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The Perfluoro-t-butyl Anion in the Synthesis of Organofluorine Compounds

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Methods for the generation and reactions of the perfluoro-t-butyl anion—a convenient model for the investigation of the chemistry of perfluoroalkyl carbanions, are examined. Syntheses based on this anion lead to the formation of a wide variety of compounds containing the $(CF_3)_3C$ group.
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I. INTRODUCTION

Reactions involving perfluoroalkyl carbanions have been acquiring increasing importance in the chemistry of organofluorine compounds, because of the comparatively high thermodynamic stability of such carbanions due to the stabilising effect of the fluorine atoms [1,2]†. The perfluoro-t-butyl anion is particularly stable. Vigorous studies on methods for the preparation of this carbanion and its reactions have led during the last 10 years to the synthesis of a wide variety of compounds containing the $(CF_3)_3C$ group. The two main pathways to the synthesis of the $(CF_3)_3C^-$ anion are heterolysis of the C–H bond in nonafluoroisobutane and the addition of the F^- anion to perfluoroisobutene. Furthermore, it is possible to employ for synthetic purposes di(perfluoro-t-butyl)mercury under the conditions of nucleophilic catalysis.

II. REACTIONS OF NONAFLUOROISOBUTANE IN THE PRESENCE OF TERTIARY AMINES

Nonafluoroisobutane $(CF_3)_3CH$ is a comparatively strong CH acid. (According to various estimates, the pK_a values are approximately 11,[1] approximately 7,[5] or approximately 20.[6]) It is normally unstable when acted upon by bases, readily eliminating fluorine atoms in the form of ions [1]. However, when nonafluoroisobutane is mixed with triethylamine, fluorine atoms are not converted into an inorganic form. It has been observed by ^1H NMR that this entails the formation of a comparatively strong hydrogen bond between the molecules of nonafluoroisobutane and triethylamine with participation of the hydrogen atom of the methine group (the chemical shift due to the hydrogen bond amounts to 1.95 p.p.m.)[7].

Although a signal due to the $(CF_3)_3C^-$ carbanion cannot be detected in the ^1H NMR spectrum, its presence in the mixture can be demonstrated by reactions with various electrophiles [8]. Thus nonafluoroisobutane can be made to take part in the Michael reaction. In the presence of triethylamine, it readily adds to the C=C bonds of acrylic systems—acrylonitrile, methyl acrylate, and acrolein[9,10]:

$$(CF_3)_3CH + NEt_3 \rightleftharpoons (CF_3)_3C^{\ominus} + \overset{\oplus}{H}NEt_3$$
$$X=CN, COOMe, CHO \quad \downarrow H_2C=CHX$$
$$(CF_3)_3CCH_2CH_2X \quad (I)$$

Further reactions of products (I) led to the formation of various compounds containing the $(CF_3)_3C$ group, such as

$(CF_3)_3CCH_2CH_2COOH$, $(CF_3)_3CCH_2CH_2CH_2OH$,
$(CF_3)_3CCH_2CH_2CH_2SH$, $(CF_3)_3CCH_2CH_2CH_2NH_2$ etc. (Ref.10).

The addition to the activated triple bond C≡C of benzoylacetylene or the acetylenedicarboxylate ester takes place just as readily [11]:

$$(CF_3)_3CH + HC\equiv CCOPh \xrightarrow[Et_3N]{} (CF_3)_3CCH=CHCOPh;$$
$$(CF_3)_3CH + H_3COCOC\equiv CCOOCH_3 \xrightarrow[Et_3N]{} (CF_3)_3C(COOCH_3)=CHCOOCH_3.$$

Nonafluoroisobutane is involved in hydroxymethylation and aminomethylation reactions [8,12]. When it was heated with paraformaldehyde in the presence of triethylamine, a low yield of perfluoro-t-butylmethanol was obtained:

$$(CF_3)_3CH + (CH_2O)_n \xrightarrow[Et_3N]{} (CF_3)_3CCH_2OH.$$

Its reaction with urotropine gave a substituted triazine (II) whose hydrolysis led to the hydrochloride of perfluoro-t-butylmethylamine:

$$(CF_3)_3CH + (CH_2)_6N_4 \xrightarrow{Et_3N} (CF_3)_3CH_2C{-}N\langle CH_2\rangle N{-}CH_2C(CF_3)_3 \xrightarrow{H_2O/HCl}$$
$$\rightarrow (CF_3)_3CCH_2NH_2\cdot HCl \quad (II)$$

Ionic halogenation [13] and tropylation [14] of nonafluoroisobutane have also been achieved:

$$(CF_3)_3CH + Br_2 \xrightarrow[C_5H_5N]{} (CF_3)_3CBr;$$
$$(CF_3)_3CH + \text{tropylium-Br} \xrightarrow[Et_3N]{} \text{cycloheptatriene-}C(CF_3)_3,\ H.$$

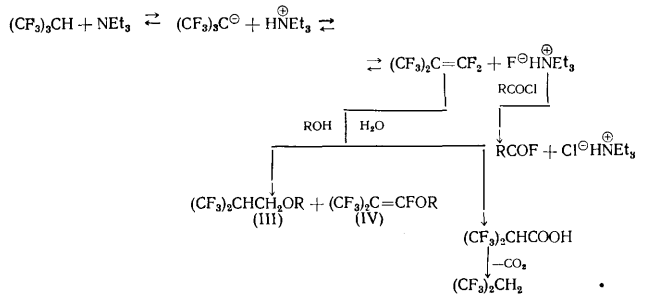
The attempt to alkylate nonafluoroisobutane by ethyl iodide in the presence of triethylamine was unsuccessful, probably because of the formation of tetraethylammonium iodide, which is incapable of alkylating monohydroperfluoroalkanes under the reaction conditions [8].

†For a discussion of the possible role of the "negative hyperconjugation" in the stabilisation of fluoro-carbanions, see Refs. 1, 3, and 4.

