Translated from *Uspekhi Khimii*, 52 976-1017 (1983) U.D.C. 547.231.412

The Synthesis and Properties of Aliphatic Fluoronitroso-compounds

I.L.Knunyants, Yu.A.Sizov, and O.V.Ukharov

The methods of synthesis and properties of aliphatic fluoronitroso-compounds are described systematically and the mechanisms of their reactions are discussed. A section is devoted to a survey of the properties and applications of copolymers of fluoronitroso-compounds.
The bibliography includes 304 references.

CONTENTS

I. Introduction 554
II. The synthesis of aliphatic fluoronitroso-compounds 554
III. The properties of aliphatic fluoronitroso-compounds 557
IV. The properties and applications of copolymers of fluoronitroso-compounds 569

I. INTRODUCTION

Compared with their non-fluorinated analogues, fluoronitroso-compounds are more electrophilic and the dissociation energy of their C–N bond is low, which led to the discovery of new reactions of both theoretical and practical importance—in particular the ready copolymerisation of fluoronitrosoalkanes with fluoro-olefins which leads to the formation of fluoronitroso-rubbers with unique properties.

This review includes data up to 1981 inclusive.

II. THE SYNTHESIS OF ALIPHATIC FLUORONITROSO-COMPOUNDS

The first representative of perfluoronitrosoalkanes, namely trifluoronitrosomethane, was obtained accidentally in 1936. Ruff and Giese[1] obtained trifluoronitrosomethane in a low yield by treating silver cyanide, containing an admixture of silver nitrate, with elemental fluorine. Interest in substances of this class was not renewed until the beginning of the 1950s when the chemistry of organofluorine substances began to develop vigorously. A series of general and special methods of synthesis, which have rendered available many aliphatic fluoronitroso-compounds, were also developed at that time.

1. Radical Reactions with Participation of Nitric Oxide

The first method of synthesis of trifluoronitrosomethane from trifluoroiodomethane and nitric oxide was proposed by Haszeldine[2]. Subsequently, this method was extended to a series of homologues of trifluoronitrosomethane[3–5]. It is based on the photochemical reaction of perfluoroalkyl iodides with nitric oxide in the presence of mercury as the acceptor of the evolved iodine:

$$R_F{-}I \xrightarrow{h\nu} \dot{R}_F + \dot{I}, \quad \dot{R}_F \xrightarrow{\dot{N}O} R_F{-}NO ,$$
$$2\dot{I} \xrightarrow{Hg} HgI_2 .$$

It is of interest that, when higher perfluoroalkyl iodides are used in this method in the absence of mercury, nitroso-compounds with a shorter fluorocarbon chain are formed in addition to the corresponding fluoronitroso-compounds[6,7]:

$$CF_3CF_2\dot{C}F_2 \xrightarrow{\dot{N}O} CF_3CF_2CF_2{-}NO; \quad 2NO \xrightarrow{h\nu} NO_2 + {}^1/_2\,N_2$$
$$CF_3CF_2\dot{C}F_2 \xrightarrow{NO_2} CF_3CF_2CF_2{-}ONO \xrightarrow[\dot{N}O]{h\nu} CF_3CF_2CF_2{-}\dot{O} \xrightarrow{O=CF_2}$$
$$\longrightarrow \underset{\underset{CF_3CF_2{-}NO}{\downarrow \dot{N}O}}{CF_3\dot{C}F_2} \xrightarrow{NO_2} CF_3CF_2{-}ONO \xrightarrow[\dot{N}O]{h\nu} CF_3CF_2{-}\dot{O} \xrightarrow{O=CF_2} \underset{\underset{CF_3{-}NO}{\downarrow \dot{N}O}}{\dot{C}F_3} .$$

The purpose of mercury therefore consists not only in binding the iodine evolved but also in binding nitrogen dioxide, which appears on disproportionation of nitric oxide[7]. The yields of fluoronitrosoalkanes synthesised by this method are fairly high but the degree of conversion is low. It has also been shown that this reaction can occur on thermal initiation[8] but with a low yield.

Perfluoroalkyl bromides can also be introduced into this reaction[9]. Unsaturated fluoronitroso-compounds have likewise been obtained in this way[10,11]:

$$\begin{matrix} CF_2{=}CF{-}I \\ \\ CF_2{=}CX{-}CF_2{-}I \end{matrix} + NO \xrightarrow[Hg]{h\nu} \begin{matrix} CF_2{=}CF{-}NO \\ (9\%) \\ CF_2{=}CX{-}CF_2{-}NO \ ; \\ X{=}F\,(24.5\%);\ X{=}H\,(34\%) . \end{matrix}$$

Fluorodinitrosoalkanes can be synthesised by the radical reaction of fluoro-olefins with nitric oxides[303,304]:

$$\underset{\underset{X}{|}}{CF_2{=}CF} + 2NO \xrightarrow{\Delta,h\nu} ON{-}\underset{\underset{X}{|}}{CF_2{-}CF}{-}NO ;$$
$$X{=}F,\ Cl,\ CF_3 .$$

Several other methods, based on a different procedure for the generation of fluoroalkyl radicals and nitric oxide, were proposed later[12–16]:

$$CF_3COOH + Cl{-}NO\ (or\ BrNO) \xrightarrow[\text{gas phase}]{h\nu} CF_3{-}NO ;$$
$$CF_3{-}CF_3\ (or\ CF_3Cl) + NO \xrightarrow[12\ MH_2]{\text{chemical plasma}} CF_3{-}NO ;$$
$$(CF_3)_2C{=}O + 2NO \xrightarrow{h\nu} 2CF_3{-}NO ;$$
$$CF_3{-}H + Cl{-}NO \xrightarrow{h\nu,\Delta} CF_3{-}NO .$$

However, the need to work in the gas phase in a closed space in apparatus transparent to ultraviolet light lowers the value of this method for the synthesis of fluoronitroso-compounds in large amounts.

2. Decarboxylation of Perfluoroacyl Nitrites

Yet another method of synthesis of fluoronitrosoalkanes, based on the thermochemical and photochemical decarboxylation of perfluoroacyl nitrites, was proposed at the beginning

of the 1950s:

$$R_F{-}C{-}O{-}NO \xrightarrow[-CO_2]{\Delta(h\nu)} R_F{-}NO \ .$$

Several methods have been put forward for the thermal decomposition of perfluoroacyl nitrites. Direct heating[5,17-22] or contact with a high-boiling inert solvent[23-25] have been proposed to reduce the risk of explosion in the process.

A version of the decarboxylation of perfluorooacyl nitrites is their photochemical decomposition[26-30]. In certain cases perfluoroacyl nitrites decompose at the instant of formation[31]:

$$(CF_3)_3C{-}\overset{\overset{O}{\|}}{C}{-}F + Na{-}ONO \xrightarrow[-NaF]{} (CF_3)_3C{-}\overset{\overset{O}{\|}}{C}{-}ONO \xrightarrow[-CO_2]{} (CF_3)_3C{-}NO \ .$$

3. The Addition of Nitrosyl Fluoride to Fluoro-olefins

A method of synthesis of perfluoronitroso-compounds by the addition of nitrosyl fluoride to fluoro-olefins was developed in the 1960s. It was shown that, on passing from tetrafluoroethylene derivatives to higher fluoro-olefins, the mechanism of the addition of nitrosyl fluoride undergoes inversion[32]. Nitrosyl fluoride readily adds to tetrafluoroethylene via an electrophilic mechanism in the presence of boron trifluoride[32,33]:

$$F{-}NO + BF_3 \rightarrow BF_4^- + NO^+ \ ;$$

$$CF_2{=}CFX \xrightarrow{NO^+} \overset{+}{C}F_2{-}CFX{-}NO \xrightarrow[-BF_3]{BF_4^-} CF_3{-}CFX{-}NO \ ;$$

X=F, Cl .

When X = F, the nitroso-compound cannot be isolated, since it immediately gives rise to an oxazetidine on reaction with a second tetrafluoroethylene molecule:

$$CF_2{=}CF_2 + F{-}NO \xrightarrow{BF_3} CF_3{-}CF_2{-}N{=}O \xrightarrow{CF_2=CF_2} CF_3{-}CF_2{-}\underset{\displaystyle CF_2-CF_2}{\overset{\displaystyle |}{N}}{-}O \ .$$

Fluoronitrosyl compounds are formed via the same mechanism from alkyl perfluorovinyl ethers and nitrosyl fluoride[33-35]:

$$RO{-}CX{=}CF_2 \xrightarrow{NO^+} RO{-}\overset{+}{C}X{-}CF_2{-}NO \xrightarrow{F^-} RO{-}CXF{-}CF_2{-}NO \ ;$$

X=F, Cl, R_F .

Nitrosyl fluorides add to higher fluoro-olefins via a nucleophilic mechanism in the presence of fluoride ions[32,36,37]:

$$CF_3{-}\underset{\displaystyle X}{\overset{\displaystyle |}{C}}{=}CF_2 \xrightarrow{F^-} CF_3{-}\underset{\displaystyle X}{\overset{\displaystyle |}{\bar{C}}}{-}CF_3 \xrightarrow[-F^-]{F-NO} (CF_3)_2C(X){-}NO \ ;$$

X=F, CF_3 .

The possibility of a radical interaction of nitrosyl fluoride with tetrafluoroethylene to form difluorocarbene when the reaction is initiated by ultraviolet radiation has been postulated[40]:

$$F{-}NO + \underset{(I)}{CF_2{=}CF_2} \xrightarrow{u.v.} \underset{(II)}{CF_2{<}^{CF_2}_{CF_2}} + \underset{(III)}{CF_3{-}\underset{\displaystyle CF_2-CF_2}{\overset{\displaystyle |}{N}}{-}O} + \underset{(IV)}{CF_3{-}CF_2{-}\underset{\displaystyle CF_2-CF_2}{\overset{\displaystyle |}{N}}{-}O} \ ;$$

$$CF_2{=}CF_2 \xrightarrow{u.v.} 2\ddot{C}F_2 \ ;$$

$$\left.\begin{array}{l} \ddot{C}F_2 + F{-}NO \xrightarrow{u.v.} \dot{C}F_3 + \dot{N}O \longrightarrow CF_3{-}NO \xrightarrow{CF_2=CF_2} \\ CF_2{=}CF_2 + F{-}NO \xrightarrow{u.v.} F{-}\underset{\displaystyle CF_2-CF_2}{\overset{\displaystyle |}{N}}{-}O \xrightarrow{\ddot{C}F_2} \dot{C}F_3 + \dot{N}(O{-}\underset{\displaystyle CF_2-CF_2}{\overset{\displaystyle |}{\ }}) \end{array}\right\} \rightarrow CF_3{-}\underset{\displaystyle CF_2-CF_2}{\overset{\displaystyle |}{N}}{-}O \ ; \quad (III)$$

$$CF_2{=}CF_2 + \ddot{C}F_2 \rightarrow \underset{(II)}{CF_2{<}^{CF_2}_{CF_2}} \ .$$

The following facts have been adduced in support of the mechanism. In the absence of ultraviolet radiation, only compound (IV) is formed:

$$CF_2{=}CF_2 + F{-}NO \rightarrow CF_3{-}CF_2{-}NO \xrightarrow{CF_2=CF_2} \underset{(IV)}{CF_3{-}CF_2{-}\underset{\displaystyle CF_2-CF_2}{\overset{\displaystyle |}{N}}{-}O} \ .$$

When a mixture of compound (I), (II), and (IV) is irradiated, compound (III) is produced in a low yield.

There have been a number of other studies[36,37,41] in which it was shown that nitrosyl fluoride adds to fluoro-olefins also in the absence of a catalyst but at temperatures above 100 °C, which lowers the yield of fluoronitroalkanes due to side reactions.

Nitrosyl fluoride adds not only to fluoro-olefins but also to other compounds with a double bond[42,43]:

$$CF_2{=}C(CF_3){-}COF \xrightarrow{F-NO} CF_3{-}\underset{\displaystyle NO}{\overset{\displaystyle |}{C}}(CF_3){-}COF$$

$$\text{F-ring-O} \xrightarrow{F-NO,\,\Delta} \text{F-ring-O(F)} \rightarrow \dot{C}F_2{-}CF_2{-}CF_2{-}COF \xrightarrow{\dot{N}O} ON{-}CF_2{-}CF_2{-}CF_2{-}COF \ .$$

4. The Addition of Nitrosyl Chloride to Fluoro-Olefins

The first attempt to add nitrosyl chloride to fluoro-olefins[44-46] led only to the formation of nitroso-compounds. However, subsequently, using Lewis acids as catalysts, it was possible to obtain chlorofluoronitroso-compounds in both liquid[47] (without irradiation) and gaseous[48-50] (with and without irradiation) phases:

$$\left.\begin{array}{l} CF_2{=}CF_2 + Cl{-}NO \xrightarrow[\text{liq. phase}]{AlCl_3} \\ CF_2{=}CF_2 + Cl{-}NO \xrightarrow[\text{gas phase}]{h\nu,FeCl_3} \end{array}\right\} \rightarrow Cl{-}CF_2{-}CF_2{-}NO \xleftarrow[\text{gas phase}]{FeCl_3} NO + CF_2{=}CF_2 \ ;$$

$$FeCl_3 + NO \rightleftarrows FeCl_3NO \xrightarrow{NO} FeCl_2NO + Cl{-}NO \xrightarrow{FeCl_3} FeCl_4NO \xrightarrow{2NO} \rightarrow FeCl_2NO + 2Cl{-}NO$$

$$CF_3{-}S{-}CF{=}CF_2 + Cl{-}NO \xrightarrow[\text{gas phase}]{h\nu} CF_3{-}S{-}\underset{\displaystyle NO}{\overset{\displaystyle |}{C}}F{-}CF_2Cl \ .$$

Nitrosyl chloride adds smoothly to fluoro-olefins in the presence of potassium fluoride[39,77]:

$$X{-}CF{=}C(CF_3)_2 \xrightarrow[-KCl]{KF,\,Cl-NO} X{-}CF_2{-}C(CF_3)_2{-}NO \ ;$$

X=F, C_2F_5 .

Fluoronitrosoalkanes can be obtained by the reaction of nitrosyl chloride with organofluorine derivatives of mercury[51] and also with 1-hydro-1-fluorosulphonyltetrafluoroethane[76]:

$$(CF_3{-}CXY)_2Hg + Cl{-}NO \xrightarrow{-HgCl_2} 2CF_3{-}CXY{-}NO \ ;$$

$$FSO_2{-}CFH(CF_3) \xrightarrow[-H^+]{\text{pyridine}} FSO_2{-}\bar{C}F(CF_3) \xrightarrow[-Cl^-]{Cl-NO} FSO_2{-}CF(CF_3){-}NO \ .$$

5. The Interaction of Nitrogen Oxides with Fluoro-olefins

It has been observed[52,53] that tetrafluoroethylene readily combines with nitrogen dioxide. Apart from a dinitroalkane and a nitronitrite, a small amount of a nitronitrosoalkane is formed under these conditions[53]:

$$CF_2{=}CF_2 + N_2O_4 \rightarrow O_2N{-}CF_2CF_2{-}NO_2 + O_2N{-}CF_2CF_2{-}ONO + O_2N{-}CF_2CF_2{-}NO \ .$$

When nitric oxide is used, the yield of the nitronitrosoalkane is higher[54-58]. As a consequence of its low reactivity, pure nitric oxide does not react with fluoro-olefins in the

dark[59]. However, on irradiation nitric oxide disproportionates with formation of nitrogen dioxide and trioxide, which initiate the subsequent radical processes.

The addition of nitric oxide to fluoro-olefins can be initiated also by adding chlorine, bromine[55], and oxygen[57]. When nitrogen oxides interact with fluoro-olefins, the NO_2 radical, which initiates the process, attacks specifically the least sterically hindered difluoromethylene group[60–66]. Whereas the interaction of perfluoropropene with nitrogen oxides[56,60,65,66] results in the formation of a small amount of a dinitroalkane in addition to the nitronitrosoalkane and the nitronitrite, in the case of perfluoroisobutene a dinitroalkane is not formed[62,63]:

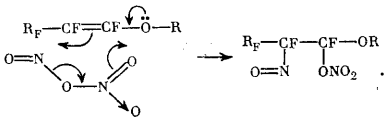
$$CF_3-CF=CF_2 \xrightarrow{N_2O_4} CF_3-\underset{NO}{CF}-CF_2-NO_2 + CF_3-\underset{ONO}{CF}-CF_2-NO_2 + CF_3-\underset{NO_2}{CF}-CF_2-NO_2 ;$$

$$(CF_3)_2C=CF_2 \xrightarrow{N_2O_4} (CF_3)_2\underset{ONO}{C}-CF_2-NO_2 + (CF_3)_2\underset{ONO}{C}-CF_2-ONO .$$

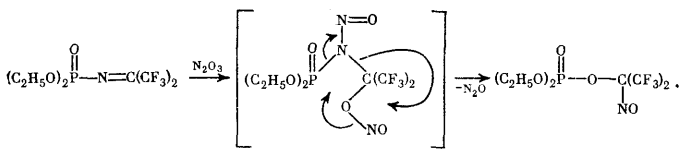
The interaction of perfluoroisobutene with nitrogen tetroxide in the presence of potassium fluoride leads to the formation of perfluoronitroso-t-butane alone[32,38]:

$$(CF_3)_2C=CF_2 \xrightarrow{F^-} (CF_3)_3C^- \xrightarrow{N_2O_4} (CF_3)_3C-N=O + NO_3^- .$$

Nitrogen dioxide adds to alkyl perfluorovinyl ethers[67] with formation of fluoronitrosonitrates:



Fluoronitrosoalkanes can also be formed by the reaction of phosphorylated imines with nitrogen trioxide[68]:



6. The Synthesis of Fluoronitro-compounds from Fluorine-containing Oximes

After the development of methods of synthesis of fluorooximes, fluoronitrosoalkanes were obtained by the Pilotti reaction[69,70]:

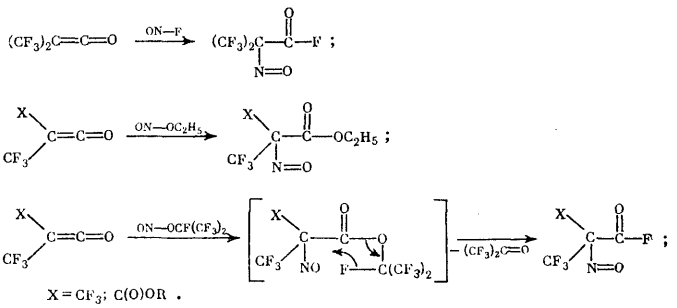
$$R_F-CF=N-OH \xrightarrow{Cl_2} \left[R_F-\underset{Cl}{CF}-\underset{Cl}{N}-OH\right] \xrightarrow{-HCl} R_F-CFCl-NO .$$

Perfluoro-2-nitrosopropane has been obtained by oxidising hexafluoroacetone oxime in anhydrous hydrogen fluoride[71]:

$$(CF_3)_2C=N-OH \xrightarrow[-H_2O]{Cr_2O_3,\ HF} (CF_3)_2CF-NO .$$

7. The Addition of Nitrosyl Fluoride and Alkyl Nitrites to Ketens

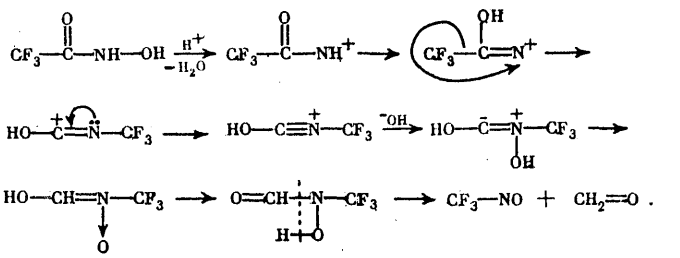
Derivatives of carboxylic fluoro-α-nitrosoacids can be obtained by the addition of nitrosyl fluoride and alkyl nitrites to ketens[72–75]:



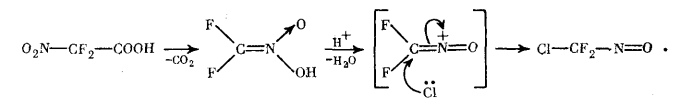
X = CF_3; C(O)OR .

