresponding β-sultone and pyrosultone together with the products of their further reactions[147]:

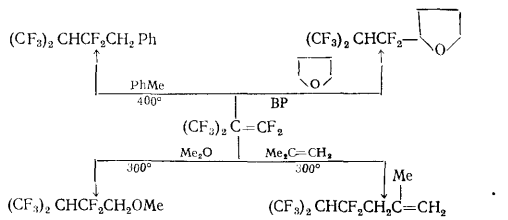


The nitration of PFIB by nitrogen oxides proceeds via a radical mechanism (Scheme 30): approximately equal amounts of the nitronitrite (L) and the dinitrite (LI) were obtained in this reaction[148]. PFIB also combines with bis(trifluoromethyl)amine oxide:[149,150]

Scheme 30



The fluoroalkylation of tetrahydrofuran by PFIB takes place with initiation by benzoyl peroxide (BP).[151] On heating, PFIB is also inserted in the C–H bonds of isobutene, toluene[152], and dimethyl ether[153]:



## V. OTHER REACTIONS

PFIB is readily oxidised by potassium permanganate in water[10]. This reaction constitutes a convenient laboratory method for the synthesis of hexafluoroacetone[154]. Among its side products, hexafluoro-α-hydroxyisobutyric acid[155] and monohydroperfluoroisobutane[10] were identified:

$$(CF_3)_2C{=}CF_2 \xrightarrow[H_2O]{KMnO_4} (CF_3)_2C(OH)_2 + (CF_3)_2\underset{OH}{\underset{|}{C}}-COOH + (CF_3)_3CH.$$

The formation of hexafluoroacetone has also been established in the reaction of PFIB with sodium nitrite in dimethylformamide[61] and with hydrogen peroxide in aqueous alkali[35]. The interaction of PFIB with fluorine oxide gives rise to the epoxy-derivative of PFIB.[38]

The hydrogenation of PFIB in the presence of a palladium catalyst leads to dihydroperfluoroisobutane (LII) as the only product[56]. When nickel is used, the main hydrogenation product is 1,1,1-trifluoro-2-trifluoromethylpropane[157]:

$$(CF_3)_2CHCF_2H \xleftarrow[Pd]{H_2} (CF_3)_2C{=}CF_2 \xrightarrow[Ni]{H_2} (CF_3)_2CHCH_3.$$
(LII)

Traces of dihydroperfluoroisobutane have also been detected in the products of the reaction of PFIB with the Hantzsch ester[23].

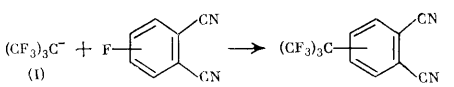
It has been shown that PFIB does not form homopolymers on radical initiation and γ-irradiation. However, the formation of copolymers with certain acrylates on initiation by acetyl peroxide has been noted[158,159]. The copolymer with tetrafluoroethylene, obtained on γ-irradiation, includes 4% of PFIB.[160] Studies of the kinetics of the copolymerisation of PFIB with tetrafluoroethylene have been described by Isamukhamedov et al.[161] and Gafurov et al.[162]

## VI. REACTIONS OF THE PERFLUORO-t-BUTYL ANION

The study of the methods of synthesis and reactions of the perfluoro-t-butyl anion (I) is associated with the possibility of synthesising a wide variety of compounds containing the $(CF_3)_3C$ group and their practical employment. This Section includes the literature on the chemistry of this anion which has not been incorporated in a special review on this topic[7] published in 1976§. It is noteworthy that the chemistry of this anion differs from the chemistry of the primary and secondary fluorocarbanions not only by its wide variety but also by specific features associated with the increased stability of the anion. The anion (I) is a more effective leaving group than, for example, the perfluoroisopropyl anion. The ease of the decarboxylation of $(CF_3)_3C-COOH$ compared with $(CF_3)_2CF-COOH$ [163] and also the instability of perfluoro-t-butylmethanols in alkaline media are consistent with this finding[164].