The benzoylation of nonafluoroisobutane could not be achieved either. On treatment with benzoyl chloride in the presence of triethylamine, it is dehydrofluorinated, yielding perfluoroisobutane [15]:

$$(CF_3)_3CH + PhCOCl + Et_3N \rightarrow (CF_3)_2C{=}CF_2 + PhCOF + Et_3\overset{\oplus}{N}HCl^{\ominus}.$$

Evidently, when nonafluoroisobutane is mixed with triethylamine, it is dehydrofluorinated, but the reaction is reversible, the equilibrium being almost completely displaced towards the starting materials (see above). Benzoyl chloride can participate in a reversible exchange reaction with triethylamine hydrofluoride, which shifts the equilibrium towards the formation of perfluoroisobutene [8,15]. A similar shift of the equilibrium can be achieved by removing perfluoroisobutene from the reaction instead of triethylamine hydrofluoride. Thus when nonafluoroisobutane reacts with methanol in the presence of triethylamine, the products are the stable ethers (III) and (IV). [15] If water is used instead of methanol, one obtains 1,1,1,3,3,3-hexafluoropropane as a result of the decarboxylation of 2,2,2-trifluoro-2-trifluoromethylpropionic acid (α-hydrohexafluoroisobutyric acid) [16]:



All these reactions take place with the intermediate formation of the perfluoro-t-butyl anion.

Thus the use of the carbanion $(CF_3)_3C^-$ generated from nonafluoroisobutane gives rise to fairly considerable synthetic possibilities. However, another method for the preparation of this carbanion—by the addition of the fluoride anion to perfluoroisobutene—is much more important for the synthesis of organofluorine compounds.

III. REACTIONS OF PERFLUOROISOBUTENE IN THE PRESENCE OF ALKALI METAL FLUORIDES

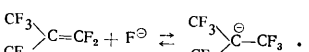
Perfluoro-olefins occupy an especially important place in the chemistry of organofluorine compounds. Owing to the electron-accepting effect of the fluorine atoms, they exhibit very marked electrophilic properties [17]. One of the most interesting reactions of perfluoro-olefins, which is being very vigorously investigated at the present time, is that with various electrophiles in the presence of fluoride ions in aprotic polar solvents. According to current ideas, the first step in this process is nucleophilic addition of the fluoride ion to the double bonds of the perfluoro-olefin with formation of a perfluoroalkyl carbanion, which then reacts with the electrophile [18]:

$$\rangle C{=}CF_2 + F^{\ominus} \rightarrow \rangle \overset{\ominus}{C}{-}CF_2{-}\overset{E^{\oplus}}{\rightarrow} \rangle \underset{E}{C}{-}CF_3 .$$

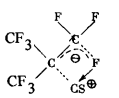
The perfluoro-olefin–alkali metal fluoride system can be regarded as a perfluoroalkyl derivative of the alkali metal. Such systems are involved in a wide range of reactions, the synthetic value of which not only largely compensates the limited applicability of perfluoroalkyl Grignard reagents, but also gives rise to additional possibilities, associated, in particular, with the use of processes such as the Wurtz reaction.

Reactions of this kind were investigated previously mainly in relation to fluorine-containing ethylenes and perfluoropropene. However, the perfluoro-t-butylanion, obtained from perfluoroisobutene, is a more convenient model for the investigation of the reactions of perfluoroalkyl carbanions. Its advantages are due to a series of factors, including the low tendency of perfluoroisobutene towards dimerisation and oligomerisation‡ and its pronounced electrophilic properties, which ensure the ease of addition of the fluoride ion. In contrast to other perfluoroalkyl carbanions, the generation of the perfluoro-t-butyl anions can be observed directly with the aid of ^{19}F NMR spectra [22].

Two characteristic multiplets, corresponding to the CF_3 and CF_2 groups (−18 and 20 p.p.m. relative to CF_3COOH), in the perfluoroisobutene spectrum are converted after the addition of caesium fluoride into a broadened singlet displaced downfield (−27 p.p.m.) relative to the CF_3COOH signal. This reaction constitutes a rapid exchange, since the above spectral change is caused by much less than the equivalent amount of caesium fluoride:



The downfield signal shift can be accounted for by a reverse redistribution of electron density via fluorine atoms to the vacant inner orbitals of the metal atom:



The perfluoro-t-butyl anion generated from perfluoroisobutene readily combines with a proton. Thus the reaction of perfluoroisobutene with hydrogen fluoride in the presence of catalytic amounts of ammonium fluoride [23] or triethylamine [15] leads to the formation of nonafluoroisobutene:

$$(CF_3)_2C{=}CF_2 \xrightarrow{+F^{\ominus}} (CF_3)_3C^{\ominus} \xrightarrow[-F^{\ominus}]{+HF} (CF_3)_3CH .$$

This reaction makes it possible to use perfluoroisobutene as a dehydrofluorinating agent [24,25].

The nucleophilic fluoroiodination of perfluoroisobutene leads to iodoperfluoroisobutane [26]:

$$(CF_3)_2C{=}CF_2 \xrightarrow{+F^{\ominus}} (CF_3)_3C^{\ominus} \xrightarrow[-I^{\ominus}]{+I_2} (CF_3)_3CI .$$

The same compound has been obtained by the reaction of perfluoroisobutene with iodine monofluoride [27].

The alkylation of the perfluoro-t-butyl anion by various alkyl halides gives rise to considerable possibilities for the synthesis of various organic compounds containing the perfluoro-t-butyl group [22,28]:

$$(CF_3)_2C{=}CF_2 + RX \xrightarrow{CsF} (CF_3)_3C{-}R ;$$
$$R{=}CH_3,\ C_4H_9,\ CH_2{=}CHCH_2;$$
$$C_6H_5CH_2,\ n\text{-}FC_6H_4CH_2,\ (C_6H_5)_2CH;$$
$$X{=}Cl,\ Br,\ I .$$

‡It is claimed, incidentally, that perfluoroisobutene is dimerised on treatment with CsF in ether or diglyme. [19-21]

3-Bromocyclohexene reacts similarly[22].