8. Other Methods of Synthesis of Fluoronitroso-compounds

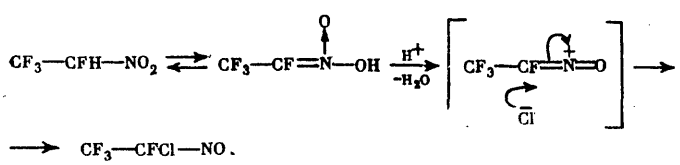
When trifluoroacetohydroxamic acid was heated *in vacuo*, trifluoronitrosomethane was obtained[79]. The following reaction mechanism is possible:



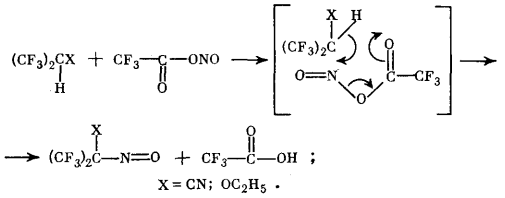
Difluoronitroacetic acid is converted into chlorodifluoronitrosomethane via several stages in a hydrochloric acid medium[80]:



When tetrafluoro-α-hydronitroethane was allowed to react with hydrogen chloride, the corresponding nitroso-compound was obtained[81]:

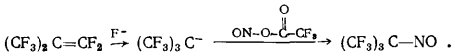


Derivatives of hexafluoro-2-nitrosoisobutyric acid can be obtained by the substitution of the hydrogen atom in the corresponding C–H acid by the nitroso-group on treatment with trifluoroacetyl nitrite[78]:



X = CN; OC_2H_5 .

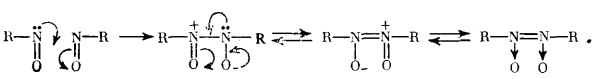
Trifluoroacetyl nitrite can also be used to synthesise fluoronitrosoalkanes from fluoro-olefins[78]:



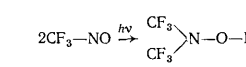
III. THE PROPERTIES OF ALIPHATIC FLUORONITROSO-COMPOUNDS

1. Characteristic Features of the Chemical Properties of Fluoronitrosoalkanes

A tendency towards dimerisation is a characteristic feature of non-fluorinated aliphatic nitroso-compounds[82,83] and most of them can exist in a monomeric form only in the melt, in solution, or in the gas phase[84]:



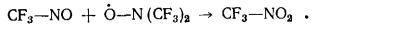
As a consequence of the decrease of the basicity of the nitrogen atom in fluoronitroso-compounds, the latter do not dimerise and they all exist exclusively in the monomeric form[84]. However, fluoronitrosoalkanes are also capable of forming dimers on irradiation but with a different structure[85]:

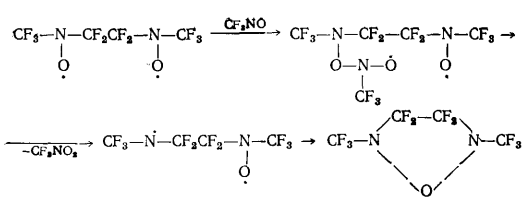


The inductive effect of the perfluoroalkyl group increases the electrophilicity of fluoronitrosoalkanes and decreases the C–N bond strength. Compared with their non-fluorinated analogues, fluoronitroso-compounds are therefore more readily reduced, are oxidised with greater difficulty, and typically undergo reactions with nucleophiles and reactions involving the dissociation of the C–N bond. In cycloaddition reactions fluoronitroso-compounds behave as active dienophiles.

2. Oxidation of Fluoronitroso-compounds

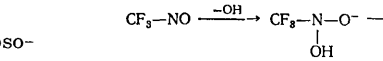
Trifluoronitrosomethane is a strong electrophile and is resistant to the action of oxidants (HNO_3, $HMnO_4$, $H_2Cr_2O_7$, and Hal_2).[86,87] The oxidation of perfluoronitrosoalkanes at 65–130 °C with hydrogen peroxide[5,7,88] and higher metal oxides[4,45] has been described. In the presence of Hopcalite trifluoronitrosomethane is oxidised only at 150–200 °C;[86] nitroxy-radicals are also capable of oxidising trifluoronitrosomethane[89,139]:





The most convenient method involves oxidation by liquid nitrogen tetroxide. Secondary fluoronitroso-compounds are then oxidised preferentially to nitro-compounds[76,90–92].

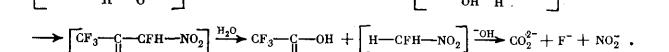
Tertiary fluoronitroso-compounds are oxidised by nitrogen tetroxide and other oxidants only to nitrites[38,39,42,62,90,93]:



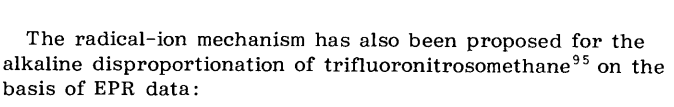
The formation of nitrites can be explained by the ready radical dissociation of the C–N bond in tertiary fluoronitroso-compounds.

3. Disproportionation of Fluoronitroso-compounds

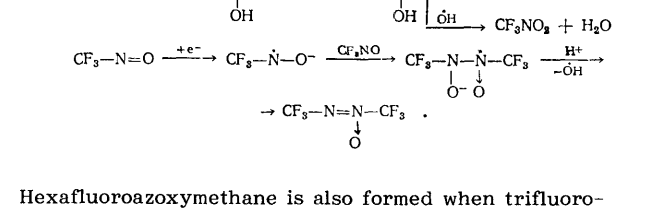
Fluoronitrosoalkanes, including trifluoronitrosomethane, undergo oxidative-reductive disproportionation over activated charcoal (at 100 °C) to perfluoronitroalkanes and perfluoroazoxyalkanes[7,88,94]:



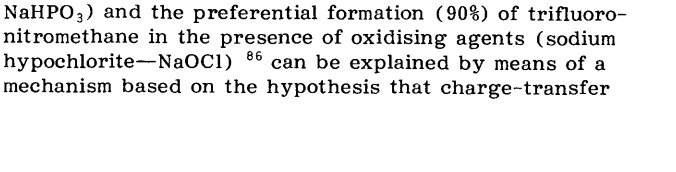
In aqueous alkalis trifluoronitrosomethane disproportionates at room temperature with formation of analogous products[7,88,94]:



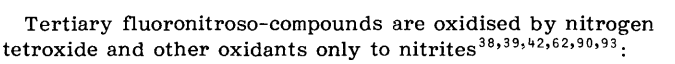
Higher homologues then decompose with formation of carboxylic acids[7,86,87]:



The radical-ion mechanism has also been proposed for the alkaline disproportionation of trifluoronitrosomethane[95] on the basis of EPR data:

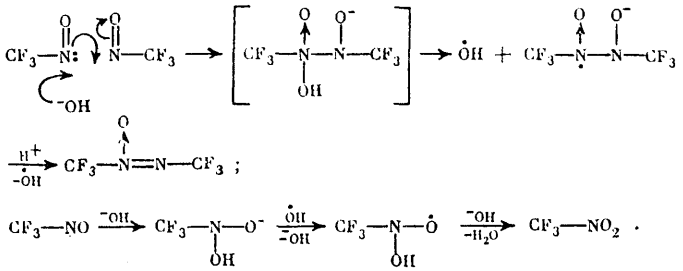


Hexafluoroazoxymethane is also formed when trifluoronitrosomethane reacts with iron pentacarbonyl[96]:



The preferential formation (90%) of hexafluoroazoxymethane in the presence of reducing agents (sodium hypophosphite—$NaHPO_3$) and the preferential formation (90%) of trifluoronitromethane in the presence of oxidising agents (sodium hypochlorite—NaOCl) [86] can be explained by means of a mechanism based on the hypothesis that charge-transfer

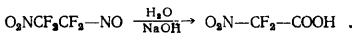
complexes are formed[97]:



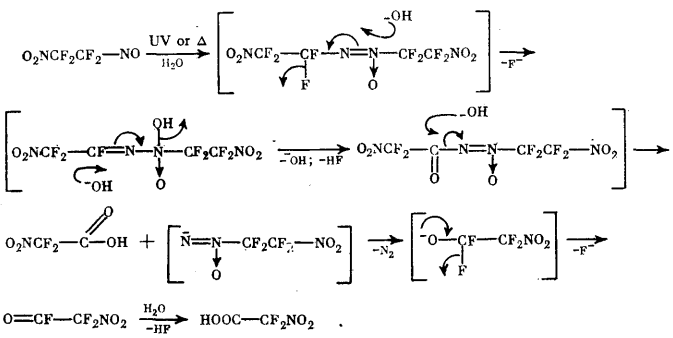
According to the authors, the reducing agent ($NaHPO_3$) binds hydroxy-radicals and prevents the formation of trifluoronitromethane, while the oxidising agent NaOCl generates hydroxy-radicals and promotes the preferential formation of trifluoronitromethane:

$$NaHPO_3 + 2\dot{O}H \rightarrow Na_2HPO_4 + H_2O \ ;$$
$$NaOCl + H_2O \rightarrow NaCl + 2\dot{O}H \ .$$

Tetrafluoro-2-nitro-1-nitrosoethane[98] hydrolyses to difluoronitroacetic acid in the presence of alkali:

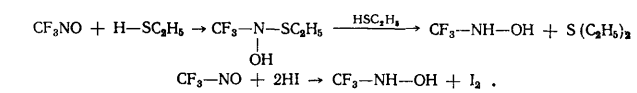


It is believed[98] that difluoronitroacetic acid is also formed in an aqueous medium on ultraviolet irradiation or on heating, via the intermediate formation of an azoxy-compound:

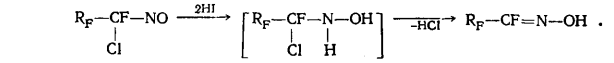


4. Reduction of Fluoronitroso-compounds

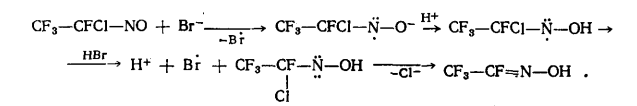
Trifluoronitrosomethane is reduced by ethanethiol and hydrogen iodide[86] to trifluorohydroxylamine, which is stable in the form of the etherate:



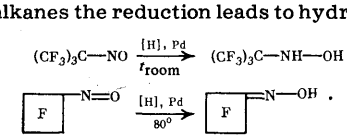
On reduction to hydroxylamine, α-chloroperfluoronitrosoalkanes[55,59] split off hydrogen halide with formation of the fluorides of perfluorohydroxamic acids:



Fluoronitrosoalkanes can be reduced also by other methods—by treating a solution of a nitrosoalkane and phenol in ether with bromine and by catalytic hydrogenation. In the former case the reducing agent is the bromide ion formed when bromine interacts with phenol[99]:



In the catalytic hydrogenation of secondary and tertiary fluoronitrosoalkanes the reduction leads to hydroxylamines[92,100]:



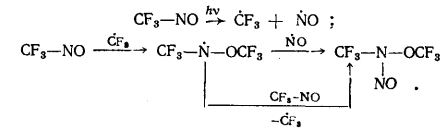
The attempts to reduce perfluoronitroso-t-butane to perfluoro-t-butylamine by hydrogenation over Raney nickel led only to the formation of perfluoromonohydro-t-butane—the product of the hydrogenolysis of the initial nitroso-compound. This finding confirms yet again the low energy of the C–N bond in tertiary fluoronitroso-compounds.

Perfluoro-t-butylhydroxylamine has been obtained in the form of the etherate by treating perfluoronitroso-t-butane with tin dichloride[101].

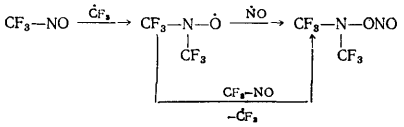
5. Pyrolysis and Photolysis of Fluoronitroso-compounds

The pyrolysis and photolysis of fluoronitroso-compounds proceed with dissociation of the C–N bond whose strength in trifluoronitrosomethane corresponds to 31–50 kcal mole^{-1} [102–106].

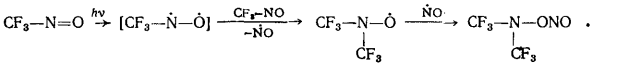
It has been suggested that in the photolysis of trifluoronitrosomethane the trifluoromethyl radical attacks the oxygen atom of the molecule of the nitroso-compound with [subsequent] formation of an *N*-nitroso-compound whose structure proved to be erroneous[107]:



A mechanism involving the attack of the nitrogen atom by the trifluoromethyl radical with formation of an *N*-nitrite, whose structure was demonstrated, was proposed later[108–109]:

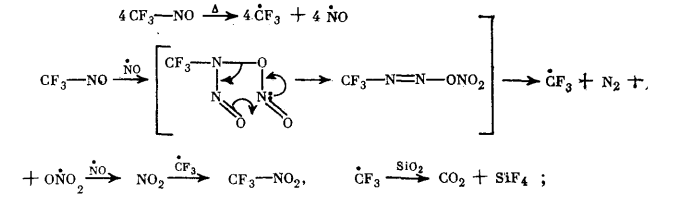


Masson[103] suggested that another primary step is also possible, in which the trifluoronitrosomethane molecule passes to an excited triplet state:



Since *N,N*-difluoro(trifluoromethyl)amine (CF_3NF_2) was not found among the products obtained on irradiation of trifluoronitrosomethane in the presence of tetrafluorohydrazine (N_2F_4), it was also concluded that there is no primary photodissociation of the C–N bond[110].

Thermal decomposition of trifluoronitrosomethane results in the formation of only trifluoronitromethane and low-molecular-weight decomposition products[111]. The following mechanism has been proposed to explain this:



or overall:

$$4CF_3{-}NO \xrightarrow{\Delta} 2CF_3{-}NO_2 + N_2 + 2\dot{C}F_3 \text{ (in the form of } CO_2 + SiF_4)\,.$$

Apart from trifluoronitromethane, tris(trifluoromethyl)-hydroxylamine and a polymeric product $(-CF_2{-}NF-)_n$ were isolated from the products of the pyrolysis of trifluoronitrosomethane at 250–300 °C:[112]

$$CF_3{-}NO \xrightarrow{250-300^\circ} \begin{cases} \longrightarrow \dot{N}O + \dot{C}F_3 \xrightarrow{\dot{C}F_3NO} CF_3{-}N(CF_3){-}\dot{O} \xrightarrow{\dot{C}F_3} CF_3{-}N(CF_3){-}OCF_3 \\ \xrightarrow{CF_3NO} CF_3{-}NO_2 + [CF_3{-}\ddot{N}] \rightarrow CF_2{=}NF \rightarrow (-CF_2{-}NF-)_n\,. \end{cases}$$

On pyrolysis, higher homologues of trifluoronitrosomethane give rise to fluoroazomethines together with nitroalkanes[41,55,112,113]. Two mechanisms have been proposed to account for this finding[41,112]:

$$\text{a) } R_F{-}CF_2{-}NO \xrightarrow{\Delta} R_F\dot{C}F_2 + \dot{N}O\ ;$$

$$R_FCF_2{-}NO \xrightarrow{R_F\dot{C}F_2} R_FCF_2{-}N(\dot{O}){-}CF_2R_F \rightarrow R_F{-}CF{=}N{-}CF_2R_F +$$

$$+ \dot{O}F \xrightarrow{R_F\dot{C}F_2NO} R_FCF_2{-}NO_2 + \dot{F} \xrightarrow{R_F\dot{C}F_2} R_F{-}CF_3\ ;$$

$$\text{(b) } (CF_3)_2CF{-}NO \xrightarrow{\Delta} (CF_3)_2\dot{C}F + \dot{N}O$$

$$(CF_3)_2CF{-}NO \xrightarrow{(CF_3)_2\dot{C}F} (CF_3)_2CF{-}N(\dot{O}){-}CF(CF_3)_2 \xrightarrow{\dot{N}O} (CF_3)_2CF{-}N(ONO){-}CF(CF_3)_2 \rightarrow$$

$$\rightarrow (CF_3)_2CF{-}\dot{N}{-}CF(CF_3)_2 + \dot{O}NO \rightleftarrows \dot{N}O_2$$

$$\xrightarrow{-RF}\downarrow\dot{R} \qquad \downarrow(CF_3)_2\dot{C}F \qquad \downarrow(CF_3)_2\dot{C}F$$

$$(CF_3)_2C{=}N{-}CF(CF_3)_2 \qquad (CF_3)_2CF{-}ONO \qquad (CF_3)_2CF{-}NO_2$$

$$\downarrow$$

$$(CF_3)_2C{=}O + F{-}NO\ ;$$

$\dot{R}$ = iso-$\dot{C}_3F_7$, $\dot{N}O$, $\dot{N}O_2$.

