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Abstract

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OXIDATION, REDUCTION, AND DISPROPORTIONATION REACTIONS OF POLYFLUORONITROSOALKANES

(Presented by Academicians I. L. Knunyants and M. I. Kabachnik, June 1, 1961)

Whereas the chemistry of aromatic nitroso compounds has been studied in considerable detail, nitrosoalkanes still remain little investigated, although in recent years a number of works have appeared devoted to methods of synthesis and to the study of certain properties of polyfluoronitrosoalkanes ($^{1-4}$). Methods for the synthesis of polyfluoronitrosoalkanes from polyfluoroolefins and nitrogen oxides, or from nitrogen oxide and halides in ultraviolet light (^{5,6}), appear to be the most accessible and have enabled us to obtain various nitroso compounds with functional groups in quantities sufficient for their detailed investigation.

Below are presented the results of a study of the polyfluorinated nitrosoalkanes synthesized by us with respect to oxidizing and reducing agents. The indicated transformations were also studied using the simplest polyfluoronitrosoalkane—trifluoronitrosomethane—as an example.

Possessing strongly pronounced electrophilic properties, polyfluorinated aliphatic nitroso compounds proved to be rather resistant to the action of acidic oxidizing agents (nitric, permanganic, and chromic acids, halides). At 150-200° Hopcalite oxidizes nitroso compounds to the corresponding polyfluoronitroalkanes:

$$R_{\mathrm{fNO}} \xrightarrow{\mathrm{MnO_2}} R_{\mathrm{fNO}}2.$$

In aqueous alkaline media trifluoronitrosomethane is slowly converted into trifluoronitromethane and hexafluoroazoxymethane:

$$3CF_3NO \to CF_3NO_2 + CF_3N_2(O)CF_3.$$

The action of aqueous alkali solutions on trifluoronitrosomethane was first described by Ruff and Giese, who erroneously assumed that trifluoronitrosomethane is isomerized in this process to difluorocarbaminoyl fluoride (^{7}). In practice, the indicated compounds are formed not in the molar ratio represented in the scheme, but with predominance of the nitro product. Thus, at room temperature with a 10% aqueous NaOH solution, the molar ratio of the products formed, $CF_3N_2(O)CF_3/CF_3NO_2$, is ~ 0.6. In the presence of oxidizing agents the yield of trifluoronitromethane increases; in the case of the use of a 10% aqueous solution of sodium hypochlorite, trifluoronitromethane is formed in more than 90% yield based on trifluoronitrosomethane. Conversely, the addition of reducing agents to the alkaline solution changes the ratio of the resulting azoxy and nitro derivatives toward an increase in the yield of hexafluoroazoxymethane. Thus, in a 10% aqueous solution of sodium hydroxide containing 10–12% sodium hypophosphite, the conversion of trifluoronitrosomethane into hexafluoroazoxymethane reaches 90%.

Haszeldine, considering the disproportionation reaction of trifluoronitrosomethane under the action of aqueous alkalis, suggests that trifluoromethylhydroxylamine is formed as an intermediate in this process ([8]).

This scheme is unconvincing, since trifluoromethylhydroxylamine is completely mineralized in alkaline media (see below).

The oxidation-reduction disproportionation of trifluoronitrosomethane may be represented, for example, by the scheme:

$$CF_3N^{(+)}{=}O^{(-)} + OH^{(-)} \rightarrow$$

$$\rightarrow \left[CF_3N\left(\frac{O^{(-)}}{OH}\right) \quad CF_3N\left(\frac{O^{(-)}}{OH}\right) \xrightarrow{CF_3N^{(+)}{=}O^{(-)}} CF_3N\left(\frac{O\cdot N(CF_3)O^{(-)}}{OH}\right)\right] \rightarrow$$

$$\rightarrow CF_3NO_2 + [CF_3N^{(-)}{-}OH]$$

$$\left[CF_3N^{(-)}{-}OH + CF_3N^{(+)}{=}O^{(-)} \rightarrow CF_3N(OH){-}N\left(\frac{O^{(-)}}{CF_3}\right)\right] \rightarrow$$

$$\rightarrow CF_3N{=}N\left(\frac{O}{CF_3}\right) + OH^{(-)}.$$

This scheme is consistent with the behavior of trifluoronitrosomethane toward nucleophilic reagents in nonaqueous media. Thus, this nitroso compound readily combines with triethyl phosphite or trimethylamine, forming at low temperatures in ether (−70°) complexes of composition 1 : 1 (in moles), which, under the action of an excess of trifluoronitrosomethane, liberate hexafluoroazoxymethane:

$$CF_3NO + \ddot{P}(OC_2H_5)_3 \rightarrow CF_3N{=}O \xrightarrow[\uparrow\ddot{P}(OC_2H_5)_3]{CF_3NO} CF_3N_2(O)CF_3 + OP(OC_2H_5)_3,$$

$$\mathrm{CF_3NO} + \mathrm{\ddot{N}(CH_3)_3} \to \mathrm{CF_3N{=}O} \xrightarrow[\uparrow \mathrm{\ddot{N}(CH_3)_3}]{\mathrm{CF_3NO}} \mathrm{CF_3N_2(O)CF_3} + [\mathrm{(CH_3)_2NH}] + \mathrm{CH_2O}.$$

These transformations resemble the known reaction of phosphinomethylenes and phosphinimides with oxidizing agents. Indeed, trifluoronitrosomethane, on interaction with the latter, forms the corresponding polyfluoroazo compounds:

$$\mathrm{(C_6H_5)_3P{=}NR} + \mathrm{CF_3NO} \to \mathrm{(C_6H_5)_3P{=}O} + \mathrm{CF_3N{=}NR},$$

where $R = \mathrm{CH_3}, \mathrm{C_6H_5}$ (see Table 1, Nos. 11, 12).

In aqueous alkaline solutions, polyfluoronitrosoalkanes decompose somewhat differently:

$$\mathrm{ClCF_2CF_2NO} \xrightarrow{\mathrm{OH}^{(-)}} \left[\mathrm{ClCF_2CF_2N}\left(\frac{\mathrm{O}^{(-)}}{\mathrm{OH}}\right) \xrightarrow{-\mathrm{F}^{(-)}} \mathrm{ClCF_2CF{=}N}\left(\frac{\mathrm{O}}{\mathrm{OH}}\right)\right] \to \mathrm{ClCF_2COOH} + [\mathrm{HNO}].$$

In reduction reactions under the action of hydrides of sulfur or phosphorus, and also hydrogen iodide in an ether or methanol medium, trifluoronitrosomethane behaves analogously to other nitroso compounds. Thus, when hydrogen iodide acts on trifluoronitrosomethane in ether, *N*-trifluoromethylhydroxylamine, comparatively stable as an etherate, is smoothly formed:

$$\mathrm{CF_3NO} + 2\mathrm{HJ} \xrightarrow{\mathrm{(C_2H_5)_2O}} \mathrm{CF_3NHOH} \cdot \mathrm{O(C_2H_5)_2} + \mathrm{J_2}.$$

When hydrogen sulfide or phosphine is used as the reducing agent in an ether medium, it is possible to isolate the primary reaction product—an unstable adduct of the hydride and the nitroso compound—which, in an excess of reducing agent, decomposes according to the scheme:

$$\mathrm{CF_3NO} + \mathrm{C_2H_5SH} \to \mathrm{CF_3N(OH)SC_2H_5} \xrightarrow{\mathrm{C_2H_5SH}} \mathrm{CF_3NHOH} + \mathrm{(C_2H_5S)_2}.$$