It is readily seen that the results of these reactions are similar to those of the Wurtz reaction; at the same time the lower reactivity of the anion $(CF_3)_3C^-$ compared with hydrocarbon carbanions makes it possible to substitute the halogen in compounds containing other reaction centres, for example in β-bromopropionitrile[28], ethylbromoacetate[29], and β-bromoethyl acetate[30]. The reaction with 1,2-dibromoethane under mild conditions leads to the formation of the product resulting from the substitution of one bromine atom by the $(CF_3)_3C$ group[30]:

$$(CF_3)_3C^{\ominus} + BrCH_2X \xrightarrow[-Br^{\ominus}]{} (CF_3)_3CCH_2X\,;$$
$$X{=}CH_2CN,\ CH_2COOEt,\ CH_2OAc,\ CH_2Br\,.$$

Perfluoro-t-butylacetic acid $(CF_3)_3CCH_2COOH$ was obtained by the hydrolysis of the corresponding ester. The dissociation constant of the acid has been determined and the Taft constant σ^* for the $(CF_3)_3C$ group (1.48) has been calculated[31]. This value proved to be much smaller than the additive constant ($\sigma^*_{(CF_3)_3C} = 3\sigma^*_{CF_3} \times 0.357 = 2.79$).

Perfluoro-t-butylethylene has been obtained by the dehydrobromination of 2-(perfluoro-t-butyl)ethyl bromide with solid alkali or by the pyrolysis of 2-(perfluoro-t-butyl)ethyl acetate[30]:

$$(CF_3)_3CCH_2CH_2Y \xrightarrow[-HY]{} (CF_3)_3CCH{=}CH_2\,;$$
$$Y{=}Br,\ OAc\,.$$

The same olefin is formed together with nonafluoroisobutane and the salt (V), containing a mesomeric anion, is formed when perfluoroisobutene reacts with oxiran in the presence of caesium fluoride[32]:

$$(CF_3)_3C^{\ominus}Cs^{\oplus} + \underset{O}{CH_2CH_2} \rightarrow (CF_3)_3CCH_2CH_2O^{\ominus}Cs^{\oplus} \xrightarrow{(CF_3)_2C=CF_2}$$
$$\rightarrow [(CF_3)_3CCH_2CH_2OCF_2\overset{\ominus}{C}(CF_3)_2]\,Cs^{\oplus} \xrightarrow{(CF_3)_2C=CF_2}$$
$$\rightarrow (CF_3)_3CCH{=}CH_2 + \overset{\oplus}{Cs}\,[O{\cdots}CF{\cdots}C(CF_3)_2]^{\ominus} + (CF_3)_3CH\,.$$

(V)

Here perfluoroisobutene behaves not only as a dehydrofluorinating agent but also as a kind of dehydrating agent. Under other conditions, perfluoro-t-butylethanol $(CF_3)_3CCH_2CH_2OH$ was isolated from the reaction mixture (after acidification).

Derivatives of perfluoro-t-butylpropionic acid have been obtained by the reaction of the perfluoro-t-butyl anion with derivatives of acrylic acid; in the case of acrylonitrile, the product of further interaction of the intermediate carbanion with a molecule of perfluoroisobutene is also formed[28]:

$$CH_2{=}CHX + (CF_3)_3C^{\ominus} \rightarrow (CF_3)_3CCH_2\overset{\ominus}{C}HX \xrightarrow{H^{\oplus}} (CF_3)_3CCH_2CH_2X$$
$$\downarrow -F^{\ominus},\ +(CF_3)_2C{=}CF_2$$
$$(CF_3)_3CCH_2\underset{CN}{CH}CF{=}C(CF_3)_2$$
$$\downarrow$$
$$(CF_3)_3CCH_2\underset{CN}{C}{=}CFCH(CF_3)_2\,;$$
$$X{=}CN,\ COOCH_3,\ CHO\,.$$

Perfluoropropene and tetrafluoroethylene react with carbon dioxide in the presence of caesium fluoride to form perfluoroisobutyric and perfluoropropionic acids respectively. The attempt to synthesise perfluoropivalic acid by carboxylating the perfluoro-t-butyl anion was unsuccessful[19]. Perfluoropivaloyl fluoride $(CF_3)_3CCOF$ is formed together with the enamine (VI) when perfluoroisobutene reacts with dimethylformamide, evidently as a result of the addition of carbonyl difluoride to perfluoroisobutene[33]:

$$(CF_3)_2C{=}CF_2 + OCHN(CH_3)_2 \rightarrow \underset{(VI)}{(CF_3)_2C{=}CHN(CH_3)_2} + (CF_3)_3CCOF\,;$$
$$(CF_3)_2C{=}CF_2 \xrightarrow{+F^{\ominus}} (CF_3)_3C^{\ominus} \xrightarrow[-F^{\ominus}]{+COF_2} (CF_3)_3COF\,.$$

Carbonyl difluoride adds to perfluoro-olefins in the presence of CsF or KF.[34-36] The perfluoroethyl and perfluoroisopropyl anions interact with carbonyl compounds, forming fluorinated alcohols[37-39]. The corresponding alcohols containing the $(CF_3)_3C$ group have been obtained by an indirect procedure—via α-halogenoethers[40]:

$$(CF_3)_3C^{\ominus} + \underset{X}{RCHOR^1} \rightarrow \underset{C(CF_3)_3}{RCHOR^1} \xrightarrow[\text{or } FSO_3H]{SO_3} \underset{C(CF_3)_3}{RCHOH}\,; \qquad R{=}H,\ Alk;\ R^1{=}Alk\,.$$

The acylation of the perfluoro-t-butyl anion has not been described (if one disregards the synthesis of perfluoropivaloyl fluoride from perfluoroisobutene and dimethylformamide; see above). However, the anion $(CF_3)_3C^-$ reacts readily with aromatic imidoyl halides:

$$(CF_3)_3C^{\ominus} + PhN{=}\underset{Cl}{C}Ar \rightarrow PhN{=}\underset{C(CF_3)_3}{C}Ar\,.$$