For the same reasons, certain reactions known for primary and secondary fluorocarbanions cannot be carried out with the anion (I), since in the presence of the $F^-$ anion these reactions are reversible and the equilibrium is displaced towards the initial compounds. This applies to the interaction of the anion (I) with benzoyl chloride[164,165] and dimethylaminotrifluorosulphurane[166]. Furthermore, as a consequence of its reversibility, the dimerisation of PFIB rarely accompanies its reactions initiated by the $F^-$ anion[7]. It is remarkable that the pseudohalogen character of the perfluoro-t-butyl group makes it possible to employ compounds of the type $CF_3C-X$ (X = Br, PhS, etc.) as electrophiles for the bromination, sulphenylation, and other similar reactions involving fluorocarbanions. It is also significant that the anion (I) in solutions is in equilibrium with free PFIB, so that the anionoid intermediates formed in the reactions of the anion (I) frequently interact with PFIB.

The anion (I) has been alkylated by $I(CH_2)_nI$ ($n = 1$ [104] and $n = 3$ or 4 [167]), $ClCH_2SCH_3$,[91] $(ClCH_2)_2O$, and $(ClCH_2)_3N$. The corresponding perfluoro-t-butyl derivative has been obtained from the anion (I) and α-chlorotetrahydrofuran[169]. The synthesis of perfluoro-t-butylphthalonitriles, which have been used to obtain phthalocyanines, has been described[170]:



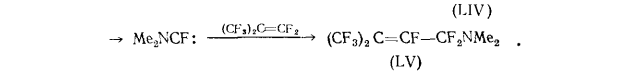
The interaction of PFIB with fluorotrimethylamine leads to the tertiary amine (LIII).[71] The anion (I) is probably formed in this case and the source of the fluoride ion is fluorotrimethylamine itself:



(LIII)

§ Except where stated otherwise, this Section deals with the reactions of the anion (I) generated by the addition of alkali metal fluorides to PFIB.

PFIB reacts in an unusual manner with α,α-difluorotrimethylamine. Fluoroamine adds reversibly under these conditions to the fluoro-olefin and compound (LIV) is formed; on heating, it decomposes into monohydroperfluoroisobutane and dimethylaminofluorocarbene, which adds to PFIB to form the amine (LV):[172]

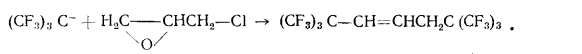


(LIV)

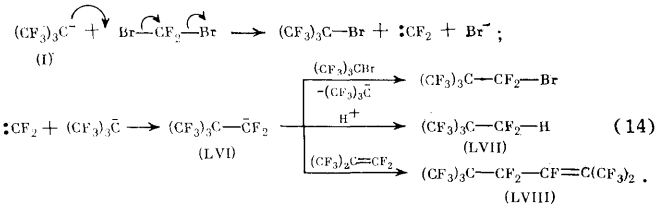


(LV)

When the anion (I) interacts with epichlorohydrin, the opening of the epoxide ring and dehydration are accompanied by the substitution of chlorine by the $(CF_3)_3C$ group[173] (for the description of the mechanism, see Gervits et al.[174]):



The replacement of bromine by the perfluoro-t-butyl group takes place in the reaction of the anion (I) with $CF_2Br_2$.[175] However, in contrast to the usual alkylation of the anion (I) where the halogen atom undergoes nucleophilic substitution, in this case the interaction proceeds via a completely different mechanism. The anion (I) is initially brominated by $CF_2Br_2$, which is accompanied by the generation of difluorocarbene to which the anion (I) and bromine are then added in a coupled reaction to form perfluoroneopentyl bromide. The hydride (LVII) and the olefin (LVIII) were detected as side products, which confirms the formation of the carbanionic intermediate (LVI):



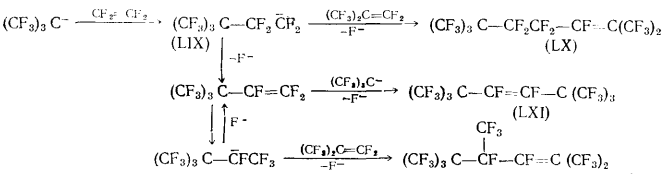
(I) (LVI) (LVII) (LVIII)