The first mechanism[112] gives rise to major doubts. It was shown later that trifluoronitrosomethane can produce on pyrolysis not only fluoroazomethines, like its higher homologues, but also hexafluoroazomethane[114]:

$$2CF_3{-}NO \xrightarrow{\Delta} CF_3{-}N(ONO){-}CF_3 \longrightarrow CF_3{-}N{=}CF_2 + F{-}NO_2$$

$$\xrightarrow{SiO_2} NO_2 + SiF_4;$$

$$2CF_3{-}NO \longrightarrow \begin{matrix} CF_3{-}N(\dot{O}){-}CF_3 \\ CF_3{-}N(\dot{O}){-}CF_3 \end{matrix} \xrightarrow{2CF_3NO} CF_3{-}N(CF_3){-}O{-}N(\dot{O}){-}CF_3 \longrightarrow$$

$$\longrightarrow CF_3{-}N{=}N{-}CF_3 + 2CF_3NO_2;$$

$$CF_3{-}NO \xrightarrow{2NO} \text{[cyclic intermediate]} \longrightarrow CF_3{-}N{=}N{-}ONO_2$$

$$\xrightarrow[-\dot{O}NO_2]{} CF_3{-}N{=}\dot{N} \xrightarrow{\dot{C}F_3} CF_3N{=}NCF_3.$$

On the basis of these data, it was concluded that trifluoronitrosomethane can be pyrolysed via the "diazonium nitrate",[111] via the dimer $(CF_3)_2N{-}ONO$,[108] and via the Andreades mechanism[41]. On thermal decomposition of α-chlorofluoronitroso-compounds[48,115], the products of the substitution of the nitroso-group by a chlorine atom were isolated together with nitroso-compounds:

$$ClCF_2{-}CFCl{-}NO \xrightarrow{\Delta} ClCF_2{-}\dot{C}FCl + \dot{N}O\ ;$$

$$ClCF_2{-}CFCl{-}NO \xrightarrow{\dot{N}O} ClCF_2{-}CFCl{-}NO_2 + {}^1/_2N_2\ ;$$

$$ClCF_2{-}CF(Cl){-}NO \xrightarrow{ClCF_2{-}\dot{C}FCl} [ClCF_2{-}\dot{C}F{-}NO] + ClCF_2{-}CFCl_2\,.$$

A study has been published recently[116] in which the compositions of the pyrolysis and photolysis products of perfluoronitrosopropane were compared. Photolysis results in a more complex mixture of decomposition products:

$$C_3F_7{-}NO \xrightarrow[24\ h]{80^\circ} \underset{(72\%)}{C_3F_7{-}N{=}CF{-}C_2F_5} + \underset{(11\%)}{C_3F_7{-}NO_2} + \underset{(7\%)}{(C_3F_7)_2N{-}OC_3F_7}\ ;$$

$$C_3F_7{-}NO \xrightarrow[18\ h]{u.v.} \left.\begin{matrix}(C_3F_7)_2N{-}ONO \\ (C_3F_7)_2N{-}NO_2\end{matrix}\right\} (30\%) + \begin{matrix}(C_3F_7)_2N{-}OC_3F_7 \\ (<30\%) \\ (C_3F_7)_2N{-}C_3F_7 \\ (<30\%) \\ (C_3F_7)_2N{-}N(C_3F_7)_2 \\ (<30\%)\end{matrix}\,.$$

In the catalytic fluorination of trifluoronitrosomethane[117] there is also a possibility of radical decomposition processes:

$$CF_3{-}NO \xrightarrow{F_2} CF_3{-}N(OCF_3){-}CF_3 + CF_3{-}N(F){-}CF_3\,.$$

An increase of the decomposition temperature of trifluoronitrosomethane from 30° to 170 °C in the presence of silver difluoride and of silver difluoride with a simultaneous supply of fluorine increases the yield of tris(trifluoromethyl)-hydroxylamine from 0 to 15% in the former case and reduces the yield from 55 to 7% in the latter case[118]:

$$CF_3{-}NO \xrightarrow{AgF_2} (CF_3)_2N{-}OCF_3 \xleftarrow[F_2]{AgF_2} CF_3{-}NO\,.$$

6. Interaction of Fluoronitroso-compounds with Radicals

(a) Interaction with Nitric Oxide

Trifluoronitrosomethane reacts with liquid nitric oxide[111] even at −100 °C with formation of trifluoronitromethane, *N*-bis(trifluoromethyl)ammonium nitrite, and nitrogen. In the gas phase the same products are formed much more slowly. A mechanism has been proposed with the intermediate formation of "diazonium nitrate":[111]

$$CF_3{-}NO \xrightarrow{2NO} \text{[cyclic intermediate]} \longrightarrow CF_3{-}N{=}N{-}ONO_2 \longrightarrow$$

$$\longrightarrow \dot{C}F_3 + N_2 + \dot{O}NO_2 \xrightarrow{\dot{N}O} 2\dot{N}O_2;$$

$$\dot{C}F_3 + \dot{N}O_2 \longrightarrow CF_3{-}NO_2;$$

$$CF_3{-}NO \xrightarrow{\dot{C}F_3} (CF_3)_2N{-}\dot{O} \xrightarrow{\dot{N}O} (CF_3)_2N{-}ONO;$$

or overall:

$$3CF_3NO + 3NO \rightarrow CF_3NO_2 + (CF_3)_2N{-}ONO + NO_2 + N_2.$$

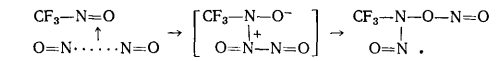
Later it was possible to detect the intermediate adduct of two nitric oxide molecules with a trifluoronitrosomethane molecule[119]:

$$CF_3{-}NO + 2NO \xrightarrow{-100^\circ} CF_3{-}N(O){-}N{=}O \xrightarrow{-50^\circ} \dot{C}F_3 + N_2 + \dot{O}NO_2\ ;$$

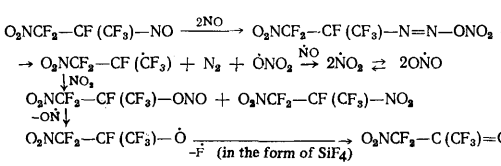
$$CF_3{-}N(ONa){-}N{=}O + CH_3O{-}NO \qquad CF_3{-}N(OH){-}N{=}O \cdot HN(C_2H_5)_2 + ON{-}N(C_2H_5)_2\,.$$

(CH₃ONa; 2HN(C₂H₅)₂)

Ginsburg et al.[119] claim reasonably that nitric oxide cannot attack trifluoronitrosomethane via a radical mechanism, since radical species were not detected by EPR at temperatures corresponding to the formation of the colourless adduct. A different pathway leading to the formation of this adduct was therefore proposed—via a complex of the trifluoronitrosomethane molecule with two nitric oxide molecules, which is stabilised as a result of electron transfer within the complex without the liberation of free radicals:

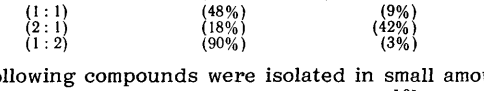


Apart from the dinitro-compound, an α-nitroketone is formed on interaction of 1-nitro-2-nitrosoperfluoropropane with nitric oxide[65]:

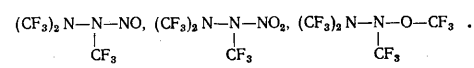


(b) Interaction with Fluoroalkyl and Other Radicals

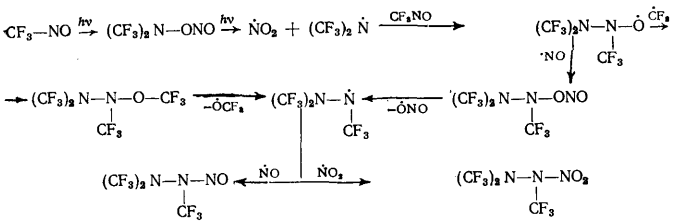
When trifluoronitrosomethane reacted with the trifluoromethyl radical, generated photochemically from trifluoroiodomethane[120,121], *N*-bis(trifluoromethyl)ammonium nitrite and tris(trifluoromethyl)hydroxylamine were obtained. The ratio of the initial reactants does not influence the ratio of the reaction products:



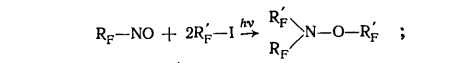
The following compounds were isolated in small amounts from the mixture of products of this reaction[121]:



In order to explain their formation, the mechanism

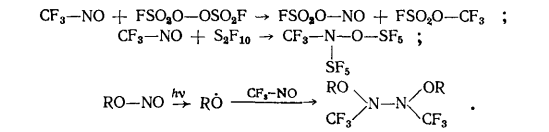


was put forward. Analogous reactions lead to both homogeneous and mixed hydroxylamines[113,122]:



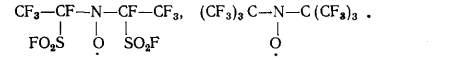
A number of studies have been devoted to the interaction of trifluoronitrosomethane with the trifluoromethyl radical, generated in different ways—by the pyrolysis of trifluoroacetyl nitrite[123], by the photolysis of hexafluoroazomethane[124], and by the photolysis of hexafluoroacetone[15].

Trifluoronitrosomethane reacts also with other substances which are readily converted into radicals[125–127]:

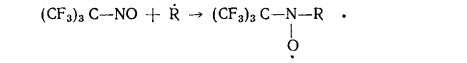


(c) Fluoronitroso-compounds as Radical-trapping Agents

On interaction with radicals, certain fluoronitrosoalkanes form relatively long-lived nitroxy-radicals which can be detected by EPR:[128,129]

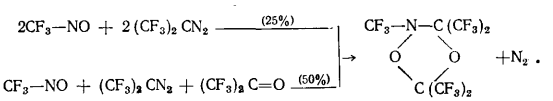


By virtue of this property, perfluoronitroso-t-butane has found applications[129–132] as a spin-trapping agent for long-lived radicals:



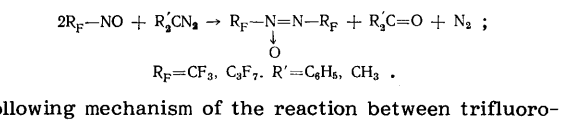
(d) Interaction With Carbenes

On interaction with bis(trifluoromethyl)azomethane, trifluoronitrosomethane gives rise to a cyclic product[133]:

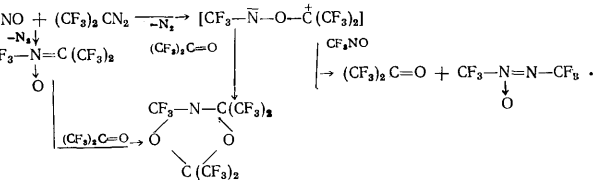


The authors suggested that hexafluoroacetone is formed as an intermediate, because the yield of the dioxazolidine increases by a factor of two when hexafluoroacetone is added to a mixture of trifluoronitrosomethane and bis(trifluoromethyl)diazomethane.

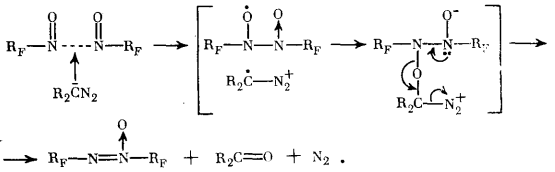
Later, other workers[134] confirmed this hypothesis also by the observation that the interaction of trifluoronitrosomethane with diphenyl- and dimethyl-diazomethanes results in the formation of a dialkyl ketone:



The following mechanism of the reaction between trifluoronitrosomethane and bis(trifluoromethyl)diazomethane has been suggested:



The authors believe that, when other diazoalkanes [Ph_2CN_2, $(CH_3)_2CN_2$] are used in this reaction, a nitrone is not formed and suggest a mechanism with charge transfer (at low temperatures in the condensed phase):



Mixed fluoroazoxyalkanes were obtained in the same study[134]:

$$CF_3{-}NO + C_3H_7{-}NO + R_2CN_2 \rightarrow CF_3{-}\underset{\downarrow O}{N{=}N}{-}C_3F_7 + CF_3{-}\underset{\downarrow O}{N{=}N}{-}C_3F_7 .$$

On reaction with diphenyldiazomethane, perfluoronitroso-t-butane gives rise to oxaziridine[135], while other fluoronitroso-alkanes react with diazoalkanes to form copolymers[136,137]:

$$(CF_3)_3C{-}N{=}O + Ph_2CN_2 \rightarrow (CF_3)_3C{-}\underset{\diagdown\,\diagup\ CPh_2}{N{-}\!\!-O} + N_2 ;$$

$$R_F{-}NO + X{-}CHN_2 \rightarrow (-\underset{R_F}{N}{-}O{-}\underset{X}{CH}-)_n + N_2 ;$$

$R_F = CF_3,\ C_3F_7;\ X = H,\ CF_3$.

Methylisonitrile deoxygenates trifluoronitrosomethane with formation of a carbodi-imide[138]:

$$CF_3{-}NO + \ddot{C}{=}N{-}CH_3 \xrightarrow[-O=C=N-CF_3]{} [CF_3{-}\ddot{N}] \xrightarrow{\ddot{C}=N-CH_3} CF_3{-}N{=}C{=}N{-}CH_3 .$$

(e) Substitution of the Nitroso-Group

Substitution of the nitroso-group by a halogen. The low energy of the C–N bond in fluoronitroso-compounds promotes easy substitution of the nitroso-group. This was first observed[115] in the thermal decomposition of 1,2-dichlorotrifluoronitrosoethane (see above). The nitroso-group is readily substituted on interaction of secondary and tertiary fluoronitrosoalkanes with halogens[76,140]:

$$\begin{matrix} CF_3 \\ FSO_2 \end{matrix}\!\!>\!CF{-}NO \xrightarrow{Br_2} \begin{matrix} CF_3 \\ FSO_2 \end{matrix}\!\!>\!CF{-}Br + BrNO ;$$

$$(CF_3)_3C{-}NO \xrightarrow{X_2} (CF_3)_3C{-}X + X{-}NO ;$$

X = Cl, Br, I .

It is of interest that the substitution of the nitroso-group in 2-chloro-trifluoro-1-nitro-2-nitrosoethane[140] occurs only on treatment with chlorine, while treatment with bromine and iodine results in the formation of a dichloro-compound, which is a disproportionation product of the initial nitrosoalkane:

$$O_2N{-}CF_2{-}CFCl{-}NO \xrightarrow{Cl_2} O_2N{-}CF_2{-}CFCl_2 + Cl{-}NO .$$

The formal substitution of the nitroso-group by a hydrogen atom takes place on hydrolysis and alcoholysis of alkyl hexafluoro-2-nitrosobutyrates[74,141] and (hexafluoroisopropyl-2-nitroso)diethyl phosphate[68] and on interaction of perfluoronitroso-t-butane with *N,N*-dimethylaniline, aniline, or ethanol[140]:

$$\begin{matrix} X \\ CF_3 \end{matrix}\!\!>\!\underset{N=O}{C}{-}C(O)OR \xrightarrow{H_2O(C_2H_5OH)} \begin{matrix} X \\ CF_3 \end{matrix}\!\!>\!\underset{H}{C}{-}C(O)OR ;$$

X = CF_3; C(O)OR

$$(C_2H_5O)_2P(O){-}\underset{N=O}{C}(CF_3)_2 \xrightarrow{H_2O(C_2H_5OH)} (C_2H_5O)_2P(O){-}\underset{H}{C}(CF_3)_2 ;$$

$$(CF_3)_3C{-}N{=}O \xrightarrow{\text{H-C}_6\text{H}_4\text{-NX}_2} (CF_3)_3C{-}H + O{=}N{-}C_6H_4{-}NX_2 ;$$

$$(CF_3)_3C{-}N{=}O \xrightarrow{\text{H-C}_6\text{H}_5\text{-OC}_2\text{H}_5} (CF_3)_3C{-}H + O{=}N{-}C_6H_5{-}OC_2H_5$$

X = H; CH_3.

Interaction with tetrafluorohydrazine. On interaction with tetrafluorohydrazine, the nitroso-group is substituted only in tertiary fluoronitroso-compounds[142–144], in which the dissociation energy of the C–N bond is lowest:

$$\begin{matrix} CF_3 \\ CF_3{-}C{-}NO \\ R \end{matrix} \xrightarrow{N_2F_4} \begin{matrix} CF_3 \\ CF_3{-}C{-}NF_2 \\ R \end{matrix} + \begin{matrix} CF_3 \\ CF_3{-}C{-}N{=}NF \\ R \end{matrix}\!\!\!\underset{O}{\downarrow} .$$

Primary and secondary fluoronitroso-compounds[142,145,146] form only fluoroazoxy-compounds via a radical mechanism[60]:

$$R_F{-}NO + N_2F_4 \longrightarrow \left[CF_3{-}\underset{NF{-}F}{N}{-}O{-}NF_2 \right] \xrightarrow{-NF_3} CF_3{-}\underset{\downarrow O}{N{=}NF} ;$$

$R_F = CF_3,\ O_2NCF_2CF_2,\ C_2H_5O{-}CFX$ (X = F, Cl, CF_3) .

Apart from fluoroazoxy-compounds, hydroxylamines and *N*-nitriles were later isolated from the products of these reactions[147]:

$$O_2N{-}CF_2CF_2{-}NO \xrightarrow{N_2F_4} O_2NCF_2CF_2{-}\underset{\downarrow O}{N{=}NF} + (O_2NCF_2CF_2)_2N{-}O{-}CF_2CF_2NO_2 +$$

$$+ (O_2NCF_2CF_2)_2N{-}ONO + CF_3{-}CF_2{-}\underset{\downarrow O}{N{=}NF} .$$

A radical-ion mechanism was proposed in the same study on the basis of EPR data for trifluoronitrosomethane[147]:

$$R_F{-}\overset{O}{\overset{\|}{N}}\cdots\cdots\overset{O}{\overset{\|}{N}}{-}R_F \rightarrow \left[R_F{-}\overset{O}{\overset{\uparrow}{N}}{-}\overset{O^-}{\overset{|}{N}}{-}R_F \right] \rightarrow R_F{-}\dot{N}{-}O^- +$$

$$F_2N{-}NF_2 \qquad\qquad F_2\overset{+}{N}{-}NF_2$$

$$+ \left[R_F{-}\overset{\dot{O}}{\overset{|}{N}}{-}\overset{+}{N}F_2 \right] \rightarrow R_F{-}\underset{\downarrow O}{N{=}NF} + NF_3 .$$

(f) Radical Reactions with Trialkyl- and Trihalogeno-silanes

In the photochemical reactions of trifluoronitrosomethane with trimethylsilane[148] and trihalogenosilanes[149], the silyl radical attacks the trifluoronitrosomethane molecule at the oxygen atom, in contrast to all other radicals:

$$CF_3{-}NO + R_3\dot{S}i \xrightarrow{h\nu} CF_3{-}\dot{N}{-}OSiR_3 \xrightarrow{R_3SiH} CF_3{-}\underset{H}{N}{-}OSiR_3 + R_3\dot{S}i ;$$

R = CH_3, Cl, F .

This reaction is also catalysed by platinum[148]:

$$(CH_3)_3SiH + Pt \rightleftarrows (CH_3)_3SiPtH \underset{\leftarrow\!\!\!\rightarrow}{\overset{(CH_3)_3SiH}{\rightleftarrows}} [(CH_3)_3Si]_2PtH_2 \xrightarrow{CF_2NO}$$

$$\rightarrow CF_3{-}NH{-}O{-}\underset{H}{Pt}[Si(CH_3)_3] \rightarrow CF_3{-}\underset{H}{N}{-}O{-}Si(CH_3)_3 + (CH_3)_3SiPtH .$$

7. Reactions with Nucleophiles

(a) Interaction with Amines

The bulk of studies in this field have been devoted to trifluoronitrosomethane. In these reactions the nitroso-group resembles the carbonyl group. Trifluoronitrosomethane reacts with primary alkylamines and cycloalkylamines to form azo-compounds[87,150,151]:

$$CF_3{-}\overset{H_2NR}{N{=}O} \longrightarrow \left[CF_3{-}\underset{O^-}{N}{-}NH_2R \longrightarrow CF_3{-}\underset{OH}{N}{-}NHR \right] \xrightarrow{-H_2O} CF_3{-}N{=}N{-}R .$$

With decrease of basicity, the reactivity of the amines falls[150]. The reactivity of various fluoronitroso-compounds increases with increasing electrophilicity[152].