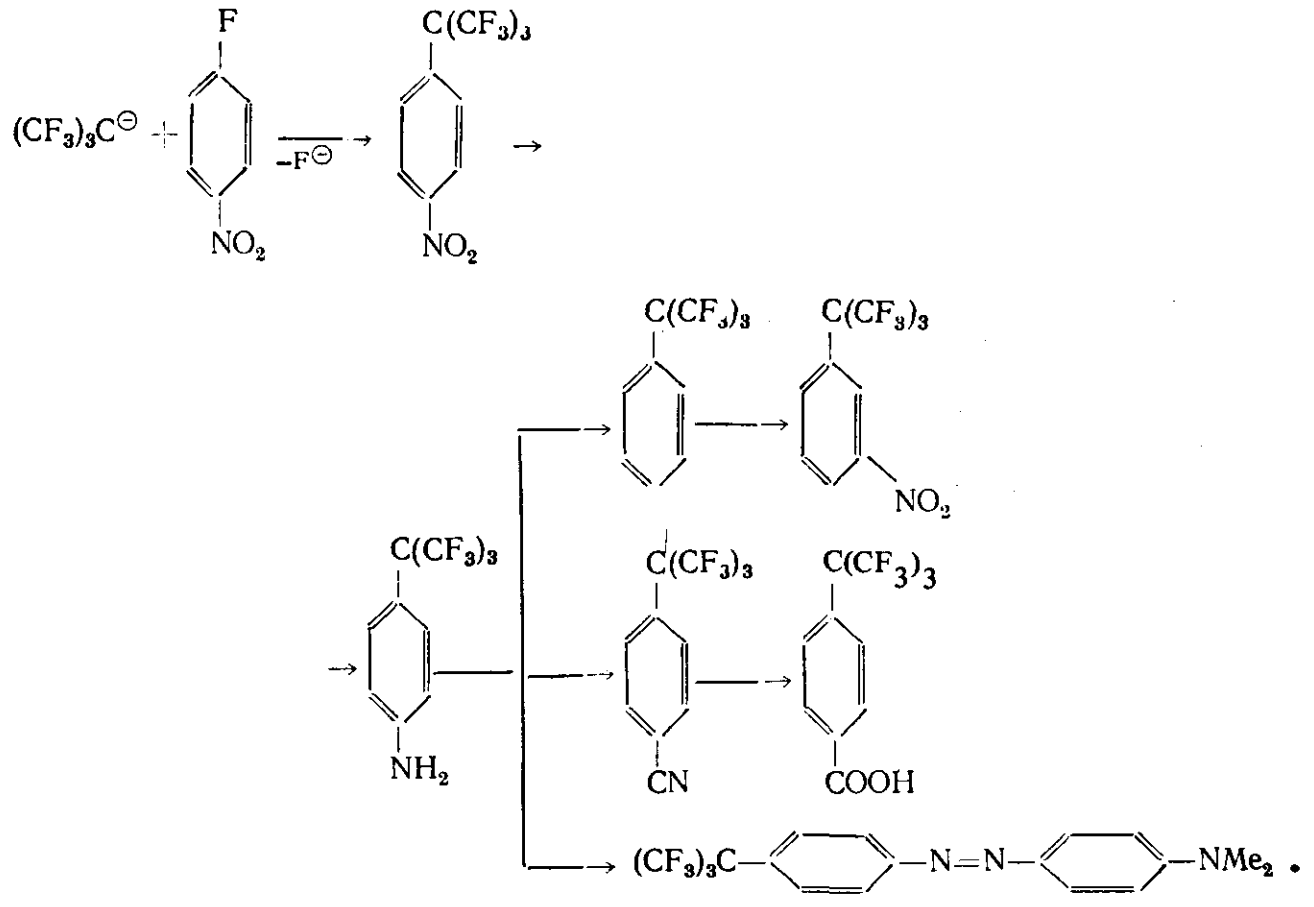
The attempts to obtain ketones by the hydrolysis of the products of this reaction proved unsuccessful[40].

The perfluoro-t-butyl anion can substitute the chlorine atom in 1-chloroacetylenes containing a fairly electronegative substituent in the 2-position[41]. Thus 1-chloro-3,3,3-trifluoropropyne reacts with the ion $(CF_3)_3C^-$ in diglyme at room temperature and chloro(phenyl)acetylene reacts at 120°C:

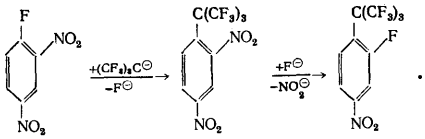
$$(CF_3)_3C^{\ominus} + ClC{\equiv}CR \rightarrow (CF_3)_3CC{\equiv}CR\,;$$
$$R{=}CF_3,\ Ph\,.$$

On the other hand 1-chlorohex-1-yne and 1-chloro-2-methoxyethyne do not react with perfluoroisobutene and caesium fluoride even under severe conditions. The perfluoroisopropyl anion does not react with either 1-chloro-3,3,3-trifluoropropyne or 1-chloro-2-phenylethyne.

