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Abstract

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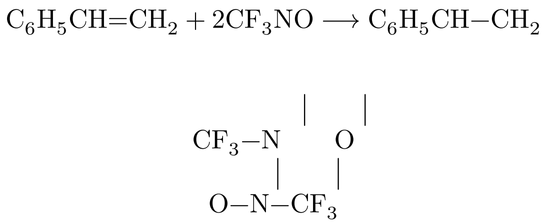
REACTIONS OF POLYFLUORINATED NITROSOALKANES WITH UNSATURATED COMPOUNDS

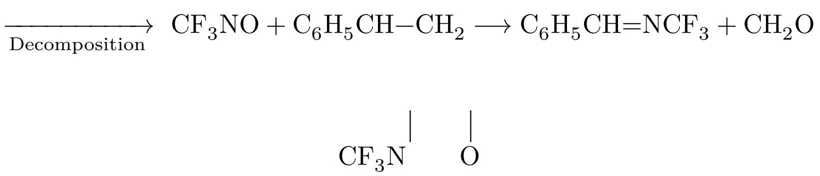
(Presented by Academician M. I. Kabachnik, June 1, 1961)

Several years ago, using difluorochloroethylene and the nitroso compound formed from it in reaction with nitrosyl chloride as examples, we first noted that polyfluorinated nitrosoalkanes readily add polyfluoroolefins, forming high polymers (^{1}). Later, analogous transformations for perfluoronitrosoalkanes and polyfluoroolefins were described in a number of papers ($^{2-7}$). The behavior of polyfluoronitrosoalkanes toward other types of unsaturated compounds had remained unstudied. In the present work, some such reactions are described using the simplest perfluorinated nitrosoalkane—trifluoronitrosomethane—as an example.

It turned out that the addition of trifluoronitrosomethane to olefins proceeds readily (in an autoclave at −70-0°C), including with derivatives not containing fluorine, such as methyl acrylate, methacrylate, and vinyl acetate, giving monomeric and polymeric products of composition 1 mole of nitroso compound per 1 mole of olefin. Styrene with trifluoronitrosomethane forms two types of products, with molar compositions styrene—nitroso compound of 1 : 1 and 1 : 2. The latter substance, upon heating to 70-80°, readily decomposes with liberation of 1 mole of nitroso compound, formaldehyde, and the corresponding imine, which illustrates the structure of the adduct (cf. the reaction of nitrosobenzene with styrene (^{8})):



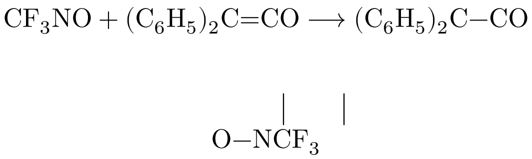
$$C_6H_5CH{=}CH_2 + 2CF_3NO \longrightarrow \begin{array}{c} C_6H_5CH{-}CH_2 \\ CF_3{-}N \quad O \\ O{-}N{-}CF_3 \end{array}$$



$$\xrightarrow[\text{Decomposition}]{} CF_3NO + C_6H_5CH{-}CH_2 \longrightarrow C_6H_5CH{=}NCF_3 + CH_2O$$

$$\begin{matrix} & | & | \\ CF_3N & & O \end{matrix}$$

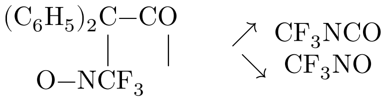
With still greater ease, trifluoronitrosomethane adds to diphenylketene (when the nitroso compound is passed into ketene under ordinary conditions), giving a cyclic derivative:



$$CF_3NO + (C_6H_5)_2C{=}CO \longrightarrow (C_6H_5)_2C{-}CO$$

$$\begin{matrix} | & | \\ O{-}NCF_3 & \end{matrix}$$

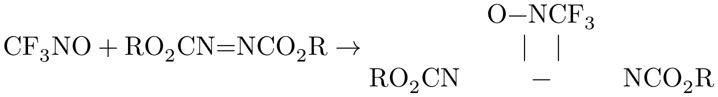
This latter compound decomposes upon heating to 300°, forming mainly trifluoromethyl isocyanate (b.p. 33°, yield 35%) and traces of trifluoronitrosomethane, which proves the structure of the adduct.



$$\begin{matrix} (C_6H_5)_2C{-}CO \\ |\quad\ | \\ O{-}NCF_3 \end{matrix} \quad \begin{matrix} \nearrow CF_3NCO \\ \searrow CF_3NO \end{matrix}$$

Like olefins, certain acetylenic compounds also enter into reaction with trifluoronitrosomethane (interaction at room temperature in an autoclave), of the type $R_FC{\equiv}CX$, where $X = Cl, Br$; $R_F = CF_3,\ CF_2Cl,\ CFCl_2$.

Upon heating trifluoronitrosomethane to 100-150° under pressure with azodicarboxylic esters, an addition reaction is also observed, leading to the formation of the corresponding four-membered ring:



$$CF_3NO + RO_2CN{=}NCO_2R \rightarrow \begin{matrix} & O{-}NCF_3 & \\ & |\quad | & \\ RO_2CN & - & NCO_2R \end{matrix}$$

In the interaction of trifluoronitrosomethane with diazoaliphatic compounds in ether at −70°, the addition reaction is accompanied by simultaneous elimination of molecular nitrogen and formation of a polymeric nitrone:

$$CF_3NO + CH_2N_2 \rightarrow [CF_3N(O)N_2CH_2] \xrightarrow{-N_2} [CF_3N(O)CH_2]_n$$

Trifluoronitrosomethane also reacts vigorously with phosphazines. Thus, on interaction (−70°) of trifluoronitrosomethane with the addition product of diazomethane to triphenylphosphine, an apparently unstable organophosphorus triazene is formed, which decomposes with liberation of nitrogen, being converted into the corresponding triphenylphosphinimine.