α-Chlorofluoronitroso-compounds react with primary amines[150] to form unstable hydroxylamines, which readily eliminate hydrogen chloride:

$$R_F{-}CFCl{-}NO + H_2NR \xrightarrow{-H_2O} R_F{-}\underset{Cl}{\underset{|}{C}}F{-}\underset{OH}{\underset{|}{N}}{-}NHR \xrightarrow{-HCl} R_F{-}CF{=}\underset{\downarrow O}{N}{-}NHR .$$

The reaction of trifluoronitrosomethane with tertiary amines[86b]

results in the formation of hexafluoroazoxymethane:

$$CF_3-N=O \xrightarrow{CF_3NO} CF_3-\underset{\downarrow}{\overset{\uparrow}{N}}(CH_3)_3 \quad CF_3-\underset{\downarrow}{N}=N-CF_3 + [(CH_3)_2NH] + CH_2=O \ .$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad O$$

The reaction of trifluoronitrosomethane with ammonia[150] leads to an unstable azo-compound, whose formation has been demonstrated by chemical transformations:

$$CF_3-NO + H_2NH \xrightarrow[-H_2O]{ROH(Et_2O)} \rightarrow [CF_3-N=NH] \begin{cases} \xrightarrow[-HCl]{Cl_2} CF_3-Cl + N_2 \\ \xrightarrow[-HCl]{ClNO} CF_3-NO + N_2 \\ \xrightarrow[-HF]{} [CF_2=N_2] \xrightarrow{P(Ph)_3} CF_2=P(Ph)_3 \ . \end{cases}$$

The interaction of trifluoronitrosomethane with hydroxylamine in an alcoholic medium leads to the formation of alkyl trifluoromethyl ether, while the product in an alcoholic alkaline medium is difluoronitromethane[150]:

$$CF_3-NO + H_2N-OH \xrightarrow{ROH} [CF_3-N=N-OH] \xrightarrow{ROH} CF_3-OR + H_2O + N_2$$
$$CF_3-NO + H_2N-OH \xrightarrow{ROH,\ -OH} \left[CF_3-\underset{HO}{\underset{|}{N}}-NH-OH\right] \xrightarrow[-HF]{} [CF_2=N-NH-OH] \rightarrow$$
$$\rightarrow NH_3 + N_2 + [CF_2=\underset{\downarrow}{\underset{O}{N}}-OH] \rightarrow CF_2H-NO_2 \ .$$

Tetrafluoro-1-nitro-2-nitrosoethane is decomposed by hydroxylamine to difluoronitroacetic acid[153], while in an alcoholic medium the alkyl ester of the acid is formed:

$$O_2NCF_2CF_2-NO + H_2N-OH \xrightarrow[-H_2O]{} [O_2NCF_2CF_2-N=N-OH] \rightarrow$$
$$\xrightarrow[-N_2]{} [O_2NCF_2CF_2-OH] \xrightarrow[-HF]{} \left[O_2NCF_2-\overset{\overset{O}{\|}}{C}-F\right] \xrightarrow[-HF]{H_2O} O_2NCF_2-COOH \ ;$$
$$O_2N-CF_2CF_2-NO + H_2N-OH \xrightarrow{ROH} O_2NCF_2CF_2-OR \rightarrow$$
$$\xrightarrow{H_2NOH} O_2NCF_2-COOR + N_2 \ .$$

The reactions of trifluoronitrosomethane with *O*-alkylhydroxylamines[150] result in the formation of azo-compounds, while the reactions with *N*-alkylhydroxylamines[154] yield azoxy-compounds:

$$CF_3-NO + H_2N-OR \xrightarrow[-H_2O]{} CF_3-N=N-OR \ ;$$
$$CF_3-NO + HO-NHR \xrightarrow[-H_2O]{} CF_3-\underset{\downarrow}{N}=N-R \ .$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad O$$

Hydrazine reacts with trifluoronitrosomethane[150,155] to form an unstable azo-compound, which decomposes under the influence of chlorine to trifluoromethyl azide:

$$CF_3-NO + H_2N-NH_2 \xrightarrow[-H_2O]{} [CF_3-N=N-NH_2] \xrightarrow{Cl_2} CF_3N_3 + 2HCl \ .$$

Like primary amines, alkyl- and acyl-hydrazines form aminoazo-compounds:

$$CF_3-NO + H_2N-NHX \xrightarrow[-H_2O]{} CF_3-N=N-NHX \ ;$$
$$X = R,\ C(O)OR$$

Trifluoronitrosomethane reacts with diamines[156] to form bisazo-compounds;

$$CF_3-NO + H_2N-(CH_2)_n-NH_2 \xrightarrow[-2H_2O]{} CF_3-N=N-(CH_2)_n-N=N-CF_3 \ .$$

The reactions of primary aromatic amines and diamines with trifluoronitrosomethane[157] also yield azo- and bisazo-compounds respectively. 2-Aminopyridine and 3-aminopyridine[158] react with trifluoronitrosomethane to give azo-derivatives, while 4-aminopyridine does not react with trifluoronitrosomethane:

$$CF_3-NO + \begin{cases} H_2N-\langle N \rangle \xrightarrow[-H_2O]{} CF_3-N=N-\langle N \rangle \\ H_2N-\langle N \rangle \xrightarrow[-H_2O]{} CF_3-N=N-\langle N \rangle \end{cases} :$$

Electron-accepting groups in the α-position with respect to the amino-group [$(H_2N)_2C=O$, H_2NCOOH] lower the nucleophilicity of such amines and prevent their reaction with trifluoronitrosomethane[159].

Electron-accepting groups in the β-position with respect to the amino-group ($H_2N-CR^1R^2-COOR$) do not prevent the formation of the azo-compound[160,161]. *p*-Aminobenzoic acid also enters into this reaction[162].

Carboxylic α,ω-fluoronitrosoacids[163] react with amines and diamines to form azo- and bisazo-compounds respectively:

$$HOOC-(CF_2)_4-NO + \begin{cases} H_2N-R \longrightarrow HOOC-(CF_2)_4-N=N-R \\ H_2N-\langle\rangle-\langle\rangle-NH_2 \rightarrow \left[HOOC-(CF_2)_4-N=N-\langle\rangle-\right]_2 \end{cases}$$

Radical-ions, formed via a charge-transfer complex, have been detected by EPR in the interaction of trifluoronitrosomethane with amines at low temperatures[164,165]:

$$CF_3-\overset{\overset{O}{\|}}{N}\cdots\cdots\overset{\overset{O}{\|}}{N}-CF_3 \rightarrow \left[CF_3-\overset{\uparrow}{\underset{H_2\dot{N}R}{N}}-\overset{O\ O^-}{\overset{|\quad|}{N}}-CF_3\right] \rightarrow CF_3-\underset{H_2NR}{\overset{\dot{O}\quad O^-}{\overset{|\quad|}{N}}}+\dot{N}-CF_3 \ .$$

On this basis, the following mechanism of the interaction of amines with trifluoronitrosomethane has been proposed[165]:

$$\left[CF_3-\overset{\uparrow}{\underset{H_2N^+R}{N}}-\overset{O\ O^-}{\overset{|\quad|}{N}}-CF_3\right] \xrightarrow[-H_2O]{} CF_3-N=N-R + CF_3-NO \ .$$

The suggested mechanism for the reaction of trifluoronitrosomethane with ammonia is

$$2CF_3-NO + NH_3 \rightarrow \left[CF_3-\overset{\uparrow}{\underset{N^+H_3}{N}}-\overset{O\ O^-}{\overset{|\quad|}{N}}-CF_3\right] \xrightarrow[-H_2O]{} \left[CF_3-\underset{NH}{\overset{O^-}{\overset{|}{N}}}-\overset{\overset{O}{\|}}{N}-CF_3\right] \rightarrow$$
$$\xrightarrow[-N_2]{} \begin{matrix} CF_3 \\ CF_3 \end{matrix}\!\!>N-OH \ .$$

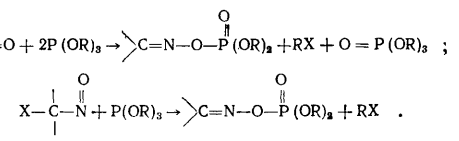
(b) Interaction with Phosphorous Acid Esters and Phospholans

The analogy between the nitroso-group and the carbonyl group is manifested strikingly also in the reactions of nitrosoalkanes with phosphorus acid esters. The Perkow reaction between α-halogenocarbonyl compounds and trialkyl phosphites is widely known[166–168]:

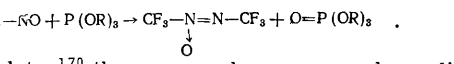
$$X-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}=O + P(OR)_3 \rightarrow \begin{matrix} \\ \end{matrix}\!\!>C=\underset{|}{\overset{|}{C}}-O-\overset{\overset{O}{\|}}{P}(OR)_2 + RX \ .$$

Allen[169] showed that geminal halogenonitro- and halogenonitroso-alkanes react analogously, forming the phosphates of

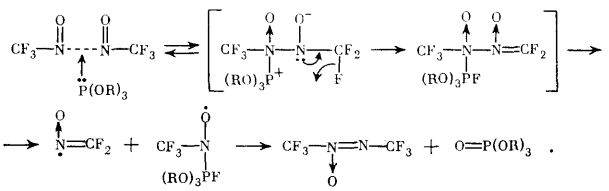
the corresponding oximes:



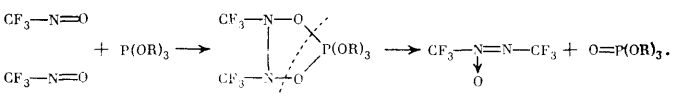
The first fluoronitroso-compound investigated in the reaction with phosphites was trifluoronitrosomethane[86]:



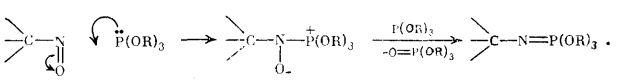
Several years later[170] the same workers proposed a radical-ion mechanism for this reaction on the basis of an EPR study:



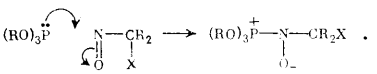
By analogy with hexafluoroacetone[171], the possibility of another version has been suggested[144]:



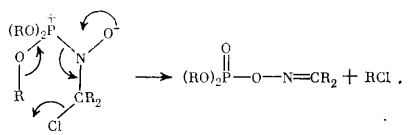
A number of general features have been established in studies of the interaction of fluoronitroso-compounds with phosphite esters[172-174]. The first step in the reaction is attack by the phosphorus atom on the nitrogen atom. Neutral phosphites react with tertiary fluoronitrosoalkanes to form phosphazo-compounds:



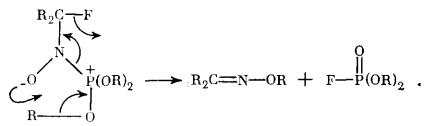
The interaction of fluoro-α-halogenonitrosoalkanes involves the intermediate formation of the *O*-anion of a hydroxylamine, whose subsequent fate depends on the nature of the halogen X:



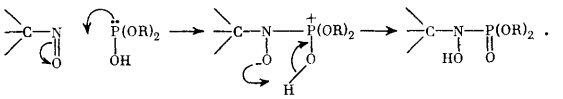
When X = Cl, the alkyl chloride is split off with formation of the products of the Allen reaction:



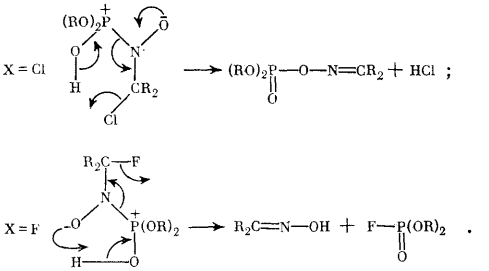
When X = F, the fluoro-oxime group acquires "pseudo-halogen" properties as a result of the high strength of the P–F bond and is split off with the alkyl group:



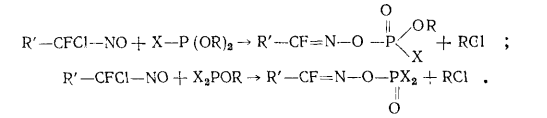
Trifluoronitrosomethane and perfluoronitroso-t-butane react with acid phosphites to form phosphorylated hydroxylamines (similarly to compounds with a carbonyl group[175,176]):



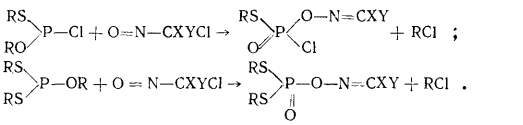
The interaction of fluoro-α-halogenonitrosoalkanes with acid phosphites results in the formation of the *O*-anion of a hydroxylamine, which splits off hydrogen chloride in the presence of a chlorine in the α-position and an oxime in the presence of a fluorine atom:



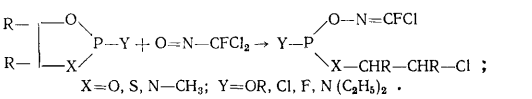
Similar reactions have been achieved with various α-chloronitrosoalkanes and halogenoalkyl phosphites[177]. In this case the products of the Allen reaction are also formed:



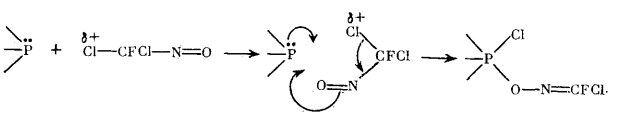
It has likewise been established that, when the alkyl halide is split off in the Allen reaction, the alkyl group is abstracted only from the alkoxy-group and not the thioalkoxy-group:



In subsequent studies[178-181] it was shown that phospholans containing at least one oxygen atom at the phosphorus atom can also enter into the Allen reaction with α-chlorofluoronitroso-compounds:

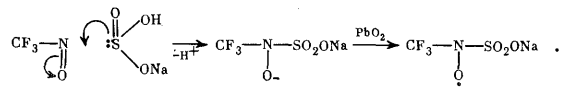


Having surveyed the available experimental data, Maleikin et al.[182] proposed a mechanism for the Allen reaction which we believe to be unlikely; it involves initial attack by the unshared electron pair of the phosphorus atom on the positively polarised chlorine atom (cf. Dyatkin et al.[174]):

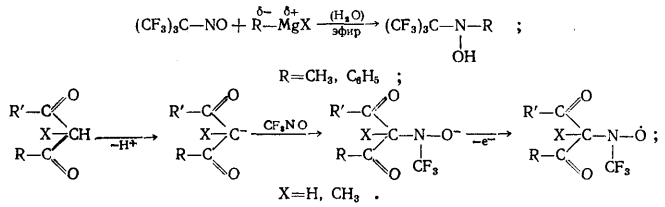


(c) Interaction with Other Nucleophiles

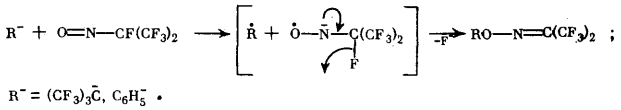
Like carbonyl compounds[183], trifluoronitrosomethane combines with sodium bisulphite[184]:



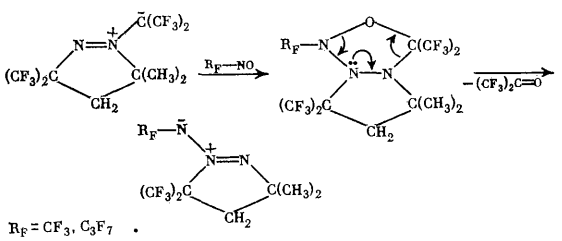
When nitrosoperfluoroalkanes were allowed to react with Grignard reagents[185] and α-diketones[186], the products of the attack by the carbanion on the nitrogen atom of the nitroso-compound were obtained:



It has been reported[187] that carbanions can attack also the oxygen atom in 2-nitrosoperfluoropropane:



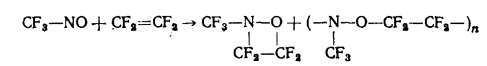
It may be that such interaction also takes places with other carbanions[188]:



8. Reactions with Unsaturated Compounds

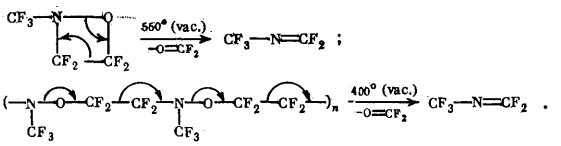
(a) Interaction with Fluoro-olefins

The development of the chemistry of fluoronitroso-compounds is perhaps most closely related to the discovery of the reaction of fluoronitrosoalkanes with fluoro-olefins from whose products copolymers with unique properties were isolated. The interaction of trifluoronitrosomethane with tetrafluoroethylene was first investigated by Barr and Haszeldine[189] in 1955:

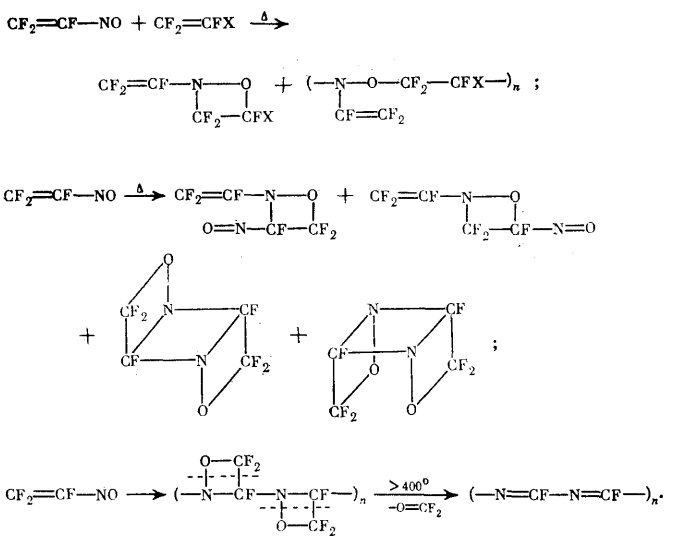


Later it was established that other fluoronitroso-compounds ($O_2NCF_2CF_2NO$,[54,190] C_2F_5NO, and $ClCF_2NO$ [46]) and fluoro-olefins ($CF_2=CFH$,[191-193] $CF_2=CFCL$,[193] $CF_2=CF-CFCl-CF_2CL$,[194] and $CF_2=CF-COF$ [195]) react analogously.

The ability of the copolymers and the oxazetidines formed simultaneously to produce on pyrolysis fluoroazomethines (in particular perfluoro-2-azapropane), with unusual chemical properties and high reactivity, whose chemistry is still being investigated, constitutes a very important property:



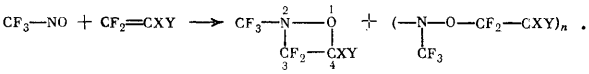
Trifluoronitrosoethylene has very interesting properties, which are a combination of those of a nitrosoalkane and a fluoro-olefin[10,196,197]. This fluoronitrosoalkene reacts with both fluoro-olefins and with itself, forming oxazetidines, polymers, and bicyclic compounds:



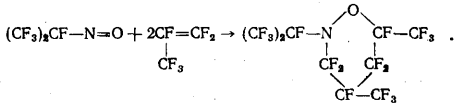
The interactions of fluoronitrosoalkanes with fluoro-olefins have a number of characteristic features.

1. At room temperature and below, a copolymer is formed preferentially, while on raising the temperature to 100 °C, the main product becomes an oxazetidine[46,54,58,189,191,194,196].

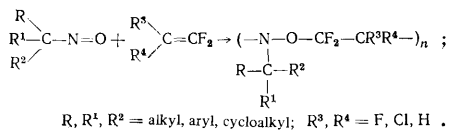
2. The interaction of fluoronitroso-compounds with asymmetric fluoro-olefins involves different modes of addition[111]. When an oxazetidine is formed, the difluoromethylene group of the olefin adds to the nitrogen atom, while on formation of a copolymer it adds to the oxygen atom:



3. Steric factors exert a significant influence on the formation of the oxazetidine[41,111]. The branching of the alkyl group of the fluoronitrosoalkane hinders the formation of the oxazetidine to a lesser extent than the branching in the fluoro-olefin. If only one of the reactants in the interaction of a fluoronitrosoalkane with a fluoro-olefin is branched in the fluorocarbon chain, an oxazetidine with a substituent predominantly in the 4-position is formed[41,65,111]. If both reactants are branched, an oxazetidine is not formed. Only in one instance has it been possible to obtain a cyclic product in the reaction of a branched fluoronitrosoalkane with a substituted fluoroethylene[198]:



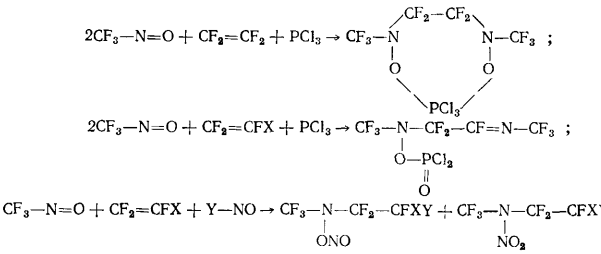
It is of interest that non-fluorinated nitroso-t-alkanes give rise to copolymers with both unsubstituted and substituted fluoro-olefins[199,200]:



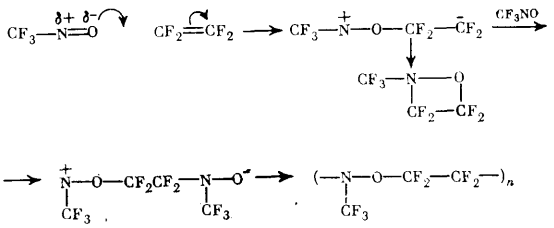
R, R^1, R^2 = alkyl, aryl, cycloalkyl; R^3, R^4 = F, Cl, H .