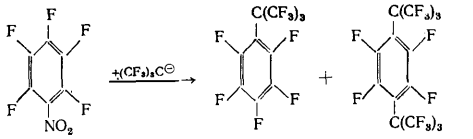
The introduction of the perfluoro-t-butyl group into an aromatic or heterocyclic ring is of definite theoretical interest in connection with the electronic and steric features of the structure of this group. The interaction of the anion $(CF_3)_3C^-$ with various aromatic and heterocyclic compounds containing a mobile halogen atom leads to the corresponding perfluoro-t-butyl substituted derivatives[42]. Thus p-nitro(perfluoro-t-butyl)benzene has been obtained from p-fluoronitrobenzene and has been used to synthesise various substituted benzenes containing the $(CF_3)_3C$ group[31]:



When the 1-fluoro-2,4-dinitrobenzene is acted upon by the perfluoro-t-butyl anion, the fluorine atom is initially substituted by the $(CF_3)_3C$ group and then the *ortho*-nitro-group, displaced from coplanarity with the benzene ring, is substituted by fluorine on being acted upon by the fluoride ion:

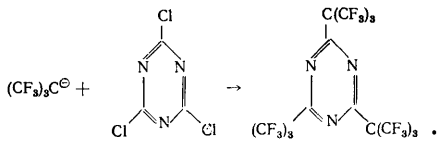


The substitution products (VII) and (VIII) have been isolated in the reaction with pentafluoronitrobenzene:

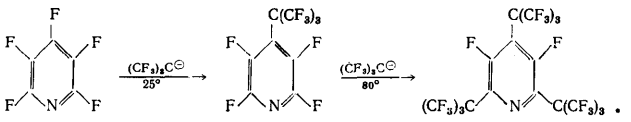


(VII) (VIII)

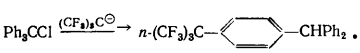
All three chlorine atoms are substituted in cyanuric acid chloride:



Depending on the conditions, the reaction with perfluoro-pyridine yields products obtained by the substitution of one or three fluorine atoms:

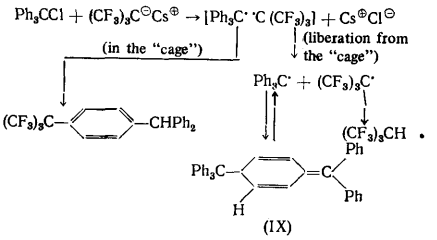


The interaction of the perfluoro-t-butyl anion with triarylmethyl halides constitutes a special case[42,43]. The reaction with chlorotriphenylmethane proceeds very readily, the chlorine atom being substituted by the perfluoro-t-butyl group. However, this is not direct substitution: the perfluoroalkyl group enters the *para*-position of one of the benzene rings:



An ESR study of this reaction (in diglyme) showed that free triphenylmethyl radicals are formed. In the presence of triphenylmethyl chloride, the concentration of the free radicals passes through a maximum and then approaches the value determined by the constant for the equilibrium between the radical and its diamagnetic dimer [Gomberg's "hexaphenylethane" (IX)].

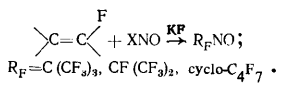
The one-electron transfer stage constitutes a general problem for nucleophilic substitution reactions[44]. The reaction of triphenylmethyl chloride with the perfluoro-t-butyl anion is the first example of proven electron transfer from a perfluoroalkyl anion. The main reaction product is formed within the cage; the triphenylmethyl radicals emerging from the cage are detected by ESR. The perfluoro-t-butyl radicals leaving the cage abstract hydrogen atoms from the solvent and form nonafluoroisobutane. The overall reaction mechanism can be represented as follows:



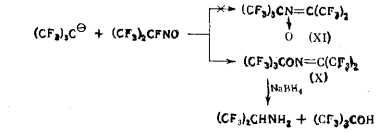
(IX)

Electron transfer is also observed in the interaction with tri-(*p*-nitrophenyl)methyl bromide, which results in the formation of the radicals $(p\text{-}O_2NC_6H_4)_3\dot{C}$ and $(CF_3)_3\dot{C}$. Since the tri-(*p*-nitrophenyl)methyl radical is incapable of dimerisation or recombination, both radicals emerge from the cage. The only organofluorine reaction product is nonafluoroisobutane; the substituted triphenylmethyl radical is stable in the absence of air[43].

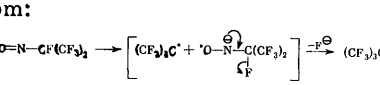
There are many other reactions for which one-electron transfer has not so far been demonstrated but is extremely probable§. Evidently the mechanism of the reaction of the perfluoro-t-butyl anion with nitrosoperfluoroalkanes can be treated from the same standpoint. It appeared strange that, in the reaction of perfluoroalkyl carbanions with nitrosyl fluoride[45,46] or nitrosyl chloride[47], further interaction of the perfluoroalkyl carbanions with the nitrosoperfluoro-compounds formed is not observed:



Subsequent studies showed that only the perfluoro-t-butyl anion is capable of involvement in the reaction with nitrosoperfluoroalkanes and only when the nitroso-group in the nitrosoperfluoro-compound is attached to a primary or secondary carbon atom[48,49]. The study of the chemical properties of the product of the reaction of the perfluoro-t-butyl anion with 2-nitrosoperfluoropropane, in particular its reduction with sodium tetrahydroborate, established that it has the structure of the *N*-perfluoro-t-butyl derivative of hexafluoroacetone oxime (X)[48] and not the perfluoronitrone (XI), as suggested previously[49]:



This unusual course of the reaction (attack by the carbanion directed to the negatively charged oxygen atom and not to the positively charged nitrogen atom, as might have been expected) can be explained if it is assumed that the first stage in this reaction is one-electron transfer from the perfluoroalkyl carbanion to the nitroso-group; the final product is then formed as a result of the elimination of the fluoride ion from the α-position relative to the nitrogen atom:



§For a discussion of the reactions of perfluoroisobutene with haloforms in the presence of the F^- ion, see the review by I. L. Knunyants and V. R. Polishchuk in this issue.

Nitrosoperfluoroisobutane without a fluorine atom in the α-position does not react with a perfluoroalkyl carbanion under comparable conditions. In the synthesis of 2-nitrosoperfluoropropane from perfluoropropene and a nitrosyl halide, the subsequent reaction of the anion $(CF_3)_2CF^-$ with nitroso-compounds is apparently unable to compete with the dimerisation and oligomerisation reactions of perfluoropropene.