(14)

The reaction of the anion (I) with chlorodifluoromethane, leading to compounds (LVII) and (LVIII), also proceeds via the intermediate formation of difluorocarbene[175]. Substitution of bromine by the $(CF_3)_3C$ group on treatment of $BrCF_2.CF_2Br$ by the anion (I) also proceeds via an elimination–addition mechanism [see Eqn.(15)].

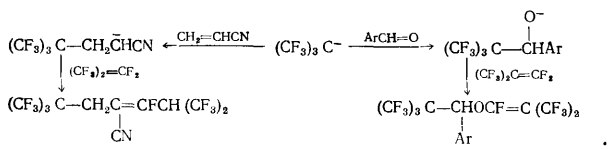
The main product of the reaction of the anion (I) with tetrafluoroethylene is the olefin (LX); the isomers (LXI) and (LXII) are formed together with this compound (Scheme 31)[176]. It is striking that the intermediate carbanion (LIX) is capable of being involved in the reaction with a second PFIB molecule in preference to the usual stabilisation pathway—the β-elimination of the $F^-$ anion:

Scheme 31

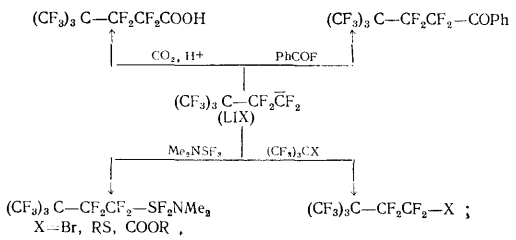


(LIX) (LX) (LXI) (LXII)

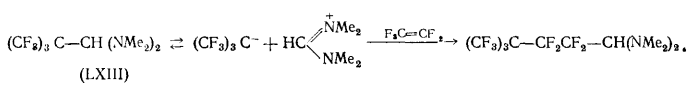
The *C*-anions[177] or *O*-anions[125], generated by the addition of $(CF_3)_3C^-$ to acrylonitrile or aromatic aldehydes respectively, are also capable of subsequent vinyl substitution reactions with PFIB:



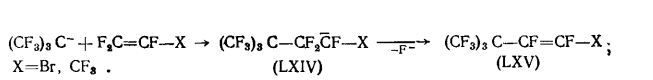
The reactions involving the coupled addition of the anion (I) to tetrafluoroethylene, which include the formation of the olefin (LX), are fairly general. Thus the intermediate carbanion (LIX) adds to the carbonyl group of $CO_2$ and substitutes the fluorine in benzoyl fluoride or in $Me_2NSF_3$.[178] It has also been possible to achieve the bromination, sulphenylation, and alkoxycarbonylation of the anion (LIX) in the condensation of PFIB with tetrafluoroethylene in the presence of CsF and compounds of the type of $(CF_3)_3CX$: [178,179]



A characteristic feature of the latter reactions is that the anion (I), participating in the initial stage where the intermediate (LIX) is generated, is liberated in the concluding stage and is not consumed in the reaction. Thus in fact the entire process constitutes the insertion of tetrafluoromethylene in the C–C, C–Br, or C–S bond catalysed by the anion (I). The anion (I) also catalyses the exchange of chlorine for fluorine in the vicinal chlorosulphide, $(CF_3)_2C(SPh)-CF_2Cl$ in its interaction with CsF.[179] Tetrafluoroethylene is also inserted in the C–C bond of the geminal diamine (LXIII) and in this case the addition of the anion (I) is not required, since the initial diamine is capable of dissociating into the anion (I) and the corresponding immonium cation[178]:

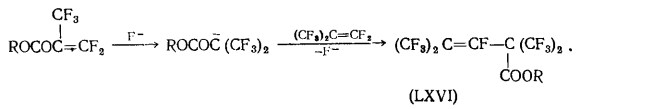


The interaction of the anion (I) with bromotrifluoroethylene[107] or hexafluoropropene[180] leads only to the vinyl substitution products (LXV). The intermediate fluorocarbanion (LXIV) is less reactive than the fluorocarbanion (LIX) and is stabilised only as a result of the β-elimination of the $F^-$ anion:



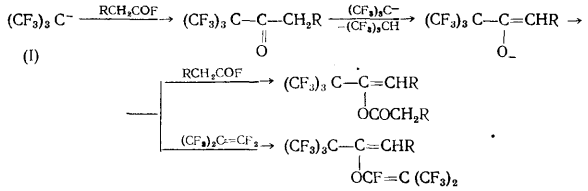
It is of interest to note that, under the conditions of thermodynamic control, the product is not the olefin (LXV, X = $CF_3$) but its isomer, namely the olefin $(CF_3)_2CFCF=C(CF_3)_2$ resulting from the interaction of PFIB with the perfluoroisopropyl anion[181]. On the other hand, the condensation of PFIB with perfluoroazapropene, catalysed by CsF, results in the formation of $(CF_3)_3C-CF=NCF_3$ regardless of the conditions[182,183].

The interaction of PFIB with perfluoromethacrylic acid esters in the presence of CsF leads to the unsaturated esters (LXVI).[107] In the given case, the reaction is propagated not by the anion (I) but by the C-anion of the hexafluoroisobutyric acid ester, apparently as a consequence of the greater ease of formation of the latter [cf.Eqn.(10)]:



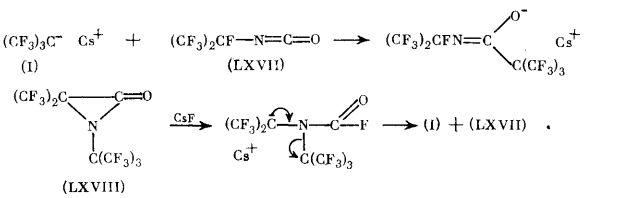
The interaction of the anion (I) with carboxylic acid halides is in general reversible because the carbonyl compounds formed are capable of decomposing in the presence of the $F^-$ anion with reformation of the initial anion (I).[165] The equilibrium position is then determined by the electrophilic properties of the carbonyl carbon atom in the reaction products. Thus the anion (I) is acylated under mild conditions by carbonic acid derivatives[165,184,185]. However, perfluoro-t-butyl phenyl ketone cannot be obtained under the usual conditions of the generation of the anion (I); in this case the reaction equilibrium is fully displaced towards the initial compounds[165]. The benzoylation of the anion (I) has been achieved only using hexamethylguanidinium as the counterion[22].

When the anion (I) is acylated by aliphatic carboxylic acid halides containing an α-hydrogen atom, the equilibrium shifts towards the reaction products, since, on treatment with the anion (I), the intermediate alkyl perfluoro-t-butyl ketones give rise to the corresponding enolates, which are then converted into the *O*-acyl and *O*-perfluoroisobutenyl derivatives[21,186]:

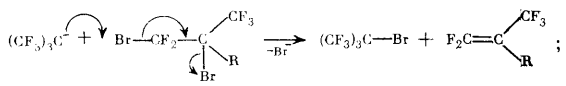


The addition of the anion (I) to the carbonyl group of perfluoroisopropyl isocyanate via Scheme 32 leads to the stable adduct of perfluoropivaloylimine and CsF. It is remarkable that the same adduct is formed when the α-lactam (LXVIII) is treated with CsF. The driving force of the latter reaction is the ease of migration of the perfluoro-t-butyl anion from the nitrogen atom to the carbon atom[187]:

Scheme 32



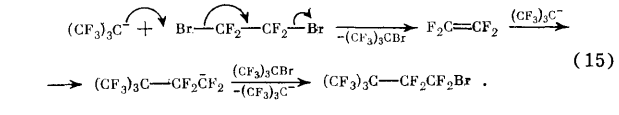
The anion (I) is brominated on treatment with elemental bromine[188]. It is of greater interest that $(CF_3)_3C-Br$ is formed also in the reactions of the anion (I) with certain compounds containing the C–Br bond. They include the *gem*-dibromopolyfluoroalkanes mentioned above. The anion (I) is also brominated when it reacts with vicinal dihalogenopolyfluoroalkanes[107]. The olefins formed together with $(CF_3)_3CBr$ undergo subsequent condensation with PFIB catalysed by the $F^-$ anion:



R=F, COOEt .