The introduction of hydrogen atoms into the tetrafluoroethylene molecule diminishes the reactivity with respect to trifluoronitrosomethane and prevents the formation of an oxazetidine[192].

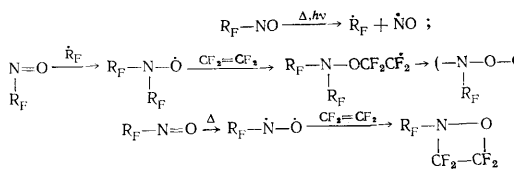
When trifluoronitrosomethane reacts with tetrafluoroethylene in the presence of phosphorus trichloride, cyclic and linear derivatives of phosphoric acid are formed, while in the presence of nitrosyl chloride or nitrogen trioxide the products are *N*-nitrites and *N*-nitro-compounds[22,201-203]:



A unanimous view on the mechanism of the reactions of fluoronitrosoalkanes with fluoro-olefins has not yet been established. An ionic mechanism was proposed initially[189]

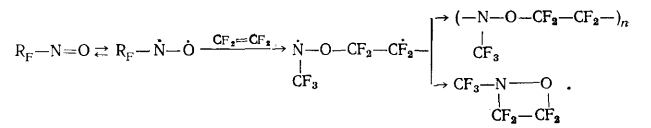


Later the same workers replaced it by a radical mechanism[7]:

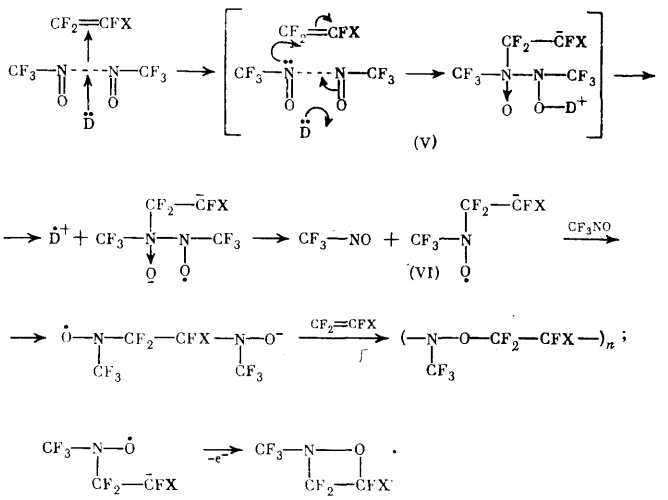


The following facts have been adduced in favour of the radical mechanism. Irradiation of the reaction mass with ultraviolet light or addition of t-butyl peroxide doubles the polymer : oxazetidine ratio. The addition of hydroquinone lowers by a factor of 2 the rate of reaction and diminishes by a factor of 8 the polymer: oxazetidine ratio.

Crawford and co-workers[193-204] also reject the ionic mechanism on the grounds that the copolymerisation takes place in an aqueous medium in the presence of classical deactivators of carbanions such as CO_2, BF_3 etherate, and $TiCl_4$ and that the presence of radical chain-transfer agents diminishes the molecular weight of the copolymer. However, they claim that the radical process is not initiated with homolytic dissociation of the C–N bond but takes place with formation of radicals arising on interaction of the fluoro-olefin with the fluoronitrosoalkane, which passes to the triplet state at the copolymerisation temperature:



The study of mixtures of trifluoronitrosomethane with various fluoro-olefins[205-207] by EPR led to the detection of paramagnetic species, which were assumed to be of the radical-ion type. Having failed to detect biradical species, whose existence had been predicted by Haszeldine and Crawford (see above), Ginsburg et al.[206] rejected the radical mechanism and proposed a radical-ion mechanism according to which a molecule of trifluoronitrosomethane, enriched by an electron donor (the OH^- species present in solution, metal ions, or the nuclophilic solvent), attacks the positively polarised difluoromethylene group of the fluoro-olefin with formation of a radical-ion, which enters into further reactions:



It was established by low-temperature thermography[207] that the formation of associated species (V) on reaction with the electron-donating medium occurs at temperatures between -130 ° and -80 °C with evolution of heat. The radical-ions (VI) are produced at higher temperatures. An electron-donating medium promotes the appearance of paramagnetic species at lower temperatures than in perfluorinated solvents or in the absence of solvents.

The size of the substituent in the fluoro-olefin does not influence significantly the ease of the above reactions. Nor is there a clear-cut correlation between the inductive influence of the substituent and the temperature at which the radical-ion is formed[207].

A detailed study of the kinetics of the copolymerisation of trifluoronitrosomethane and tetrafluoroethylene[208] again confirmed the hypothesis of the radical mechanism of the copolymerisation reaction. It was shown that the rate of formation of the copolymer obeys the equation

$$\partial [C]/\partial t = K_1 [CF_3{-}NO]^{3/2} [CF_2 = CF_2] \quad .$$

This equation is also valid for the gas phase and for a homogeneous solution in fluorocarbon solvents at temperatures between -36° and -80 °C with different ratios of the initial reactants. On the basis of this equation, the possibility of a 1 : 1 complex of the monomers is rejected, since the rate of

formation of the copolymer would then have been proportional to $[CF_3NO]^{1/2}$, and the following mechanism is proposed:

$$3CF_3{-}NO \rightarrow \dot{R}^1 + \dot{R}^2$$
$$\dot{R}^1 + CF_2{=}CF_2 \rightarrow R^1{-}CF_2\dot{C}F_2,\ \dot{R}^2 + CF_2{=}CF_2 \rightarrow R^2{-}CF_2\dot{C}F_2\ ;$$

for chain initiation,

$$R{-}CF_2\dot{C}F_2 + N{=}O \rightarrow R{-}CF_2CF_2{-}\underset{CF_3}{N}{-}\dot{O} \xrightarrow{CF_2=CF_2} R{-}CF_2CF_2{-}\underset{CF_3}{N}{-}O{-}CF_2\dot{C}F_2\ .$$

for chain propagation, and

$$2\,(R^1{-}\underset{CF_3}{N}{-}\dot{O}) \rightarrow \text{copolymer}$$

for chain termination. This mechanism requires a steady-state concentration of the radicals proportional to $[CF_3NO]^{3/2}$, which agrees with experiment. It has been suggested that the chain propagation proceeds via the interaction of $R^1{-}\underset{CF_3}{N}{-}\dot{O}$ with tetrafluoroethylene. The presence of this radical has been confirmed rigorously by EPR. The radical $R^1{-}\underset{CF_3}{N}{-}O{-}CF_2{-}\dot{C}F_2$ evidently reacts very rapidly with trifluoronitrosomethane, since it has not been detected in the EPR spectra even in a mixture of trifluoronitrosomethane with an excess of tetrafluoroethylene. The radical-ions mentioned above[207] were not detected in the above study and chain propagation via an ionic mechanism is thought to be unlikely.

In the proposed mechanism[208] the structures of the radicals $\dot{R}^1$ and $\dot{R}^2$ were not established but their concentration is proportional to $[CF_3NO]^{3/2}$, which clearly confirms the three-step initiation mechanism. The rate of formation of these radicals depends greatly on the nature of the solvent, which does not agree with earlier ideas concerning the initiation of the process in the homolysis of the C–N bond in trifluoronitrosomethane. It is also emphasised that the usual radical process initiators do not accelerate the copolymerisation in this instance. However, it has been established that the bis(trifluoromethyl)nitroxy-radical initiates specifically the copolymerisation of trifluoronitrosomethane and tetrafluoroethylene.

Kinetic studies[208,209] of the formation of oxazetidine showed that the rate of its formation obeys the equation

$$\partial[O]/\partial t = K_2[CF_3NO][CF_2{=}CF_2]\ .$$

The authors concluded that this is not a radical-chain process, since the kinetic data are consistent with a four-centre transition state but do not enable one to distinguish between a concerted mechanism and an ionic transition state.

A version of radical initiation was proposed[210] on the basis of the electronic spectra of copolymers of trifluoronitrosomethane and fluoro-olefins and the results of calculations by the INDO SCFMO method. It involves thermal excitation of the trifluoronitrosomethane molecule to the triplet state with subsequent addition of a fluoro-olefin molecule to the nitrogen or oxygen atom:

$$CF_3{-}N{=}O \xrightarrow{\Delta} CF_2{-}\dot{N}{-}\dot{O}\ ;$$

$$CF_3{-}\dot{N}{-}\dot{O} + CF_2{=}CF_2 \begin{cases} \rightarrow \dot{N}{-}O{-}CF_2{-}\dot{C}F_3 \quad (A) \\ \quad\ \ CF_3 \\ \rightarrow \dot{O}{-}\underset{CF_3}{N}{-}CF_2{-}\dot{C}F_2 \quad (B)\ ; \end{cases}$$

$$CF_3{-}N{=}O + \begin{cases} \dot{N}{-}O{-}CF_2{-}\dot{C}F_2 \xrightarrow{CF_3-NO} \dot{N}{-}O{-}CF_2CF_2O{-}\underset{CF_3}{N} \quad (C) \\ \quad\ \ CF_3 \quad (A) \\ \qquad\qquad \rightarrow \dot{N}{-}O{-}CF_2CF_2{-}\underset{CF_3}{N}{-}O \quad (D) \\ \dot{O}{-}\underset{CF_3}{N}{-}CF_2{-}\dot{C}F_2 \xrightarrow{CF_3-NO} \dot{O}{-}\underset{CF_3}{N}{-}CF_2CF_2{-}\underset{CF_3}{N}{-}\dot{O} \quad (E)\ . \\ \quad\ \ CF_3 \quad (B) \end{cases}$$

The excitation energy of the trifluoronitrosomethane was estimated as 28 kcal mol^{-1}, which is sufficient for the operation of the proposed mechanism. A regularity was observed in the spectra of the copolymers $(-\underset{CF_3}{N}{-}O{-}CF_2{-}CFX)_n$, indicating that, apart from the radical D (which is the main one), there is a possibility of the formation also of other radicals (C and E).

Simultaneously with the studies of Crabtree and co-workers[208,209] and Clark et al.[210], a report was published in 1972 [211] concerning the interaction of trifluoronitrosomethane with fluoro-olefins in a condensed phase in the presence of halogens and sulphur dichloride as copolymerisation initiators:

$$CF_3{-}NO + CF_2{=}CFR \xrightarrow{XX'} X{-}CF_2{-}CFR{-}(-\underset{CF_3}{N}{-}O{-}CF_2{-}CFR-)_n{-}X'\ ;$$
$$XX' = Cl_2,\ Br_2,\ I_2,\ SCl_2\ .$$

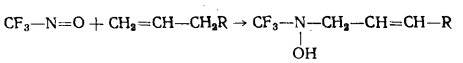
A radical mechanism has been proposed for this reaction. On the basis of the analysis of the EPR spectra, it is claimed that the reaction is initiated by the trifluoromethyl radical arising from a charge-transfer complex in which the halogen molecule functions as the donor.

However, the authors[211] claim that this is a special case and that in general the copolymerisation of trifluoronitrosomethane with fluoro-olefins takes place via an ionic and not a radical mechanism and the latter is possible only under special conditions (for example, in the presence of halogens). Thus the problem of the mechanism of the interaction of fluoronitrosoalkanes with fluoro-olefins has still not been ultimately resolved at the present time but one should note that the evidence for radical copolymerisation is fairly convincing.

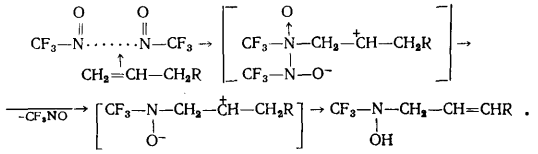
(b) Interaction with Perfluoro-olefins

Between 1962 and 1974, experimental data were accumulated on the interaction of trifluoronitrosomethane with various alkenes[138,205,212–214]. It was found that non-fluorinated olefins have only partially the same properties as their fluorinated analogues in relation to fluoronitrosoalkanes. Among all the alkenes investigated, only styrene[138], vinyl acetate[205], and methyl acrylate[214] react with trifluoronitrosomethane to form oxazetidines, while only ethylene[192] forms a copolymer by reaction with trifluoronitrosomethane with a yield of 75% in 22 months at 20 °C.

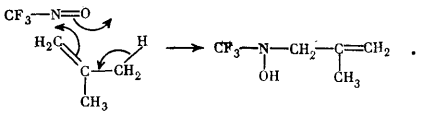
All other olefins form alkenyltrifluoromethylhydroxylamines on reaction with trifluoronitrosomethane:



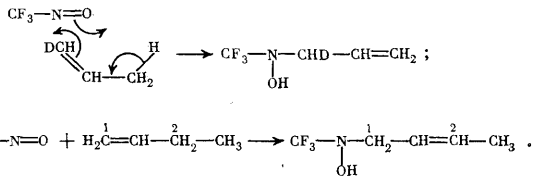
A mechanism postulating the intermediate formation of donor–acceptor charge-transfer complexes was proposed for these reactions[215]:



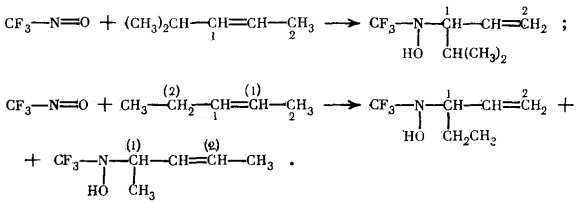
Haszeldine and co-workers[212] proposed a mechanism for the interaction of trifluoronitrosomethane with isobutene involving nucleophilic attack by a carbon atom in the unsaturated bond on the nitrogen atom of the fluoronitrosoalkane:



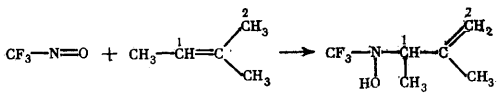
Subsequently they developed this mechanism in greater detail. It was shown in relation to 20 alkenes that in these reactions the C(1) carbon atom attacks the nitrogen atom of trifluoronitrosomethane and that hydrogen is transferred from C(2) to the oxygen atom[216]†:



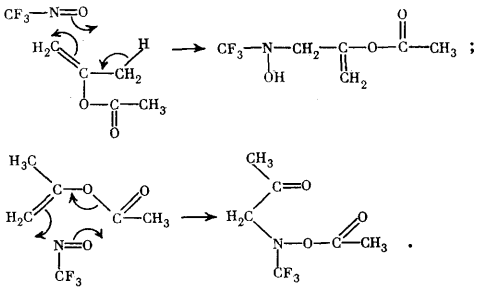
Allyl hydrogen is transferred from the least substituted carbon atom:



The least substituted carbon atom in the unsaturated bond attacks the nitrogen atom:

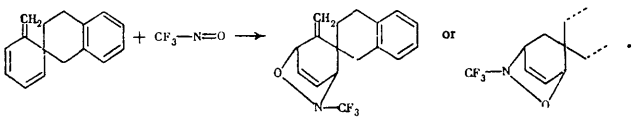


Attack on the nitrogen atom of trifluoronitrosomethane by the methylene group of isopropenyl acetate leads to the formation of two products:



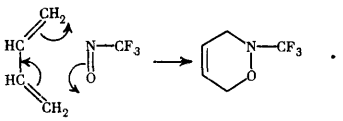
(c) Interaction with Dienes

Trifluoronitrosomethane is one of the most reactive dienophiles in Diels–Alder reactions[217]. This was first observed when the [2 + 4] cyclic adduct of trifluoronitrosomethane with spiro-di-o-xylylene was obtained[218]:

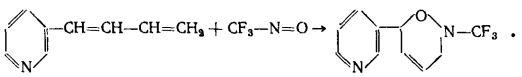


Later it was shown[219] that a copolymer is also formed under these conditions.

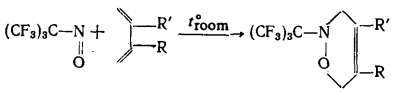
Trifluoronitrosomethane readily reacts with butadiene at -78 °C and an oxazine is formed in 97% yield:



A similar reaction takes place also with β-butadienylpyridine[220]:



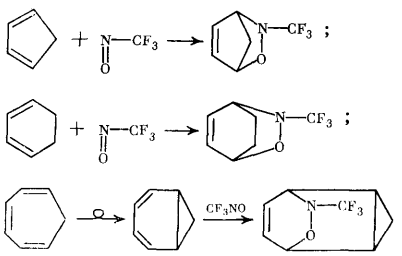
On the other hand, nitroso-t-butane does not react with dienes at all, while its perfluoro-analogue forms oxazines on reaction with butadiene and its derivatives[185] at room temperature:



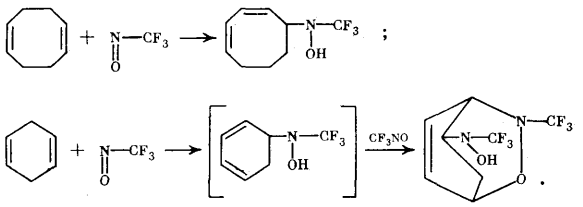
Apart from the oxazine, a copolymer is also formed in this reaction[221]. The ratio of the cyclic product to the copolymer increases as the reaction temperature is reduced, while in the interaction of fluoronitroso-compounds with fluoro-olefins the opposite behaviour is observed (see above).

† The numeral 1 designates the carbon atom attacking the nitrogen atom. The numeral 2 designates the carbon atom from which the hydrogen atom migrates.

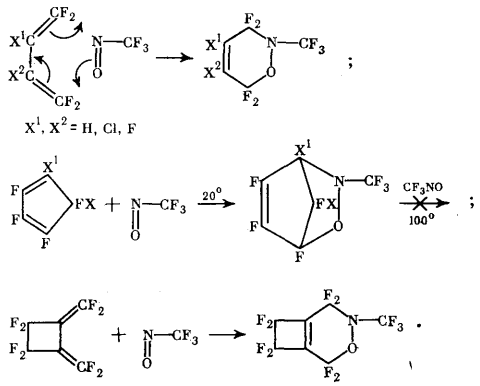
Cyclic conjugated dienes also enter into the Diels–Alder reaction with trifluoronitrosomethane[216,222]:



Non-conjugated cyclic dienes form hydroxylamines on reaction with trifluoronitrosomethane[216] as a result of the attack of the carbon atoms of the double bond on the nitrogen atom and the migration of the allyl hydrogen atom to the oxygen atom:



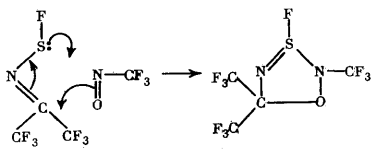
Trifluoronitrosomethane is capable of functioning as the dienophile also in relation to conjugated fluorine-containing aliphatic[194,223,224] and cyclic dienes[225–288]:



Hexafluorobutadiene reacts with various fluoronitroso-compounds more slowly than butadiene[221]. The reaction with trifluoronitrosomethane is slower by a factor of 40 and that with tetrafluoro-1-nitro-2-nitrosoethane by a factor of 600.