The formation of difluoro(perfluoro-t-butyl)amine in the reaction of perfluoroisobutene with tetrafluorohydrazine in the presence of potassium fluoride can also be treated as a one-electron transfer [50]:

$$(CF_3)_2C{=}CF_2 + N_2F_4 \xrightarrow[150^\circ]{KF} (CF_3)_3C{-}NF_2 + N_2 + NF_2 .$$

In this case, the perfluoro-t-butyl anion is oxidised by the difluoroamino-radical:

$$(CF_3)_3C^\ominus \xrightarrow[-NF_2^\ominus]{+\dot{N}F_2} (CF_3)_3C^\cdot \xrightarrow{+\dot{N}F_2} (CF_3)_3C{-}NF_2 .$$

The range of reactions for which a one electron transfer mechanism is extremely probable¶ can be supplemented by the interaction of perfluoroalkyl carbanions with diazonium salts leading to arylazoperfluoroalkanes [52,53]:

$$R_F^\ominus + N{\equiv}\overset{\oplus}{N}{-}C_6H_5 \rightarrow R_F{-}N{=}N{-}C_6H_5 + Cl^\ominus ;$$

$$Cl^\ominus$$

$$R_F = (CF_3)_3C,\ (CF_3)_2CF,\ \text{cyclo-}C_4H_7 .$$

Like other perfluoroalkyl anions, the perfluoro-t-butyl anion reacts with elemental sulphur under relatively mild conditions. Generally speaking, the reactions of perfluoroalkyl carbanions with sulphur proceed in different ways, leading to a wide variety of sulphur derivatives, the formation of which may be accounted for by the reactions of the perfluoroalkylmercaptide anions formed initially [54-57,76]. Depending on the structure of the initial olefin and the reaction conditions, these species can undergo the following transformations: (a) they can eliminate a fluoride anion from the α-position relative to the sulphur atom, forming a perfluorothiocarbonyl compound; (b) they can be oxidised by sulphur to a perfluoroalkanethiyl radical and can give rise to di(perfluoroalkyl) di- and poly-sulphides; (c) they can react with the fluoro-olefin via the vinyl substitution mechanism, forming an alkenyl perfluoroalkyl sulphide:

$$R_F^\ominus + S \rightarrow R_FS^\ominus ;$$

$$\text{(a)}\ -\overset{|}{\underset{F}{C}}{-}S^\ominus \xrightarrow{-F^\ominus} \diagdown C{=}S ;$$

$$\text{(b)}\ R_FS^\ominus \xrightarrow[-S^{2\ominus}]{+S} R_FS^\cdot \rightarrow R_FS_nR_F ;$$

$$\text{(c)}\ R_FS^\ominus + CF_2{=}C\diagup \xrightarrow{-F^\ominus} R_FSCF{=}C\diagup .$$

In the case of perfluoroisobutene, the possibility of the elimination of a fluoride ion from the α-position is ruled out. The perfluoro-t-butylmercaptide anion is oxidised to the corresponding radical, which is converted into the trisulphide (XII); the sulphide ion formed interacts with perfluoroisobutene, forming the dimer of bis(trifluoromethyl)thioketen (XII) [76,96]:

$$(CF_3)_2C{=}CF_2 \underset{-F^\ominus}{\overset{+F^\ominus}{\rightleftarrows}} (CF_3)_3C^\cdot \xrightarrow{+S} (CF_3)_3CS^\ominus \xrightarrow[-S^{2\ominus}]{+S} (CF_3)_3CS^\cdot$$

$$\downarrow{+S^{2\ominus}, -F^\ominus} \qquad \downarrow{+S}$$

$$(CF_3)_3CS_3C(CF_3)_3 \quad \text{(XII)}$$

$$(CF_3)_2C{=}C{=}S \rightarrow (CF_3)_2C{=}C\underset{S}{\overset{S}{\diagup\diagdown}}C{=}C(CF_3)_2 .$$

(XIII)

The reaction of perfluoroisobutene with potassium sulphide [57] or with salts of thiolic acids constitutes a preparative method for the synthesis of the thioketen dimer (XIII) [58,59]:

$$(CF_3)_2C{=}CF_2 \xrightarrow[-MF]{RSM} (CF_3)_2C{=}C(F){-}S{-}R \xrightarrow{-RF} (CF_3)_2C{=}C{=}S \rightarrow \text{(XIII)} .$$

The best result was obtained with potassium diethyl phosphorodithioate [58]:

$$(CF_3)_2C{=}CF_2 \xrightarrow[-KF,\ -(EtO)_2P(S)F]{+(EtO)_2P(S)SK} (CF_3)_2C{=}C\underset{S}{\overset{S}{\diagup\diagdown}}C{=}C(CF_3)_2 .$$

(XIII)

It is interesting to note, that, when this reaction is carried out with potassium thiocyanate, the thiocyanate ion exhibits the properties of an ambident nucleophile [60]:

$$(CF_3)_2C{=}CF_2 \xrightarrow{KSCN} \begin{cases} \xrightarrow[\text{sulpholane}]{} \text{(XIII)} \\ \xrightarrow[\text{benzonitrile}]{} (CF_3)_2C{=}CFN{=}C{=}S . \end{cases}$$