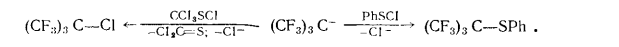
In contrast to those reactions where the anion (I) behaves as a debrominating agent, its interaction with $CF_2BrCHFBr$ leads to the dehydrobromination of the latter[107].

The reaction of the anion (I) with dibromotetrafluoroethane constitutes a special case[107]. As a result of the debromination of the vicinal dibromide by the anion (I), the reaction leads to the formation of perfluoro-t-butyl bromide and tetrafluoroethylene, which reacts further via a coupled nucleophilic addition mechanism:

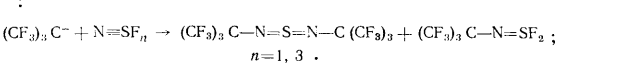


(15)

The anion (I) is smoothly sulphenylated by ethanesulphene, arenesulphene[189-191], and dialkylaminosulphene[189] chlorides. The reaction constitutes a convenient method of synthesis of perfluoroalkyl sulphides and perfluoroalkanesulphenamides. On the other hand, the interaction of the anion (I) with sulphene chlorides having electron-accepting substituents leads only to its chlorination[189]:



Areneselenyl chlorides react with the anion (I) analogously to arenesulphenyl chlorides[191]. Perfluoroalkylation at the nitrogen atom with the aid of the anion (I) was achieved when the latter reacted with thiazyl fluoride and thiazyl trifluoride[192]:



$CF_3COONO$ has been proposed as the nitrosating agent for the anion (I).[193]

Thus it follows from the data examined that the reactions of the anion (I) constitute a fairly general method of synthesis of compounds containing the $(CF_3)_3C$ group. Certain compounds of this type have been suggested as gas-transferring media[167,194,195] and as monomers for the synthesis of thermostable silicone elastomers[196,197]. Compounds containing the $(CF_3)_3C-CF_2$ group have been synthesised by the reaction of the anion (I) with $CF_2Br$.[175] Reactions involving the coupled addition of the anion (I) to tetrafluoroethylene have led in their turn to a pathway towards the synthesis of the higher homologues—compounds with the $(CF_3)_3C-CF_2CF_2$ group. These compounds are of interest because they provide a method for the introduction of functional groups into fluoroolefins with a simultaneous increase of the length of their hydrocarbon chains[178].

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The data presented in this review show that, in terms of its importance for the chemistry of organofluorine compounds, PFIB is fully comparable with the most important fluoroolefins such as tetrafluoroethylene and hexafluoropropene. Whereas the latter are industrially important and are manufactured on a large scale, PFIB has found extensive applications, despite the limitations associated with its high toxicity, in the laboratory synthesis of functional organofluorine compounds of many types. The most important of these include hexafluoroacetone[198], derivatives of α-hydrohexafluoroisobutyric and perfluoromethacrylic acids[33], bis(trifluoromethyl)keten[32] and its imines[72], acetals[199], and aminals[79], allenes[103], and various heterocyclic compounds with *gem*-trifluoromethyl groups.

At the same time PFIB proved to be a convenient model compound for the solution of various problems associated with the nucleophilic reactions of fluoro-olefins such as the relative contributions of addition and vinyl and allyl substitution processes, the application of nucleophilic catalysis in addition and cycloaddition reactions, etc. Thus the development of the chemistry of PFIB has in many respects determined the general advances in the study of fluorine-containing compounds of various types, apart from purely practical results.

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