A radical-ion mechanism of the interaction of trifluoronitrosomethane with polyfluorinated and non-fluorinated dienes has been put forward on the basis of EPR spectra[222] (analogously to the mechanism described above).

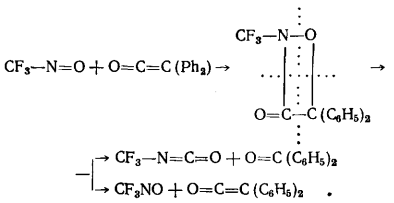
An unusual [2 + 3] cycloaddition takes place on interaction of trifluoronitrosomethane with hexafluoroacetone fluorosulphenylimine[229]:



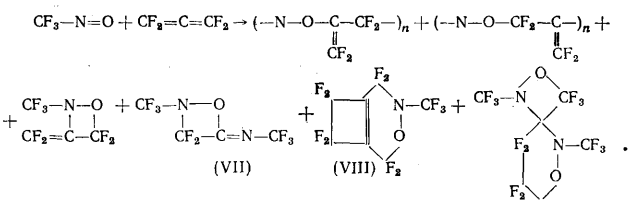
(d) Interaction with Cumulenes

The interaction of fluoronitroso-compounds with cumulenes has been investigated only in relation to trifluoronitrosomethane. Like other unsaturated compounds, cumulenes are capable of forming oxazetidines and polymers on reaction with trifluoronitrosomethane.

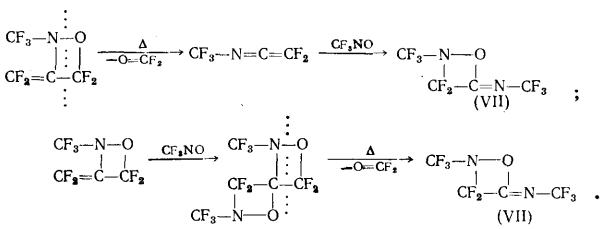
Diphenyl ketone reacts with trifluoronitrosomethane to form an oxazetidine, which can be pyrolysed via two pathways[138]:



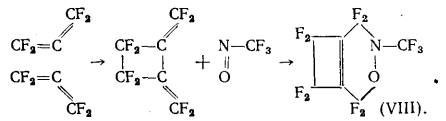
Tetrafluoroallene reacts with trifluoronitrosomethane to form a complex mixture of substances[230], from which polymers, oxazetidines, oxazines, and spiro-compounds were isolated:



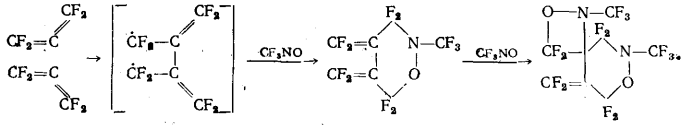
The formation of compound (VII) is explained by the following mechanisms:



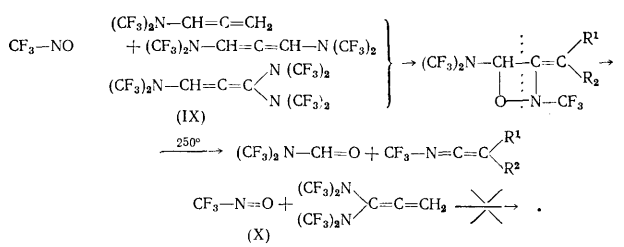
Compound (VIII) is formed from the tetrafluoroallene dimer as described by Banks et al.[228]:



The following mechanism has been postulated to account for the formation of spiro-compounds:

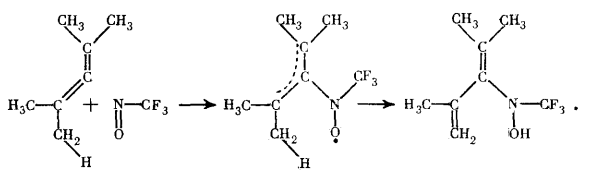


N,N-Bis(trifluoromethyl)aminoallenes react with trifluoronitrosomethane to form only oxazetidines[231,232] whose pyrolysis yields bis(trifluoromethyl)formamide and cumulated



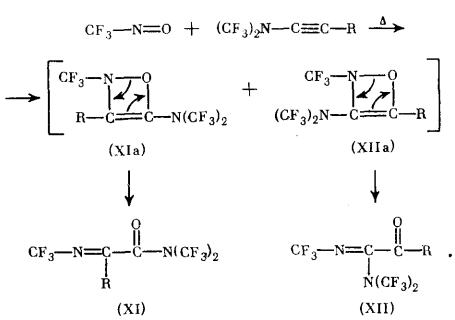
For reasons which are obscure[232], compound (X) does not enter into this reaction, while its close structural analogue (IX) reacts with trifluoronitrosomethane to form an oxazetidine.

Tetramethylallene forms the corresponding hydroxylamine on interaction with trifluoronitrosomethane[233]. The authors suggest the possibility of a mechanism involving a biradical:



(e) Interaction with Acetylenes

The reaction of fluoronitroso-compounds with acetylenes has been studied in only one instance[234]. The formation of the products of the reaction of trifluoronitrosomethane with bis(trifluoromethyl)aminoacetylenes has been explained by the intermediate formation of oxazetidines:



When R = H, Br, or CF_3, the main product is compound (XI), evidently as a consequence of the preferential formation of the less sterically hindered oxazetidine (IXa), whereas for R = $N(CF_3)_2$ only one reaction product is naturally obtained.

IV. THE PROPERTIES AND APPLICATIONS OF COPOLYMERS OF FLUORONITROSO-COMPOUNDS

Data on the copolymers of fluoronitrosoalkanes with fluoro-olefins first appeared in 1955.[189,235] The copolymers immediately attracted much attention having shown a series of interesting and useful properties—resistance to concentrated sulphuric acid, 50% potassium hydroxide solution, and hot aqueous alkali[189], thermal stability in air up to 200 °C, and retention of elasticity at −30 °C.[236]

Further studies yielded a large number of copolymers of fluoronitrosoalkanes with various unsaturated compounds. Whereas the number of studies on the chemical properties of fluoronitrosoalkanes has decreased appreciably in recent years, in the field of copolymers of fluoronitro-compounds publications have continued to appear up to the present time in which further new properties and applications of these substances are described.

Several reviews have been devoted in recent years to the synthesis and properties of the copolymers of fluoronitroso-alkanes[237–242].

All the copolymers of fluoronitrosoalkanes can be divided by convention into three large groups.

1. The copolymers of fluoronitrosomethane and tetrafluoroethylene.
2. The copolymers of other fluoronitrosoalkanes and various fluoro-olefins.
3. Ternary copolymers.

1. The Copolymers of Trifluoronitrosomethane and Tetrafluoroethylene

It was noted above that the preferential formation of the copolymer relative to the oxazetidine in the interaction of trifluoronitrosomethane with tetrafluoroethylene takes place at 0 °C and below. Depending on the copolymerisation conditions, a liquid[189,235] or solid[236,243] copolymer can be obtained. Usually efforts are made to obtain rubber-like copolymers with a molecular weight in excess of 10^6.

The copolymers of trifluoronitrosomethane with tetrafluoroethylene $(-N(CF_3)-O-CF_2-CF_2-)_n$ are highly resistant to chemical reagents and ozone-induced and natural ageing, are frost resistant (the glass point of the copolymer with a molecular weight in excess of 10^6 is −51 °C), and their properties remain unchanged for a long time at 200 °C. The vulcanisates are resistant to aromatic and aliphatic hydrocarbons, alcohols, ethers, aldehydes, ketones, and concentrated acids, do not ignite, and when placed in a flame evolve pyrolysis products which quench the flame[244,245]. Such copolymers do not ignite even in pure oxygen[241]. They are soluble only in halogenoalkanes, cyclic perfluoro-ethers, and perfluorotributylamine. In the presence of strong bases, for example, triethylamine, the copolymer readily decomposes[242]. Difluorophosgene and perfluoro-2-azapropene are formed on radiolysis and thermal and photochemical decomposition of the copolymer[246].

The inadequate thermal and radiation stability limit the applications of these copolymers. The usual vulcanising agents, employed for hydrocarbon elastomers[241], are unsuitable for them. However, it has been observed that triethylenetetramine and hexamethylenediamine form a network structure in cured rubbers based on raw nitroso-rubbers[247,248].

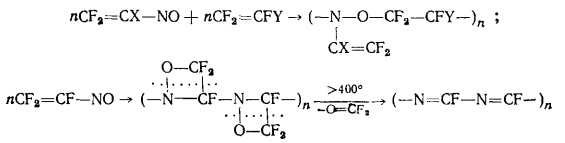
Fillers are used to improve the strength of the copolymers. The most effective is finely ground silica (in the case of amine vulcanisation)[241].

Vulcanisation and addition of various fillers[244,247,249–252] resulted in elastic and thermoplastic copolymers virtually without residual deformation, which are useful as protective coatings and articles[249,253], lubricants[254], and protective low-temperature coatings resistant to highly corrosive oxidants, for example, ClF_3.[250,251]

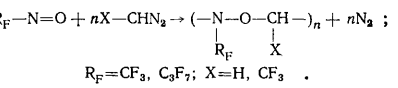
2. The Copolymers of Other Fluoronitrosoalkanes and Different Fluoro-olefins

Thermostable[255,256] and elastic[257] copolymers, which can be used as lubricants and protective coatings for metals[258], have been obtained by the copolymerisation of various perfluoronitrosoalkanes with fluoroethylenes.

Among fluorovinyl nitroso-compounds[259,260], elastic and thermostable polymers have been synthesised by copolymerisation and homopolymerisation:



Copolymers with satisfactory thermal and corrosion stabilities, which can be used as films, protective coatings, gaskets, and washers, have been synthesised from trifluoronitrosomethane and diazoalkanes[136,137]:



The study of the thermal stabilities of raw fluoronitrosorubbers *in vacuo* and in oxygen[261] established that the perfluoro-copolymers are more stable in oxygen.

The vulcanisation of certain raw fluoronitroso-rubbers improves their resistance to solvents and halogen-containing oxidants[262].

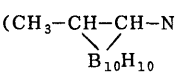
The introduction of various functional groups into the copolymer chain also promotes the appearance of useful properties in the copolymers and improves their capacity for vulcanisation. Both olefins with functions groups [CH_2–C(–CH_3)–$COOCH_3$, CH_2=CH–CN, and CH_2=CH–C_6H_5;[263] CF_2=CF–SO_2F;[264] CF_2=C=CXY;[265,266] CH_2=CH–CH=CH_2;[267] CF_2=CF$(CF_2)_n$–COONa;[268] CF_2=CF–OR [269]] and fluoronitrosoalkanes [O=N–CF_2–COF;[270] O=N–CF_2–$COOCH_3$;[271] O=N–$(CF_2)_n$–COOH [272]] are used in the copolymerisation reaction.

Such copolymers have satifactory thermal and chemical stabilities and can be used as lubricants, waxes, and elastomers[265–268]. Copolymers with improved resistance to oxidants have been obtained[270,271]. Some of them can be used as cation-exchange membranes in the electrolysis of alkali metal halides[272].

3. Ternary Copolymers

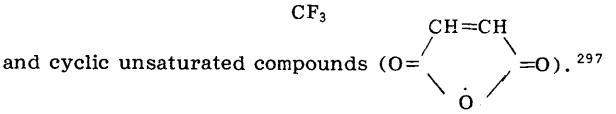
Yet another effective and widely used method for the introduction of functional groups into the polymer chain of raw nitroso-rubbers involves the use in the copolymerisation, apart from the fluoronitrosoalkane and the fluoro-olefin, of a third monomer having an alkenyl or nitroso-group at one end of the molecule and the required functional group at the other. Such copolymers are referred to as ternary polymers or terpolymers.

The most common "third" monomers are nitroso-compounds with functional groups, which consist of carboxylic perfluoronitrosoacids [O=N–$(CF_2)_n$–COOH],[273–282] methyl esters of carboxylic fluoronitrosoacids [O=N–$(CFX)_n$–$COOCH_3$],[283,284] aromatic fluoronitroso-compounds[285–288], aromatic non-fluorinated nitroso-compounds[289], nitrosoethers (O=N–CF_2–CFCl–O–C_2H_5),[290] and 1-methyl-2-nitrosocarbaborane

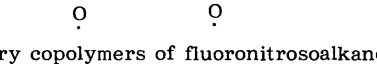


[291]

The following olefins with functional groups have been used: acrylic acid[292,293], unsaturated carboxylic fluoroacids and their esters, metal salts, amides, and nitriles [CF_2=CF–$(CF_2)_n$–A, where A = COOH, COOR, COOM, $CONH_2$, or CN),[294] unsaturated polyether carboxylic fluoroacids and their nitriles, fluorides, esters, metal salts, and dialkylamides [CF_2=CF–O–CF_2–(CFX–O–$CF_2)_m$–$(CFX)_n$–$(CF_2$–O–$CFX)_l$–A, where A = COOH, CN, COF, COOR, COOM, or $CONR_2$],[295] unsaturated fluoroethers with a sulphonyl fluoride group (CF_2=CF–CF_2–CF(–CF_3)–O–CF_2–CF_2–SO_2F),[296]



Such polymers can be vulcanised with metal oxides, metal salts of organic and organofluorine acids (chromium trifluoroacetate), epoxy-compounds[241], poly(butadiene)di-isocyanate [O=C=N–$(CH_2$–CH=CH–$CH_2)_n$–N=C=O] [298] and perfluoro-2,5-diazahexane-2,5-dioxy-biradical



[299,300]

The ternary copolymers of fluoronitrosoalkanes have perhaps the widest range of useful properties among all the copolymers of fluoronitroso-compounds. The unique property of the nitroso-polymers—incombustibility in pure oxygen—has led to their wide-scale employment in the Apollo spaceship[241].

The ternary copolymers have the following properties.

1. Satisfactory chemical and thermal stability[279,287,290,297] and suitability for use as lubricants, washers, and gaskets.
2. High elasticity and tensile strength[273,284–286,288]. Some of them have a relative elongation ranging from 150 to 950% with retention of a high tensile strength[280,281].
3. Thermoplasticity and capacity for being moulded[275,278]. At the same time they are resistant to oxidants such as nitrogen tetroxide[278].
4. The ability to "remember" their initial shape and to recover it on heating[276].
5. A modulus of hardness of 5–200 km cm^{-2} (they are used for the coating of artificial dentures)[301].
6. Elasticity and resistance to the components of rocket fuels (N_2H_4, N_2O_4, ClO_3F, N_2F_4, and ClF_3). They are therefore used in rocket engineering as shutters in the exhaust chambers for the retention of the rocket fuel and oxidant[240,274,277,285,302].
7. Properties permitting their use as binders for rocket fuels and explosives[281,292,293].
8. Properties permitting their employment as cation-exchange membranes in the electrolysis of alkali metal halides[295,296].

However, in planning the applications of such copolymers, one must bear in mind that they evolve toxic gases on decomposition—difluorophosgene, perfluoro-2-azapropene[241], and other fluoroazamethines.

REFERENCES

1. O.Ruff and M.Giese, Ber., 1936, **69B**, 684.
2. R.N.Haszeldine, Nature, 1951, **168**, 1028.
3. J.Banus, Nature, 1952, **171**, 173.
4. R.N.Haszeldine, J.Chem.Soc., 1953, 2075.