In the presence of catalytic amounts of potassium fluoride, perfluoropropene gives a satisfactory yield of virtually only one sulphur-containing product—the dimer of perfluorothioacetone (XIV), which is formed as a result of the elimination of the F^- ion from the perfluoroisopropylmercaptide ion (XV); in the presence of large amounts of potassium fluoride, there is a significant increase of the yield of the disulphide (XVI) and of the unsaturated sulphide (XVII) [76]:

$$CF_2{=}\underset{CF_3}{\overset{|}{C}}{-}CF_2CF_2CF_3 \xrightarrow{+(XV)} (CF_3)_2CFSCF{=}\underset{CF_3}{\overset{|}{C}}CF_2CF_2CF_3 ; \quad \text{(XVII)}$$

$$\uparrow +CF_2{=}CF_2$$

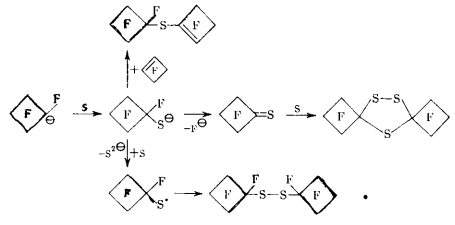
$$(CF_3)_2CF^\ominus \xrightarrow{+S} (CF_3)_2C{-}S^\ominus \xrightarrow{-F^\ominus} (CF_3)_2C{=}S \rightarrow \underset{CF_3}{\overset{CF_3}{\diagup}}C\underset{S}{\overset{S}{\diagup\diagdown}}C\underset{CF_3}{\overset{CF_3}{\diagdown}} ;$$

$$\text{(XV)} \qquad \downarrow{-S^{2\ominus}, +S} \qquad \text{(XIV)}$$

$$(CF_3)_2CFS^\cdot \rightarrow (CF_3)_2FC{-}S{-}S{-}CF(CF_3)_2 .$$

(XVI)

The reaction of perfluorocyclobutene with sulphur and KF leads to a similar result, but in this instance the elimination of the fluoride ion from the perfluorocyclobutylmercaptide anion is somewhat difficult, because the formation of perfluorothiocyclobutanone (XVIII)—a compound with a semicyclic double bond—is energetically less favourable; accordingly there is an increase in the yield of compounds containing the perfluorocyclobutylthio-group, i.e. the unsaturated sulphide (XIX) and the disulphide (XX) [56,76]:



(XIX)

(XX)

The reactions of perfluoroalkyl carbanions give rise to considerable possibilities for the preparation of fluorine-containing organomercury compounds [61-63]. In contrast to the electrophilic mercuration reaction known previously [54,64-66], such reactions may be called "nucleophilic mercuration of fluoro-olefins". Depending on the nature of the reagent and the reactions conditions, they make it possible to obtain fully substituted or mixed

¶The formation of perfluorocarboxylic acid nitriles from fluoro-olefins and dicyanogen in the presence of alkali metal fluorides also probably includes a one-electron transfer stage [51].

perfluoroalkyl derivatives of mercury. Thus perfluoroisobutene reacts with mercury trifluoroacetate in the presence of KF, giving a high yield of di(perfluoro-t-butyl)-mercury and the reaction with trifluoromethylmercury trifluoroacetate leads to trifluoromethyl(perfluoro-t-butyl)mercury [63]:

$$(CF_3)_2C{=}CF_2 + KF \begin{cases} \xrightarrow{Hg(OCOCF_3)_2} [(CF_3)_3C]_2Hg \\ \xrightarrow{CF_3HgOCOCF_3} (CF_3)_3C{-}Hg{-}CF_3 . \end{cases}$$

It is noteworthy that fluorides—HgF_2 and phenylmercury fluoride—add to perfluoroisobutene in the absence of a catalyst [62], behaving themselves as sources of the fluoride ion; one cannot, however, rule out the possibility that the addition can proceed in this case also via a cyclic four-centre mechanism.

The reaction of perfluoroisobutene with mercury(II) chloride in the presence of KF proceeds less vigorously and stops at the stage involving the formation of perfluoro-t-butylmercury chloride [62]:

$$(CF_3)_2C{=}CF_2 + HgCl + KF \xrightarrow{DMF} (CF_3)_3CHgCl \not\rightarrow [(CF_3)_3C]_2Hg .$$

Evidently the more covalent character of the Hg–Cl bond compared with the Hg–F and Hg–$OCOCF_3$ bonds is manifested here.

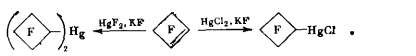
In contrast to perfluoroisobutene, perfluoropropene acted upon by potassium fluoride and mercury(II) chloride can form, depending on the reaction conditions, both fully substituted and mixed derivatives of mercury: the reaction in dimethylformamide leads to di(perfluoroisopropyl)-mercury and that in the less polar dimethoxyethane yields perfluoroisopropylmercury chloride [62]:

$$CF_3CF{=}CF_2 + HgCl_2 + KF \begin{cases} \xrightarrow{DMF} [(CF_3)_2CF]_2Hg \\ \xrightarrow{DME} (CF_3)_2CFHgCl . \end{cases}$$

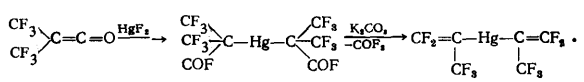
The formation of the symmetrical compound indicates a higher reactivity of the perfluoroisopropyl anion compared with the perfluoro-t-butyl anion. This is confirmed directly by the displacement of perfluoroisobutene from perfluoro-t-butylmercury chloride on treatment with perfluoropropene in the presence of KF [62]:

$$CF_3CF{=}CF_2 + (CF_3)_3CHgCl \xrightarrow{F^{\ominus}} [(CF_3)_2CF]_2Hg + Cl^{\ominus} + (CF_3)_3C^{\ominus}$$
$$\downarrow$$
$$(CF_3)_2C{=}CF_2 + F^{\ominus} .$$

Fluoro-olefins containing not only a terminal double bond but also an inner double bond can be involved in the nucleophilic mercuration reaction. Thus perfluorocyclobutene, the mercuration of which could not be achieved under the conditions of the electrophilic reaction [65], in the presence of KF interacts with mercury(II) fluoride and chloride, forming respectively di(perfluorocyclobutyl)-mercury and perfluorocyclobutyl mercury chloride [62]:



Bis(trifluoromethyl)keten, a powerful electrophile, combines with mercury(II) fluoride in the absence of a catalyst [67]. Treatment of the adduct with potassium carbonate leads to the formation of di(perfluoroprop-2-enyl) mercury:



The analogous reaction of perfluoroalkyl carbanions with silver salts can be used to synthesise various perfluoroalkyl derivatives of silver. These compounds were obtained for the first time by the addition of silver fluoride to fluoro-olefins [68–71]; the fluoro-olefin–fluoride ion–$AgOCOCF_3$ system is, however, much more effective. Together with perfluoroisobutene, perfluoropropene, and perfluorocyclobutene, it proved possible to introduce into this reaction chlorotrifluoroethylene [72,73]:

$$\left.\begin{matrix} (CF_3)_2C{=}CF_2 \\ CF_3CF{=}CF_2 \\ cyclo\text{-}C_4F_6 \\ CF_2{=}CFCl \end{matrix}\right\} + MF + AgOCOCF_3 \rightarrow \left\{\begin{matrix} (CF_3)_3CAg \\ (CF_3)_2CFAg \\ cyclo\text{-}C_4H_7Ag \\ CF_3CFClAg \end{matrix}\right. ;$$
$$M{=}K, Cs .$$

On the other hand, the attempt to add silver fluoride as such to chlorotrifluoroethylene was unsuccessful [68]. Evidently, silver fluoride, which is a fairly covalent compound, adds via a four-centre mechanism, while in the case of a perfluoroalkyl carbanion only an ionic reaction takes place.

A ^{19}F NMR study of compounds R_FAg showed that exchange reactions involving perfluoroisopropylsilver are much slower than those involving perfluoro-t-butylsilver [73]. This difference can be explained by the coordination of the lone electron pairs of the fluorine atoms in the α-position of perfluoroisopropylsilver to the vacant electronic orbitals of the silver atoms.

The "steric" interaction of the geminal halogen atoms and the metal is also indicated by data obtained from the ^{19}F NMR spectra of perfluoroalkyl derivatives of mercury in solvents with different solvating capacities [74]. It has been shown that the constant for the spin–spin interaction between the mercury atom and the β-fluorine atom increases with increase of the solvating capacity of the solvent and that the opposite behaviour obtains for the fluorine atom in α-position. Evidently the donor solvent molecule competes with the α-fluorine atom in the interaction with the unfilled orbitals of the mercury atom, which leads to a decrease of the steric contribution to the quantity

$$J_{^{199}Hg\text{-}C\text{-}^{19}F} .$$

IV. SYNTHESES BASED ON DI(PERFLUORO-t-BUTYL)-MERCURY

It is well known that, in contrast to their non-fluorinated analogues, perfluoroalkylmercury compounds are extremely stable in relation to electrophiles. Their reactions with such reagents either proceed with difficulty or not at all [65]. This is shown, in particular, by the finding that the best method for their purification is distillation from concentrated sulphuric acid [62]. However, under the conditions of nucleophilic catalysis, the reactivity of perfluoroalkyl mercury compounds in reactions with electrophiles increases significantly, the most convenient catalysts being alkali metal fluorides [75,76].

Evidently the fluoride ion is coordinated via its lone electron pairs to the mercury atom, but, in contrast to other halides, this coordination does not lead to the complete displacement of the perfluoroalkyl carbanion (and the decomposition of perfluoroalkylmercury), increasing merely the carbanionic character of the carbon atom linked to mercury; as a result, the complex formed in the process

$$F^{\ominus} + R_F{-}Hg{-}R_F \rightleftharpoons R_F{\cdots}Hg{-}R_F$$
$$\ominus$$

enters into the reaction and not the free carbanion.

Thus reactions of di(perfluoroalkyl)mercury with various electrophiles become possible. For example, di(perfluoro-t-butyl)mercury and di(perfluoroisopropyl)-mercury become desymmetrised by mercury(II) chloride in the presence of potassium fluoride:

$$(R_F)_2Hg + HgCl_2 \xrightarrow{KF} R_FHgCl\ ;$$
$$R_F = (CF_3)_3C,\ (CF_3)_2CF\ .$$

Potassium fluoride also catalyses the reactions of these mercury perfluoroalkyls with iodine:

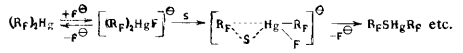
$$(R_F)_2Hg + I_2 \xrightarrow{KF} R_FI + HgI_2\ ;$$
$$R_F = (CF_3)_3C,\ (CF_3)_2CF\ .$$

It is noteworthy that di(perfluoro-t-butyl)mercury reacts with iodine in dimethylformamide also in the absence of a catalyst, probably due to the readily polarisability of iodine in a polar solvent; however, this reaction is much slower than in the presence of the fluoride ion.

When di(perfluoro-t-butyl)mercury and di(perfluoroisopropyl) mercury are heated with sulphur in dimethylformamide in the presence of potassium fluoride, mercury di(perfluoroalkyl)mercaptides are formed:

$$(R_F)_2Hg + S \xrightarrow{KF} (R_FS)_2Hg\ ;$$
$$R_F = (CF_3)_3C,\ (CF_3)_2CF\ .$$

The interaction of di(perfluoroalkyl)mercury with sulphur, catalysed by potassium fluoride, is remarkable in that it proceeds quite unambiguously—mercury perfluoroalkylmercaptides are the only reaction products. This finding suggests that the reaction with electrophiles proceeds within the limits of the complex $(R_F)_2Hg.KF$ without the involvement of the free carbanion:



Otherwise products of the oxidation of the perfluoroalkylmercaptide anion (di- and poly-sulphides) would have appeared in the reaction medium. Thus one may say that perfluoroalkylmercury compounds serve as a store of perfluoroalkylcarbanions and the experimental results obtained using the above method for their generation can differ from the results obtained in a fluoro-olefin–fluoride ion system.

In all the reactions enumerated above, di(perfluoro-t-butyl)mercury is much more reactive than di(perfluoroisopropyl)mercury. If one assumes that the catalytic activity of the fluoride ion is determined by its coordination to the mercury atom, the lower reactivity of perfluoroisopropylmercury can be accounted for not only by the destabilising effect of the fluorine atom in the α-position relative to the carbanionic centre but also by the competing intramolecular coordination of the mercury atom to the geminal fluorine atom.

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