Polyfluoronitroalkanes can readily be prepared by the conjugated nitrofluorination of fluoro olefins [1]. Study of chemical properties of the compounds obtained has shown that the introduction of several fluorine atoms into a nitroalkane leads to a polyfluoronitroalkane which differs in reactivity from its non-fluorinated analog. Thus, for the acid hydrolysis of polyfluoronitroalkanes, leading to \( \alpha \)-fluoro carboxylic acids, more severe conditions are required [2]. Moreover, an alkoxymethylation reaction, unusual for nitroalkanes, has been observed for 1,1,1-trifluoronitroethane under the conditions of the Mannich reaction, leading to fluorine-containing nitro ethers [3].

It was found that 1,1,1-trifluoronitroethane undergoes the analogous reaction (alkylthio) methylation in presence of 1-butanethiol, a secondary amine hydrochloride, and paraform with formation of butyl 3,3,3-trifluoro-2-nitropropyl sulfide [1]:

\[
\text{CF}_3\text{CH}_2\text{NO}_2 + \text{CH}_2\text{O} + (\text{C}_2\text{H}_5)_2\text{NH} \cdot \text{HCl} \overset{\text{CH}_{3}\text{SH}}{\longrightarrow} \text{CF}_3\text{CH}(\text{NO}_2)\text{CH}_2\text{SC}_4\text{H}_9
\]

Difference in reactivity between polyfluoronitroalkanes and the usual nitro compounds was observed by us in a number of other cases. For example, the chlorination or bromination of the sodium salt of 1,1,1-trifluoronitroethane in sodium hydroxide solution leads exclusively to 1,1,1-trifluoro-2,2-dihalo-2-nitroethanes:

\[
\text{CF}_3\text{CH}_2\text{NO}_2 + \text{X}_2 \rightarrow \text{CF}_3\text{CX}_2\text{NO}_2
\]

The halogenation of the usual nitroalkanes under these conditions leads only to \( \alpha \)-monohalo nitro compounds [4]. The formation of \( \alpha \), \( \alpha \)-dihalo nitro compounds in the halogenation of 1,1,1-trifluoronitroethane is probably to be explained on the view that the sodium salt of 1,1,1-trifluoronitroethane and the immediately formed \( \alpha \)-monohalo nitro compound disproportionate at a much greater rate than their nonfluorinated analogs:

\[
\text{CF}_3 - \text{CH} = \text{NOONa} + \text{X}_2 \rightarrow \text{CF}_3 - \text{CHX} - \text{NO}_2 + \text{NaX}
\]

\[
\text{CF}_3 - \text{CH} = \text{NOONa} + \text{CF}_3 - \text{CHX} - \text{NO}_2 \rightarrow \text{CF}_3 - \text{CH}_2 - \text{NO}_2 + \text{CF}_3 - \text{CX} = \text{NOONa}
\]

\[
\text{CF}_3 - \text{CX} = \text{NOONa} + \text{X}_2 \rightarrow \text{CF}_3 - \text{CX}_2 - \text{NO}_2 + \text{NaX}
\]

It was shown by gas-liquid chromatography that after the halogenation of the sodium salt of 1,1,1-trifluoronitroethane the reaction mixture contains only 1,1,1-trifluoronitroethane and the 1,1,1-trifluorodihalo-2-nitroethane. The formation of the \( \alpha \)-monohalo nitro compound was not detected. The yields of 1,1-dibromo- and 1,1-dichloro-2,2,2-trifluoro-1-nitroethanes for molar proportions of trifluoronitroethane, alkali, and bromine or chlorine of 1:1:1 were about 80% on the amount of trifluoronitroethane that reacted. Since the separation of the products by fractionation is difficult, it is desirable to carry out the halogenation with excess of alkali and halogen.
The difference in reactivity between polyfluoronitroalkanes and the usual nitro compounds is also shown up clearly in Nef's reaction. It is known that the direct Nef reaction cannot be brought about with 1,1,1-trifluoro-3-nitropropane [5, 6]. We found that 1,1,1-trifluoronitroethane also does not form the corresponding trifluoroacetaldehyde under the usual conditions for this reaction (0°C and the action of 10% H2SO4). It is interesting that even under the action of 30% H2SO4 at 40°C only the regeneration of trifluoronitroethane from its sodium salts occurs. On the other hand, the regeneration of the usual nitro compounds from their salts occurs only under very mild conditions (action of weak acids -CO2, HONH2·HCl, and others at between -10 and 0°C). We succeeded in obtaining trifluoroacetaldehyde by the direct Nef reaction by adding a 1N aqueous solution of the sodium salt of 1,1,1-trifluoronitroethane to excess of 80% H2SO4 at 95-100°C. The necessity for more severe conditions to bring about Nef reaction as also the acid hydrolysis of trifluoronitroethane [2], is explained by the fact that the aci form of trifluoronitroethane, which is the intermediate form in these reactions, is a stronger acid than its nonfluorinated analogs. The dissociation of this stronger acid as a base is naturally more difficult:

\[
\begin{align*}
\text{CF}_3\text{CH} &= \text{NOONa}^+ \quad &\text{CF}_3\text{CH} &= \text{NOOH} \quad &\text{CF}_3\text{CH} &= \text{N} = \text{O}^+ \\
& \text{H}_2\text{O}^- \quad &[\text{CF}_3\text{CH} &= \text{N} = \text{O}]^- \quad &\text{HNO} \quad &\text{CF}_3\text{CHO} \\
& \text{OH} \\
& \text{OH} \\
& \text{CF}_3\text{C} &= \text{NOH} \quad &\text{H}_2\text{O} \quad &\text{CF}_3\text{COOH}
\end{align*}
\]

It must be mentioned that in the reaction of the sodium salt of trifluoronitroethane with sulfuric acid not only trifluoroacetaldehyde is formed, but also trifluoroacetic acid, i.e., acid hydrolysis occurs simultaneously. Further rise in reaction temperature and in sulfuric acid concentration leads, as would be expected, to the predominance of acid hydrolysis, and at 140°C with 95% H2SO4 the only reaction product is trifluoroacetic acid.

The basic dissociation of the aci forms of nitro compounds in presence of strong acids also occurs in a number of other cases. Thus, through the intermediate formation of the cation (II) it is possible to explain the formation of 1-chlorotetrafluoro-1-nitrosoethane when 1,1,1,2-tetrafluoronitroethane is heated with concentrated hydrochloric acid:

\[
\begin{align*}
\text{CF}_3\text{CFH} &= \text{NO}_2 \quad &\text{CF}_3\text{CF} &= \text{NOOH} \quad &\text{CF}_3\text{CF} &= \text{N} = \text{O}^+ \\
& \text{Cl}^- \\
& \text{Cl}^- \\
& \text{Cl}^- \\
& \text{Cl}^- \\
\end{align*}
\]

The reaction of 1,1,1,2-tetrafluoronitroethane with concentrated hydrochloric acid requires a temperature of 100°C, but at this temperature the nitrosoalkane formed decomposes rapidly and the yield is only 30-40%. In presence of alcohol the reaction goes already at 70°C and the yield of 1-chlorotetrafluoro-1-nitrosoethane attains 90%.

The above scheme for the reaction of 1,1,1,2-tetrafluoronitroethane with hydrochloric acid is analogous to the scheme proposed earlier for the formation of chlorodifluoronitrosomethane when a mixture of difluoronitroacetic and hydrochloric acids is heated [7]. However, we were unable to obtain difluoronitrosomethane by the direct reaction of difluoronitromethane even when the mixture was heated to 150°C. In an analogous way the α-chloro nitroso compound was not formed in the action of hydrochloric acid on 2H-hexafluoro-2-nitropropane. Neither were we able to prepare the corresponding α-halo nitroso compound by the action of hydrogen bromide and hydrogen fluoride on 1,1,1,2-tetrafluoronitroethane.

We also studied the oxidation of polyfluoronitroalkanes. In the oxidation of 1,1,1-trifluoronitroethane with permanganate under mild conditions (neutral medium at 0°C), trifluoroacetaldehyde hydrate was formed in 40% yield together with trifluoroacetic acid:

\[
\begin{align*}
\text{CF}_3\text{CH} &= \text{NO}_2 \quad &\text{CF}_3\text{CHO} \quad &\text{H}_2\text{O} \quad &\text{CF}_3\text{COOH}
\end{align*}
\]

Under more severe conditions (acid medium, 30°C) 1,1,1-trifluoronitroethane, as also 1,1,1,2-tetrafluoronitroethane, is oxidized by permanganate to trifluoroacetic acid.