5. J.Banus, J.Chem.Soc., 1953, 3755.
6. D.A.Barr, W.C.Francis, and R.N.Haszeldine, Nature, 1956, **177**, 785.
7. D.A.Barr and R.N.Haszeldine, J.Chem.Soc., 1956, 3416.
8. J.Jander and R.N.Haszeldine, J.Chem.Soc., 1954, 912.
9. R.N.Haszeldine, US P.3 083 237 (1960); Chem.Abs., 1964, **60**, 1588.
10. C.E.Griffin and R.N.Haszeldine, Proc.Chem.Soc., 1959, 369.
11. P.Tarrant and J.Savory, J.Org.Chem., 1963, **28**, 1728.
12. W.J.Fraser, US P.3 398 072 (1964); Chem.Abs., 1968, **69**, 76 618.
13. M.Schmeisser, Z.anorg.Chem., 1975, **418**, 109.
14. J.C.Amphlett and L.J.Maculey, Canad.J.Chem., 1976 **54**, 1234.
15. G.G.A.Perkins, E.R.Austin, and F.W.Lampe, J.Chem. Phys., 1978, **68**, 4357.
16. J.E.Paustian and H.Burwasser, US P.2 616 359 (1968); Chem.Abs., 1972, **77**, 49 785.
17. R.N.Haszeldine and J.Jander, J.Chem.Soc., 1953, 4172.
18. R.E.Banks, R.N.Haszeldine, and M.K.McCreath, Proc.Chem.Soc., 1961, 64.
19. C.W.Taylor, T.J.Brice, and R.L.Wear, J.Org.Chem., 1962, **27**, 1064.
20. B.P.1 014 221 (1961); Chem.Abs., 1966, **64**, 8033.
21. C.W.Taylor, US P.3 342 874 (1961); Chem.Abs., 1968, **68**, 21 546.
22. V.A.Ginsburg, L.L.Martynova, M.F.Lebedeva, B.T.Tetel'baum, and A.N.Medvedev, Zhur.Obshch. Khim., 1967, **37**, 1077.
23. G.H.Crawford and D.E.Rice, US P.3 162 692 (1963); Chem.Abs., 1965, **62**, 10 336.
24. J.E.Paustian and M.M.Fein, US P.3 335 192 (1965); Chem.Abs., 1968, **68**, 21 515.
25. J.E.Paustian and M.M.Fein, B.P.1 132 327 (1966).
26. J.D.Park, R.W.Rosser, and J.R.Lacher, J.Org. Chem., 1962, **27**, 1462.
27. J.D.Park, US P.3 162 590 (1961); Chem.Abs., 1965, **62**, 9010.
28. G.H.Crawford and D.E.Rice, US P.3 192 246 (1961); Chem.Abs., 1965, **63**, 8206.
29. R.E.Banks, M.G.Barlow, R.N.Haszeldine, and M.K.McCreath, J.Chem.Soc.C, 1966, 1350.
30. H.A.Brown, N.Knoll, and D.E.Rice, U.S.Dept.Comp., Office Tech.Serv., A.D., 1962, 418 638; Chem.Abs., 1964, **60**, 14 709.
31. Yu.A.Cheburkov and I.L.Knunyants, Izv.Akad.Nauk SSSR.Ser.Khim., 1967(4), 829.
32. B.L.Dyatkin, E.P.Mochalina, R.A.Bekker, S.R.Sterlin, and I.L.Knunyants, Tetrahedron, 1967, **23**, 4291.
33. B.L.Dyatkin, E.P.Mochalina, R.A.Bekker, S.R.Sterlin, and I.L.Knunyants, Zhur.Vses.Khim.Obshch.im. Mendeleeva, 1966, **11**, 598.
34. B.L.Dyatkin, R.A.Bekker, Yu.S.Konstantinov, and I.L.Knunyants, Dokl.Akad.Nauk SSSR, 1965, **165**, 1305.
35. B.L.Dyatkin, R.A.Bekker, and I.L.Knunyants, Izv. Akad.Nauk SSSR, Ser.Khim., 1965(6), 1121.
36. I.L.Knunyants, E.G.Bykhovskaya, V.N.Frosin, and Ya.M.Kisel', Dokl.Akad.Nauk SSSR, 1960, **132**, 123.
37. B.L.Dyatkin, E.P.Mochalina, R.A.Bekker, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1966(3), 585.
38. B.L.Dyatkin, E.P.Mochalina, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1967(2), 469.
39. K.V.Scherer, T.F.Terranova, and D.D.Lawson, J.Org.Chem., 1981, **46**, 2379.
40. S.Andreades, Chem.Ind., 1962, 782.
41. S.Andreades, J.Org.Chem., 1962, **27**, 4163.
42. Yu.A.Cheburkov, N.Mukhmadaliev, and I.L.Knunyants, Dokl.Akad.Nauk SSSR, 1965, **165**, 127.
43. S.Andreades, J.Org.Chem., 1962, **27**, 4157.
44. A.Yu.Yakubovich, V.A.Shpanskii, and A.L.Lemke, Dokl.Akad.Nauk SSSR, 1954, **96**, 773.
45. R.N.Haszeldine, B.P.770 618 (1957); Chem.Abs., 1957, **51**, 14 790.
46. D.A.Barr and R.N.Haszeldine, J.Chem.Soc., 1960, 1151.
47. A.I.Totov, Dokl.Akad.Nauk SSSR, 1963, **149**, 619.
48. J.D.Park, A.P.Stefani, and J.R.Lacher, J.Org.Chem., 1961, **26**, 4017.
49. J.D.Park, A.P.Stefani, and J.R.Lacher, J.Org.Chem., 1961, **26**, 3319.
50. W.S.Durreele, E.C.Stump, G.Westmoreland, and C.D.Padgett, J.Polymer Sci., 1965, **A3**, 4065.
51. P.Tarrant and D.E.O'Connor, J.Org.Chem., 1964, **29**, 2012.
52. I.L.Knunyants and A.V.Fokin, Dokl.Akad.Nauk SSSR, 1956, **111**, 1035.
53. I.L.Knunyants and A.V.Fokin, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1957(12), 1439.
54. J.M.Birchall, A.J.Bloom, R.N.Haszeldine, and C.J.Willis, Proc.Chem.Soc., 1959, 367.
55. V.A.Ginsburg, N.F.Privezentseva, V.A.Shpanskii, N.P.Rodionova, S.S.Dubov, A.M.Khokhlova, S.V.Makarov, and A.Ya.Yakubovich, Zhur.Obshc. Khim., 1960, **30**, 2409.
56. J.D.Park, A.P.Stefani, G.H.Crawford, and J.R.Lacher, J.Org.Chem., 1961, **26**, 3316.
57. A.V.Fokin, A.T.Uzun, and A.I.Bol'shakova, USSR P. 168 677 (1962); Byul.Izobret., 1965(5), 20.
58. J.M.Birchall, A.J.Bloom, R.N.Haszeldine, and C.J.Willis, J.Chem.Soc., 1962, 3021.
59. V.A.Ginsburg, N.F.Privezentseva, N.P.Rodionova, S.S.Dubov, S.P.Makarov, and A.Ya.Yakubovich, Zhur.Obshch.Khim., 1960, **30**, 2406.
60. I.L.Knunyants, A.V.Fokin, and V.A.Komarov, Zhur. Vses.Khim.Obshch.im.Mendeleeva, 1962, **7**, 709.
61. M.Hauptschein and R.E.Oesterling, J.Org.Chem., 1963, **28**, 1279.
62. I.L.Knunyants and B.L.Dyatkin, Izv.Akad.Nauk SSSR, Ser.Khim., 1964(5), 923.
63. I.L.Knunyants, B.L.Dyatkin, A.V.Fokin, and V.A.Komarov, Izv.Akad.Nauk SSSR, Ser.Khim., 1964(8), 1425.
64. A.V.Fokin, V.A.Komarov, I.N.Sorochkin, and S.M.Davydova, Zhur.Vses.Khim.Obshch.im.Mendeleeva, 1965, **10**, 354.
65. E.Bagley, J.M.Birchall, and R.N.Haszeldine, J.Chem. Soc.C, 1966, 1232.
66. I.L.Knunyants, A.V.Fokin, and V.A.Komarov, Izv. Akad.Nauk SSSR, Ser.Khim., 1966(3), 466.
67. B.L.Dyatkin, R.A.Bekker, and I.L.Knunyants, Dokl. Akad.Nauk SSSR, 1966, **166**, 106.
68. L.N.Kryukov, L.Yu.Kryukova, V.L.Isaev, R.N.Sterlin, and I.L.Knunyants, 1979, **247**, 115.
69. I.L.Knunyants, E.G.Bykhovskaya, and V.N.Frosin, Zhur.Vses.Khim.Obshch.im.Mendeleeva, 1964, **9**, 598.
70. I.L.Knunyants, L.S.German, I.N.Rozhkov, and B.L.Dyatkin, Izv.Akad.Nauk SSSR, Ser.Khim., 1966(2), 250.
71. B.L.Dyatkin, E.P.Mochalina, and I.L.Knunyants, Izv. Akad.Nauk SSSR, Ser.Khim., 1965(9), 1715.

72. N.Mukhamadaliev, Yu.A.Cheburkov, and I.L.Knunyants, Izv.Akad.Nauk SSSR., Ser.Khim., 1965(11), 1982.
73. M.D.Bagramova, N.S.Mirzabekyants, Yu.A.Cheburkov, and I.K.Knunyants, Izv.Akad.Nauk SSSR,Ser.Khim., 1976(6), 1326.
74. L.Yu.Kryukova, L.N.Kryukov, V.L.Isaev, R.N.Sterlin, and I.L.Knunyants, Zhur.Vses.Khim.Obshch.im. Mendeleeva, 1977, **32**(3), 356.
75. L.Yu.Kryukova, L.N.Kryukov, V.L.Isaev, R.N.Sterlin, and I.L.Knunyants, Zhur.Vses.Khim.Obshch.im. Mendeleeva, 1977, **22**, 454.
76. G.A.Sokol'skii, S.S.Dubov, A.N.Medvedev, L.I.Ragulin, S.N.Chelobov, Yu.M.Shalaganov, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1972(1), 129.
77. I.L.Knunyants, "Sintezy Ftororganicheskikh Soedinenii" (Syntheses of Organofluorine Compounds), Izd.Khimiya, Moscow, 1973, p.24.
78. V.L.Isaev, L.Yu.Mal'kevich, T.D.Truskanova, R.N.Sterlin, and I.L.Knunyants, Zhur.Vses.Khim. Obshch.im.Mendeleeva, 1975, **20**(2), 233.
79. I.L.Knunyants and G.A.Sokol'skii, Dokl.Akad.Nauk SSSR, 1960, **132**, 605.
80. I.L.Knunyants, A.V.Fokin, V.S.Blagoveshchenskii, and Yu.M.Kosyrev, Dokl.Akad.Nauk SSSR, 1962, **146**, 1088.
81. I.L.Knunyants, L.S.German, and I.N.Rozhkov, Izv. Akad.Nauk SSSR, Ser.Khim., 1966(12), 2111.
82. B.G.Gowenlock and J.Trotman, J.Chem.Soc., 1956, 1670.
83. K.Nakamoto and R.E.Rundle, J.Amer.Chem.Soc., 1956, **78**, 1113.
84. J.H.Boyer, in "The Chemistry of the Nitro and Nitroso Groups" (Edited By H.Feuer) (Translated into Russian), Izd.Mir, Moscow, 1972, p.186.
85. A.H.Dinwoodie and R.N.Haszeldine, J.Chem.Soc., 1965, 1675.
86. A.Ya.Yakubovich, V.A.Ginsburg, S.P.Makarov, V.A.Shpanskii, N.F.Privezentseva, L.N.Martynova, B.V.Kir'yan, and A.L.Lemke, Dokl.Akad.Nauk SSSR, 1961, **140**, 1352.
87. A.H.Dinwoodie and R.N.Haszeldine, J.Chem.Soc., 1965, 2266.
88. J.Jander and R.N.Haszeldine, Naturwiss., 1953, **40**, 579.
89. R.E.Banks, R.N.Haszeldine, and M.J.Stevenson, J.Chem.Soc.C, 1966, 901.
90. B.L.Dyatkin, R.A.Bekker, and I.L.Knunyants, Dokl. Akad.Nauk SSSR, 1966, **168**, 1319.
91. R.A.Bekker, B.L.Dyatkin, and I.L.Knunyants, Izv. Akad.Nauk SSSR, Ser.Khim., 1966(1), 194.
92. B.L.Dyatkin, S.R.Sterlin, and I.L.Knunyants, Zhur. Vses.Khim.Obshch.im.Mendeleeva, 1968, **13**, 468.
93. S.R.Sterlin, B.L.Dyatkin, and I.L.Knunyants, USSR P.482 432 (1974); Byul.Izobret., 1975, **52**(32), 63.
94. J.Jander and R.N.Haszeldine, J.Chem.Soc., 1954, 919.
95. V.A.Ginsburg, A.N.Medvedev, M.F.Lebedeva, S.S.Dubov, and A.Ya.Yakubovich, Zhur.Obshch. Khim., 1965, **35**, 1418.
96. A.S.Filatov and M.A.Englin, Zhur.Obshch.Khim., 1969, **39**, 763.
97. V.A.Ginsburg, L.L.Martynova, and M.N.Vasil'eva, Zhur.Org.Khim., 1971, **7**, 2074.
98. A.V.Fokin, Yu.M.Kosyrev, and A.T.Uzun, Zhur. Obshch.Khim., 1966, **36**, 119.
99. B.L.Dyatkin, A.A.Gevorkyan, and I.L.Knunyants, Zhur.Obshch.Khim., 1966, **36**, 1326.
100. I.L.Knunyants, B.L.Dyatkin, and E.P.Mochalina, Izv.Akad.Nauk SSSR, Ser.Khim., 1965(6), 1091.
101. E.G.Bykhovskaya, Candidate's Thesis in Chemical Sciences, VAKhZ, Moscow, 1963.
102. J.Mason, J.Chem.Soc., 1957, 3904.
103. J.Mason, J.Chem.Soc., 1963, 4537.
104. P.J.Carmichael, B.G.Gowenlock, and A.F.Christopher, J.Chem.Soc., Perkin Trans.II, 1853.
105. K.Glaenzer, M.Maier, and J.Troe, Chem.Phys.Letters, 1979, **61**, 175.
106. F.Lahmani, C.Lardeux, and D.Solgadi, J.Photochem., 1981, **15**, 37.
107. J.Jander and R.N.Haszeldine, J.Chem.Soc., 1954, 696.
108. R.N.Haszeldine and B.J.H.Mattison, J.Chem.Soc., 1957, 1741.
109. A.H.Dinwoodie and R.N.Haszeldine, J.Chem.Soc., 1965, 1675.
110. R.C.White and L.J.Parcell, J.Phys.Chem., 1965, **69**, 4409.
111. D.A.Barr, R.N.Haszeldine, and C.J.Willis, J.Chem. Soc., 1961, 1351.
112. A.Ya.Yakubovich, S.P.Makarov, V.A.Ginsburg, N.F.Privezentseva, and L.L.Martynova, Dokl.Akad. Nauk SSSR, 1961, **141**, 125.
113. R.E.Banks, M.G.Barlow, R.N.Haszeldine, and M.K.McCreath, J.Chem.Soc., 1965, 7203.
114. R.E.Banks, M.G.Barlow, R.N.Haszeldine, and M.K.McCreath, J.Chem.Soc., 1965, 7209.
115. D.E.O'Connor and P.Tarrant, J.Org.Chem., 1964, **29**, 1793.
116. R.E.Banks, W.T.Flowers, and R.N.Haszeldine, J.Fluorine Chem., 1979, **13**(3), 267.
117. J.M.Shreeve, NASA Accession No.65-14 984, Rept. No.AD 607 616. Avail CFSTI, 1964; Chem.Abs., 1965, **63**, 14 362.
118. J.M.Shreve and D.P.Babb, J.Inorg.Nuclear Chem., 1967, **29**(7), 1815.
119. V.A.Ginsburg, L.L.Martynova, and M.N.Vasil'eva, Zhur.Obshch.Khim., 1967, **37**, 1083.
120. A.H.Dinwoodie and R.N.Haszeldine, J.Chem.Soc., 1965, 1681.
121. R.N.Haszeldine and A.E.Tipping, J.Chem.Soc.C, 1966, 1236.
122. M.G.Barlow and K.W.Cheung, J.Fluorine Chem., 1978, **12**, 35.
123. R.Gibbs, R.N.Haszeldine, and R.F.Simmons, J.Chem. Soc., Perkin Trans.II, 1972, 773.
124. Tan Hiok-Seng and F.W.Lampe, J.Phys.Chem., 1973, **77**, 1335.
125. V.A.Ginsburg, A.A.Tumanov, L.V.Abramova, and A.D.Koval'chenko, Zhur.Obshch.Khim., 1968, **38**, 1195.
126. M.D.Vorob'ev, A.S.Filatov, and M.A.Englin, Zhur. Org.Khim., 1973, **9**, 324.
127. D.H.R.Barton, R.L.Ronald, R.H.Hesse, M.M.Pechet, and F.J.Frank, J.Chem.Soc., Perkin Trans.I, 1974, 2344.
128. G.A.Sokol'skii, L.I.Ragulin, and I.L.Knunyants, Dokl.Akad.Nauk SSSR, 1971, **196**, 124.
129. R.Kh.Freidlina, I.I.Kandror, and R.G.Gasanov, Uspekhi Khim., 1978, **47**, 508 [Russ.Chem.Rev., 1978(3)].
130. R.G.Gasanov, I.I.Kandror, and R.Kh.Freidlina, Izv. Akad.Nauk SSSR, Ser.Khim., 1975(9), 2135.
131. R.G.Gasanov, I.I.Kandror, and R.Kh.Freidlina, Dokl. Akad.Nauk SSSR, 1976, **226**, 342.
132. V.E.Zubarev, V.N.Belovskaya, and L.T.Bugaenko, Uspekhi Khim., 1979, **48**, 1361 [Russ.Chem.Rev., 1979(8)].

133. J.Varwig and R.Mews, Angew.Chem., 1977, **89**(9), 675.
134. R.E.Banks, W.T.Flowers, and R.N.Haszeldine, J.Chem.Soc., Perkin Trans.I, 1979, 2765.
135. D.P.Del'tsova, N.P.Gambaryan, and E.P.Lur'e, Izv. Akad.Nauk SSSR, Ser.Khim., 1979(8), 1788.
136. R.N.Haszeldine, R.E.Banks, and W.T.Flowers, B.P.981 347 (1961); Chem.Abs., 1965, **62**, 10 636.
137. R.N.Haszeldine, R.E.Banks, and W.T.Flowers, B.P.1 149 233 (1965); Chem.Abs., 1969, **71**, 39 066.
138. S.P.Makarov, V.A.Shpanskii, V.A.Ginsburg, A.I.Shchekotikhin, A.S.Filatov, L.L.Martynova, and I.V.Pavlovskaya, Dokl.Akad.Nauk SSSR, 1962, **142**, 596.
139. R.E.Banks, K.C.Eapen, R.N.Haszeldine, A.V.Holt, T.Myerscough, and S.Smith, J.Chem.Soc., Perkin Trans.I, 1974, 2532.
140. B.L.Dyatkin, A.A.Gevorkyan, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1965(10), 1873.
141. I.L.Knunyants and Yu.A.Cheburkov, Fluorine Chem. Rev., 1967, **1**(1), 112.
142. I.L.Knunyants, B.L.Dyatkin, and R.A.Bekker, Dokl. Akad.Nauk SSSR, 1966, **170**, 337.
143. R.A.Bekker, B.L.Dyatkin, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1967(5), 1060.
144. B.L.Dyatkin, Doctoral Thesis in Chemical Sciences, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1967.
145. J.W.Frazer and B.E.Holder, J.Inorg.Nuclear Chem., 1962(24), 45.
146. J.W.Frazer and V.L.Duval, J.Inorg.Nuclear Chem., 1963(25), 1066.
147. A.N.Medvedev, K.N.Smirnov, S.S.Dubov, and V.A.Ginsburg, Zhur.Obshch.Khim., 1968, **38**, 2462.
148. A.C.Delany, R.N.Haszeldine, and A.E.Tipping, J.Chem.Soc.C, 1968, 2537.
149. A.A.Kirpichnikova, V.G.Noskov, M.A.Sokal'skii, and M.A.Englin, Zhur.Obshch.Khim., 1973, **43**, 1862.
150. S.P.Makarov, A.Ya.Yakubovich, V.A.Ginsburg, A.S.Filatov, M.A.Englin, N.F.Privezentseva, and T.Ya.Nikiforova, Dokl.Akad.Nauk SSSR, **141**, 357.
151. A.S.Filatov, S.P.Makarov, and A.Ya.Yakubovich, Zhur.Obshch.Khim., 1967, **37**, 837.
152. V.A.Ginsburg and N.F.Privezentseva, Zhur.Obshch. Khim., 1968, **38**, 832.
153. A.V.Fokin and A.T.Uzun, Zhur.Obshch.Khim., 1966, **36**, 117.
154. V.A.Ginsburg, L.L.Martynova, N.F.Privezentseva, and Z.A.Buchek, Zhur.Obshch.Khim., 1968, **38**, 2505.
155. S.P.Makarov, A.Ya.Yakubovich, A.S.Filatov, M.A.Englin, and T.Yu.Nikiforova, Zhur.Obshch.Khim., 1968, **38**, 709.
156. A.S.Filatov and M.A.Englin, Zhur.Obshch.Khim., 1968, **38**, 26.
157. S.P.Makarov, A.S.Filatov, and A.Ya.Yakubovich, Zhur.Obshch.Khim., 1967, **37**, 158.
158. V.A.Ginsburg and M.N.Vasil'eva, Zhur.Org.Khim., 1973, **9**, 1080.
159. M.A.Englin and A.S.Filatov, Zhur.Obshch.Khim., 1968, **38**, 1409.
160. V.A.Ginsburg and M.N.Vasileva, Zhur.Org.Khim., 1973, **9**, 2028.
161. V.A.Ginsburg and M.N.Vasileva, USSR P.370 202 (1971); Byul.Izobret., 1973(11), 73.
162. V.A.Ginsburg, M.N.Vasil'eva, and N.S.Mirzabekova, Zhur.Vses.Khim.Obshch.im.Mendeleeva, 1974, **19**, 579.
163. L.V.Sankina, L.I.Kostikin, and V.A.Ginsburg, Zhur. Org.Khim., 1972, **8**, 1365.
164. V.A.Ginsburg, A.N.Medvedev, S.S.Dubov, and M.F.Lebedeva, Dokl.Akad.Nauk SSSR, 1966, **167**, 1083.
165. V.A.Ginsburg, A.N.Medvedev, M.F.Lebedeva, M.N.Vasil'eva, and L.L.Martynova, Zhur.Obshch.Khim., 1967, **37**, 611.
166. N.Perkow, Ber., 1954, **87**. 755.
167. F.W.Lichtentahler, Chem.Rev., 1961, **61**, 607.
168. I.L.Vladimirova, A.F.Grapov, and V.I.Lomakina, in "Reaktsii i Metody Issledovaniya Organicheskikh Soedinenii" (Reactions and Methods for the Investigation of Organic Compounds), Izd.Khimiya, Moscow, 1966, p.16.
169. J.F.Allen, J.Amer.Chem.Soc., 1957, **79**, 3071.
170. V.A.Ginsburg, A.N.Medvedev. N.S.Mirzabekova, and M.F.Lebedeva, Zhur.Obshch.Khim., 1967, **37**, 620.
171. E.M.Rokhlin, Yu.V.Zeifman, Yu.A.Cheburkov, N.P.Gambaryan, and I.L.Knunyants, Dokl.Akad.Nauk SSSR, 1965, **161**, 1356.
172. I.L.Knunyants, E.G.Bykhovskaya, B.L.Dyatkin, V.N.Frosin, and A.A.Gevorkyan, Zhur.Vses.Khim. Obshch.im.Mendeleeva, 1965, **10**, 472.
173. E.P.Mochalina, B.L.Dyatkin, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1966(12), 2247.
174. B.L.Dyatkin, E.P.Mochalina, Yu.S.Konstantinov, S.R.Sterlin, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1967(10), 2297.
175. V.S.Abramov, Dokl.Akad.Nauk SSSR, 1950, **73**, 487.
176. W.F.Barthel, P.A.Giang, and S.A.Hall, J.Amer.Chem. Soc., 1954, **76**, 4186.
177. I.V.Martynov, Yu.L.Kruglyak, and N.F.Privezentseva, Zhur.Obshch.Khim., 1967, **37**, 1125.
178. Yu.L.Kruglyak, S.I.Maleikin, and I.V.Martynov, Zhur.Obshch.Khim., 1969, **39**, 1265.
179. I.V.Martynov, Yu.L.Kruglyak, G.A.Leibovskaya, Z.I.Khramova, and O.G.Strukov, Zhur.Obshch.Khim., 1969, **39**, 996.
180. Yu.L.Kruglyak, S.I.Maleikin, and I.V.Martynov, Zhur. Obshch.Khim., 1972, **42**, 811.
181. S.I.Maleikin, M.A.Sokal'skii, Yu.L.Kruglyak, and I.V.Martynov, Zhur.Obshch.Khim., 1972, **42**, 302.
182. S.I.Maleikin, V.I.Yakutin, M.A.Sokal'skii, Yu.L.Kruglyak, and I.V.Martynov, Zhur.Obshch. Khim., 1972, **42**(4), 807.
183. J.D.Roberts and M.C.Caserio, in "Basic Principles of Organic Chemistry" [2nd Edition (Benjamin 1977)] (Translated into Russian), Izd.Mir, Moscow, 1978, Vol.1, p.479.
184. R.E.Banks and R.N.Haszeldine, J.Chem.Soc., Perkin Trans.I, 1974, 721.
185. A.A.Gevorkyan, B.L.Dyatkin, and I.L.Knunyants, Zhur.Vses.Khim.Obshch.im.Mendeleeva, 1965, **10**, 707.
186. B.L.Booth, D.J.Edge, R.N.Haszeldine, and R.G.G.Holmes, J.Chem.Soc., Perkin Trans.II, 1977, 7.
187. B.L.Dyatkin, L.G.Martynova, I.V.Martynov, and S.R.Sterlin, Tetrahedron Letters, 1974, 273.
118. D.Bell and A.E.Tipping, J.Fluorine Chem., 1978, **11**, 567.
119. D.A.Barr and R.N.Haszeldine, J.Chem.Soc., 1955, 1881.
190. R.N.Haszeldine, B.P.906 825 (1959); Chem.Abs., 1963, **58**, 1346.
191. R.N.Haszeldine and C.J.Willis, B.P.843 795 (1960); Chem.Abs., 1961, **55**, 4027.
192. R.E.Banks, R.N.Haszeldine, H.Sutcliffe, and C.J.Willis, J.Chem.Soc., 1965, 2506.
193. G.H.Crawford, J.Polymer Sci., 1960(45), 259.
194. R.E.Banks, M.G.Barlow, and R.N.Haszeldine, J.Chem.Soc., 1965, 6149.