Table 1

No.	Compound	B.p., °C/mm	d_{20}^{20}	n_D^{20}	Found, % C	Found, % H	Found, % N	Found, % F	Found, % Cl	Found, % Br	Calculated, % C	Calculated, % H	Calculated, % N	Calculated, % F	Calculated, % Cl	Calculated, % Br
1	CF$_3$(N$_2$O)CF$_2$CF$_2$NO$_2$ *	75	1,4220	—	14,03 14,27	—	15,20 15,23	50,73 50,25	—	—	13,9	—	16,2	51,4	—	—
2	CF$_3$(N$_2$O)CF$_2$CF$_2$Cl *	61—62	1,540	1,3370	14,95 15,17	—	11,29	51,35 52,36	14,57	—	14,5	—	11,2	53,7	14,3	—
3	CF$_3$(N$_2$O)CF$_2$CF$_2$Br *	74	1,722	1,3382	12,62 13,39	—	10,11 10,03	44,60 44,19	—	26,92 27,10	12,2	—	9,6	45,4	—	27,3
4	CF$_3$N(O)=NCH$_3$	15/150	1,3049	—	17,43	2,17 1,70	—	44,75 44,15	—	—	18,7	1,2	—	44,5	—	—
5	CF$_3$N(O)NC$_2$H$_5$	53—54	1,18	—	23,69 23,94	3,51	18,84 18,45	39,15 39,78	—	—	23,9	3,5	19,7	40,0	—	—
6	CF$_3$N(O)NC$_3$H$_7$ (iso)	60—62	1,145	—	30,36 30,54	4,13	17,73	36,20 36,42	—	—	30,8	4,5	18,0	36,5	—	—
7	CF$_3$N(O)NC$_6$H$_5$	63/5	1,345	1,4830	48,50 48,93	2,93	14,93 14,32	28,92 29,07	—	—	49,5	2,64	14,7	30,0	—	—
8	CF$_3$NHOH(C$_2$H$_5$)$_2$O **	5—7/5	—	—	34,54	6,76 6,60	7,96	32,07 32,19	—	—	34,0	6,8	8,0	32,6	—	—
9	CF$_3$N(CH$_3$)OCH$_3$	8—10/2	1,022	1,3445	42,00	8,26 8,18	7,09 6,89	28,59 29,45	—	—	41,5	7,9	6,9	28,0	—	—
10	CF$_3$N(OH)CONHC$_6$H$_5$	m.p. 146	—	—	44,19 43,74	2,90 3,02	12,76 12,60	25,70 25,25	—	—	43,5	3,10	12,6	25,9	—	—
11	CF$_3$N=NCH$_3$	3,5	—	—	21,78	3,42	25,7	50,20 50,51	—	—	21,4	2,68	25,0	50,4	—	—
12	CF$_3$N=NC$_6$H$_5$	41/7	1,2522	1,4660	48,05	2,91	16,79	31,59	—	—	48,20	2,88	16,10	32,40	—	—

* The position of the oxygen atom in the azoxy group was not established.
** The substance reacts with glass.

The reduction of α-H-polyfluoronitrosoethane, ClCF$_2$CFHNO, proceeds similarly.

As indicated earlier [5,6], in the case of α,α-dihalogenonitroso compounds $R_{fCX}2NO$ (where $X = F, Cl$), the hydroxylamine derivatives formed are unstable and, on decomposing, are converted into acid fluorides of the corresponding hydroxamic acids:

$$R_{fCX}2NO \xrightarrow{\text{HJ}} [R_{fCX}2NHOH] \xrightarrow{-HX} R_{fCX} = NOH.$$

N-Trifluoromethylhydroxylamine is one of the few known compounds containing the CF_3NH grouping. This compound is thermally unstable and decomposes, giving trifluoronitrosomethane and hydroxylamine fluoride in low yield.

Diazomethane methylates *N*-trifluoromethylhydroxylamine with formation of *N*-trifluoromethyl-*N,O*-dimethylhydroxylamine. Phenyl isocyanate also gives the corresponding derivative (Table 1, Nos. 9, 10).

The reaction of trifluoromethylhydroxylamine with nitroso compounds proved to be of interest; it leads to previously little-known polyfluorinated azoxy compounds:

$$R_{fNO} + CF_3NHOH \rightarrow R_{fN}2(O)CF_3 + H_2O.$$

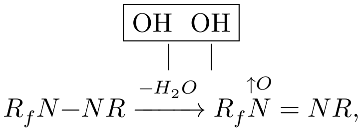
Along with the principal direction of this reaction described above, oxidative-reductive disproportionation is observed, leading to the formation of trifluoronitrosomethane and acid fluorides of the corresponding hydroxamic acids:

$$R_{fCF}2NO + CF_3NHOH \rightarrow CF_3NO + [R_{fCF}2NHOH] \rightarrow R_{fCF} = NOH.$$

In the reaction of polyfluorinated nitroso compounds with fluorine-free *N*-alkyl-(aryl)-hydroxylamines, the corresponding polyfluoroazoxy compounds are formed analogously:

$$R_{fNO} + RNHOH \rightarrow R_f\overset{\downarrow O}{N} = NR.$$

Investigation of the structure of the substances obtained by IR and mass spectrometry showed that the elimination of the elements of water from the primary product of interaction of the nitroso compound and hydroxylamine proceeds according to the scheme



$$\overset{\boxed{\text{OH}\ \ \text{OH}}}{\overset{|\quad\ |}{R_fN{-}NR}} \xrightarrow{-H_2O} R_f\overset{\uparrow O}{N} = NR,$$

which illustrates the great ease of proton abstraction from the hydroxyl adjacent to the electrophilic R_f-group. The constants of the compounds synthesized for the first time are presented in Table 1.

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Note: Figure translations are in progress. See original paper for figures.