195. R.E.Banks, R.N.Haszeldine, M.J.Stevenson, and B.G.Willoughby, J.Chem.Soc.C, 1969, 2119.
196. C.E.Griffin and R.N.Haszeldine, J.Chem.Soc., 1960, 1398.
197. R.N.Haszeldine, B.P.963 634 (1953); Chem.Abs., 1964, **61**, 13 313.
198. S.Andreades, US P.3 248 394 (1960); Chem.Abs., 1966, **65**, 15 392.
199. R.N.Haszeldine, R.E.Banks, and M.K.McCreath, Dutch P.287 467 (1963); Chem.Abs., 1965, **63**, 3072.
200. R.N.Haszeldine, R.E.Banks, and M.K.McCreath, B.P.982 660 (1961); Chem.Abs., 1965, **62**, 10 547.
201. A.Ya.Yakubovich, P.O.Gitel', Z.N.Lagutina, and F.N.Chelobov, Zhur.Obshch.Khim., 1966, **36**, 163.
202. V.A.Ginsburg, L.L.Martynova, M.F.Lebedeva, S.S.Dubov, A.N.Medvedev, and B.I.Tetel'baum, Zhur. Obshch.Khim., 1967, **37**, 1037.
203. V.A.Ginsburg and M.F.Lebedeva, USSR P.210 127 (1966); Byul.Izobret., 1968(6), 19.
204. G.H.Crawford, D.E.Rice, and B.F.Landrum, J.Polymer Sci., 1963, **A1**(1), 565.
205. V.A.Ginsburg, S.S.Dubov, A.N.Medvedev, L.L.Martynova, V.I.Tetel'baum, M.N.Basil'eva, and A.Ya.Yakubovich, Dokl.Akad.Nauk SSSR, 1963, **152**, 1104.
206. V.A.Ginsburg, A.N.Medvedev, L.L.Martynova, M.N.Vasil'eva, M.F.Lebedeva, S.S.Dubov, and A.Ya.Yakubovich, Zhur.Obshch.Khim., 1965, **35**, 1924.
207. V.A.Ginsburg, A.N.Medvedev, S.S.Dubov, P.O.Gitel', V.V.Smolyanitskaya, and G.E.Nikolaenko, Zhur. Obshch.Khim., 1969, **39**, 282.
208. J.D.Crabtree, R.N.Haszeldine, A.J.Parker, K.Ridings, R.R.Simmons, and S.Smith, J.Chem.Soc., Perkin Trans.II, 1972, 111.
209. J.D.Crabtree, R.N.Haszeldine, K.Ridings, and R.F.Simmons, J.Chem.Soc., Perkin Trans.II, 1972, 119.
210. D.T.Clark, D.Kilcast, W.J.Feast, and W.K.R.Musgrave, J.Polymer Sci., A, 1972, **10**, 1637.
211. V.A.Ginsburg, A.N.Medvedev, P.O.Gitel', Z.N.Lagutina, L.L.Martynova, M.F.Lebedeva, and S.S.Dubov, Zhur.Org.Khim., 1972, **8**, 500.
212. R.E.Banks, M.G.Barlow, and R.N.Haszeldine, J.Chem. Soc., 1965, 714.
213. V.A.Ginsburg, L.L.Martynova, S.S.Dubov, V.I.Tetel'baum, and A.Ya.Yakubovich, Zhur.Obshch.Khim., 1965, **35**, 851.
214. V.A.Ginsburg, A.N.Medvedev, M.F.Lebedeva, and L.L.Martynova, Zhur.Org.Khim., 1974, **10**, 1416.
215. V.A.Ginsburg, A.N.Medvedev, L.L.Martynova, P.O.Gitel', and G.E.Nikolaenko, Zhur.Org.Khim., 1972, **8**, 486.
216. M.G.Barlow, R.N.Haszeldine, and K.W.Murray, J.Chem.Soc., Perkin Trans.I, 1980, 1960.
217. D.R.A.Perry, Fluorine Chem.Rev., 1967, **1**, 253.
218. L.A.Freede, J.Org.Chem., 1961, **26**, 2606.
219. L.A.Freede, US P.3 242 205 (1959); Chem.Abs., 1966, **64**, 19 520.
220. G.Cimbollek, H.Nowak, Z.Simane, and K.O.Freisberg, BRD P.2 248 989 (1972); Chem.Abs., 1974, **81**, 13 529.
221. A.V.Fokin, A.T.Uzun, and O.V.Dement'eva, Zhur. Obshch.Khim., 1967, **37**, 831.
222. V.A.Ginsburg, A.N.Medvedev, S.S.Dubov, M.F.Lebedeva, M.N.Vasil'eva, and L.L.Martynova, Zhur.Obshch.Khim., 1967, **37**, 2203.
223. A.Ya.Yakubovich, S.M.Rozenshtein, and S.E.Vasyukov, USSR P.173 771 (1963); Byul.Izobret., 1965(16), 35.
224. A.Ya.Yakubovich, S.M.Rozenshtein, S.E.Vasyukov, V.I.Tetel'baum, and V.I.Yakutin, Zhur.Obshch.Khim., 1966, **36**, 728.
225. R.E.Banks, A.C.Harrison, R.N.Haszeldine, and K.G.Orrell, Chem.Comm., 1965(3), 41.
226. R.E.Banks, A.C.Harrison, R.N.Haszeldine, and K.G.Orrell, J.Chem.Soc.C, 1967, 1608.
227. R.N.Haszeldine, R.E.Banks, M.Bridge, D.W.Roberts, and N.I.Tucker, J.Chem.Soc.C, 1970, 2531.
228. R.E.Banks, R.N.Haszeldine, and D.R.Taylor, J.Chem. Soc., 1965, 978.
229. J.Varwig and R.Mews, J.Chem.Res.C, 1977(10), 245.
230. R.E.Banks, R.N.Haszeldine, and D.R.Taylor, J.Chem. Soc., 1965, 5602.
231. D.H.Coy, R.N.Haszeldine, and A.E.Tipping, J.Chem. Soc.D, 1970, 456.
232. D.H.Coy, R.N.Haszeldine, M.J.Newlands, and A.E.Tipping, J.Chem.Soc., Perkin Trans.I, 1973, 1561.
233. H.A.Chia, B.E.Kirk, and D.R.Taylor, Chem.Comm., 1971, 1144.
234. J.Freear and A.E.Tipping, J.Chem.Soc.C, 1969, 1963.
235. D.A.Barr and R.N.Haszeldine, Nature, 1955, **175**, 991.
236. D.A.Barr, R.N.Haszeldine, and C.J.Willis, Proc.Chem. Soc., 1959, 230.
237. M.C.Henry, C.B.Griffis, and E.C.Stump, Fluorine Chem.Rev., 1967, **1**, 1.
238. E.C.Stump and C.D.Padgett, US Clearinghouse Fed. Sci.Techn.Inform., 1967, AD-666 801; Chem.Abs., 1968, **69**, 97 543.
239. J.Green, Encycl.Polymer Sci.Technol., 1968(9), 322.
240. K.M.D.Saijwany and J.Labdev, Sci.and Technol., 1971, **A9**, 1.
241. L.J.Fetters, in "Fluoropolymers" (Translated into Russian), Izd.Mir, Moscow, 1975, p.146.
242. H.J.Fabris and J.G.Sommer, Rubber Chem.and Technol., 1977, **50**, 523.
243. J.B.Rose, B.P.789 254 (1958); Chem.Abs., 1958, **52**, 9644.
244. J.C.Montromoso, C.B.Griffis, and G.H.Crawford, Khim.i Tekh.Polimerov, 1961(12), 124.
245. D.D.Lawson and J.D.Ingham, J.Polymer Sci., 1968, **B6**, 181.
246. A.R.Shultz, N.Knoll, and G.A.Morneau, J.Polymer Sci., 1962, **62**, 211.
247. J.C.Montromoso, C.B.Griffis, A.Wilson, and G.H.Crawford, Rubber Plastics Age, 1961, **42**, 514.
248. J.E.Smith and G.T.Perkins, Rubber Plastics Age, 1961, **42**, 59.
249. J.Day, R.Sinnott, and D.K.Thomas, B.P.1 153 491 (1966); Chem.Abs., 1969, **71**, 40 036.
250. J.Green, N.B.Levine, and R.C.Keller, B.P.1 040 352 (1965); Chem.Abs., 1967, **66**, 11 670.
251. J.Green, N.B.Levine, and R.C.Keller, US P.3 282 884 (1963); Chem.Abs., 1967, **66**, 19 585.
252. G.H.Ball, I.O.Saler, J.V.Pustinger, and H.S.Wilson, US Clearinghouse Fed.Sci.Tech.Inform., 1967, AD 672 523; Chem.Abs., 1969, **70**. 38 641.
253. G.H.Crawford, US P.3 072 592 (1960); Chem.Abs., 1963, **58**, 8119.
254. B.P.914 452 (1959); Chem.Abs., 1963, **58**, 12 737.
255. R.E.Banks and R.N.Haszeldine, B.P.1 140 525 (1965); Chem.Abs., 1969, **70**, 58 780.
256. R.N.Haszeldine and C.J.Willis, B.P.901 206 (1958); Chem.Abs., 1962, **57**, 12 726.
257. B.P.943 224 (1959); Chem.Abs., 1964, **60**, 7009.
258. G.H.Crawford, US P.3 213 009 (1961); Chem.Abs., 1966, **64**, 6869.

259. R.N.Haszeldine, US P.3 058 961 (1969); Chem.Abs., 1963, **58**, 3585.
260. C.A.Barson and C.R.Patrick, British Plastics, 1963, **36**(2), 70.
261. J.M.Cox, B.R.Wright, and W.W.Wright, J.Appl. Polymer Sci., 1964, **8**, 2935.
262. French P.1 434 310 (1965); Chem.Abs., 1966, **65**, 18 812.
263. R.N.Haszeldine, R.E.Banks, and H.Sutcliffe, B.P.1 015 781 (1961); Chem.Abs., 1966, **64**, 12 843.
264. R.E.Banks, G.M.Haslam, R.N.Haszeldine, and A.Peppin, J.Chem.Soc.C, 1966, 1171.
265. R.N.Haszeldine, R.E.Banks, and D.R.Taylor, B.P. 1 024 849 (1963); Chem.Abs., 1966, **64**, 17 749.
266. R.N.Haszeldine, R.E.Banks, and D.R.Taylor, US P. 3 322 744 (1964).
267. R.N.Haszeldine, R.E.Banks, and H.Sutcliffe, B.P. 979 428 (1961); Chem.Abs., 1965, **62**, 11 934.
268. Daikin Kogyo, B.P.1 110 007 (1964); Chem.Abs., 1968, **69**, 3312.
269. P.G.Schuman, NASA Contract Rep., 1966, NASA-CR-93 172. From.Sci.Techn.Aerosp.Rep., 1968, **6**(7), 957; Chem.Abs., 1969, **71**, 92 434.
270. R.A.Falk, US P.3 600 438 (1968); Chem.Abs., 1971, **75**, 152 739.
271. N.Mayes and R.Michaels, US P.3 660 367 (1968); Chem. Abs., 1972, **77**, 35 997.
272. H.Ukihashi, T.Asawa, M.Yamabe, and H.Miyake, Japan.Kokai, 7 718 483; Chem.Abs., 1977, **86**, 196 963.
273. C.B.Griffis and M.C.Henry, Mater.VII Symp.Natl. SAMPE Symp., Los Angeles, 1964; Chem.Abs., 1965, **62**, 5418.
274. J.Green, N.B.Levine, and W.Sheehan, Rubber Chem. Technol., 1966, **39**, 1222.
275. G.H.Crawford and D.E.Rice, US P3 321 454 (1963); Chem.Abs., 1967, **67**, 33 659.
276. US Dept.of the Army. B.P.1 134 888 (1964); Chem. Abs., 1969, **70**, 29 911.
277. M.B.Levine, Rubber Age, 1969, **101**(5), 45.
278. J.Green, N.B.Levine, and W.R.Sheehan, US P. 3 427 279 (1966); Chem.Abs., 1969, **70**, 69 150.
279. S.M.Toy, W.D.English, W.E.Crane, and M.S.Toy, J.Macromol.Sci.Chem., 1969, **3**, 1355.
280. N.Mayes and R.Michaels, US P.3 637 814 (1968); Chem.Abs., 1972, **76**, 128 459.
281. N.B.Levine, J.Green, and W.R.Sheehan, US P. 3 649 609 (1968); Chem.Abs., 1972, **77**, 36 027.
282. J.W.Martin and E.A.Burns, US P.3 733 295 (1970); Chem.Abs., 1973, **79**, 54 660.
283. W.H.Olier and E.C.Stump, US P.3 472 822 (1966); Chem.Abs., 1969, **71**, 125 714.
284. J.E.Green and R.Michaels, US P.3 725 374 (1970); Chem.Abs., 1973, **79**, 6521.
285. J.Green, N.Mayes, and E.Cottrill, Amer.Chem.Soc. Dev.Polymer Chem., Preprints, 1966, **7**(2), 1084; Chem.Abs., 1967, **66**, 76 699.
286. J.M.Green, N.Mayes, and E.Cottrill, J.Macromolec. Sci., 1967, **1A**(7), 1387.
287. H.Mark, Allgem.und prakt.Chem., 1967, **18**, 7.
288. J.Green and J.A.Castellano, US P.3 573 267 (1968); Chem.Abs., 1971, **75**, 7121.
289. P.Tarrant, E.C.Stamp, and C.D.Padgett, Polymer Prepr.Amer.Chem.Soc.Div.Polymer Chem., 1971, **12**(1), 391; Chem.Abs., 1973, **78**, 31 051.
290. N.Mayes and R.A.Falk, US P.3 679 755 (1968); Chem. Abs., 1972, **77**, 141 180.
291. J.M.Kauffman, J.Green, M.S.Cohen, M.M.Fein, and E.L.Cottrill, J.Amer.Chem.Soc., 1964, **86**, 4210.
292. N.Mayes and J.Green, US P.3 393 104 (1965); Chem. Abs., 1968, **69**, 45 028.
293. N.Mayes and J.Green, US P.3 657 336 (1969); Chem. Abs., 1972, **77**, 4966.
294. Y.Kometani and M.Tatemoto, US P.3 654 245 (1968).
295. H.Ukihashi, T.Asawa, M.Yamabe, and H.Miyake, BRD P.2 638 791 (1975); Chem.Abs., 1977, **86**, 130 044.
296. M.Yamabe, H.Miyake, and K.Arai, Japan.Kokai 7 705 889 (1975); Chem.Abs., 1977, **86**, 140 933.
297. R.J.Jones, US P.3 761 453 (1972); Chem.Abs., 1974, **80**, 15 682.
298. R.A.Meyers and E.A.Burns, US P.3 759 868 (1970); Chem.Abs., 1974, **80**, 48 974.
299. R.E.Banks and R.N.Haszeldine, BRD P.2 304 650 (1972); Chem.Abs., 1974, **80**, 28 198.
300. R.E.Banks, R.N.Haszeldine, P.Mitra, T.Myerscough, and S.Smith, J.Macromol.Sci.Chem., 1974, **A8**, 1325.
301. K.Kidoh and N.Bannai, B.P.2 027 043 (1978); Chem. Abs., 1980, **93**, 80 094.
302. J.Green, N.B.Levine and R.C.Keller, Ind.Eng.Chem. Prod.Res.Develop., 1963, **2**, 126; Chem.Abs., 1963, **59**, 3709.
303. B.P.983 486 (1965); Chem.Abs., 1965, **62**, 11 932.
304. G.H.Crawford, US P.3 436 384 (1969); Chem.Abs., 1969, **70**, 107 017.