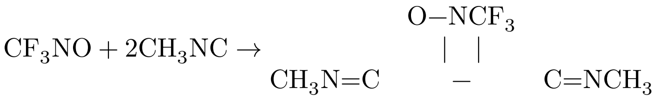
$$(C_6H_5)_3P{=}N{-}N{=}CH_2 + CF_3NO \rightarrow CH_2O + [(C_6H_5)_3P{=}N{-}N{=}NCF_3] \rightarrow$$

$$\xrightarrow{-N_2} (C_6H_5)_3P{=}NCF_3$$

This compound is also formed on interaction of triphenylphosphine with trifluoromethyl azide under the same conditions.

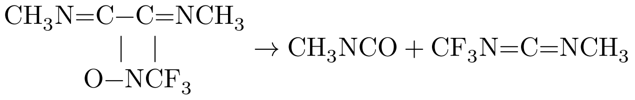
$$(C_6H_5)_3P + CF_3N_3 \rightarrow [(C_6H_5)_3PN_3CF_3] \xrightarrow{-N_2} CF_3N{=}P(C_6H_5)_3$$

The interaction of trifluoronitrosomethane with alkylcarbylamines proved to be of interest. Thus, on heating the nitroso compound with methylcarbylamine in an autoclave to +25°, as a result of a vigorously proceeding reaction, a compound is formed, apparently of cyclic structure:



$$CF_3NO + 2CH_3NC \rightarrow \begin{array}{c} O{-}NCF_3 \\ |\quad| \\ CH_3N{=}C \quad - \quad C{=}NCH_3 \end{array}$$

On thermal decomposition of the latter in vacuum at 350-400°, polyfluorinated dimethylcarbodiimide and methyl isocyanate are formed:



$$\begin{array}{c} CH_3N{=}C{-}C{=}NCH_3 \\ |\quad| \\ O{-}NCF_3 \end{array} \rightarrow CH_3NCO + CF_3N{=}C{=}NCH_3$$

The transformations of trifluoronitrosomethane with unsaturated compounds that have been investigated indicate a great tendency of the N=O group toward numerous addition reactions with both nucleophilic and electrophilic compounds. In this connection it was of interest to compare, within a series of polyfluorinated compounds, such genetically close unsaturated groupings as N=O, N=N (see (10)) and N=C.

For this purpose, some addition reactions analogous to those described above were examined for polyfluorinated azomethines $CF_3N{=}CF_2$ (b.p. −33°), $CF_3N{=}CFCl$ (b.p. −5°), obtained on pyrolysis of the addition products of trifluoronitrosomethane to tetrafluoro- and trifluorochloroethylene (the boiling points of the corresponding oxazetidines are −7° and +30°), and also difluoroformimine (9).

In all the listed polyfluorocarbylamine fluorides, the capacity of the C=N group for addition of the indicated unsaturated compounds proved to be considerably suppressed. In the reaction of trifluoromethylcarbylamine fluoride with diphenylketene (in an autoclave at 180° for 12 h), instead of the addition product, a dimer of the starting carbylamine fluoride of the structure $CF_3N{=}CFN(CF_3)_2$ was isolated (cf. (11)). This product is formed in almost quantitative yield on interaction, in the cold (−70-50°), of trifluoromethylcarbylamine fluoride with pyridine. In the reaction with aniline, this subst–

Table 1

Newly synthesized compounds

No.	Compound	bp (mp), °C/mm	d_{20}^{20}	n_D^{20}	Found C, %	Found H, %	Found N, %	Found F, %	Found Cl(Br), %	Found OCH₃, %	Calculated C, %	Calculated H, %	Calculated N, %	Calculated F, %	Calculated Cl(Br), %	Calculated OCH₃, %
1	$CF_3NO \cdot CH_2{=}C(CH_3)COOCH_3$	59/5	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	28.65	–	15.47	36.39	4.03	7.10	28.6	–	15.6
2	$2CF_3NO \cdot C_6H_5CH{=}CH_2$	mp 71			[illegible]	[illegible]	[illegible]	39.44 39.25	–		40.0	2.65	4.65	38.00	–	–
3	$CF_3NO \cdot C_6H_5CH{=}CH_2$ *	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	–	–	53.5	3.95	6.90	28.0	–	–
4	[illegible]	37/2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Cl13.89	–	[illegible]	–	6.10	50.00	Cl15.60	–
5	[illegible]	48/2	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	–	[illegible]	–	5.17	41.90	Br29.40	–
6	[illegible]	50/2	[illegible]	[illegible]	–		6.15	42.00	–	–	–	–	5.75	39.00	–	–
7	[illegible]	57/2	[illegible]	[illegible]	–		5.27	[illegible]	–	–	–	–	5.36	29.10	–	–
8	[illegible]	60/3	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	21.09	–		30.76	3.65	15.40	20.87	–	–
9	$[CF_3N(O)CH_2]_5$ **	mp 95			21.80	1.77	11.10	48.50	–	–	21.20	1.77	12.40	50.3	–	–
10	$(C_6H_5)_3P = NCF_3$	mp 162			–	–	[illegible]	16.53	–	–	–	–	4.05	16.52	–	–
11	[illegible]	52 – 54/44	[illegible]	[illegible]	33.81	[illegible]	[illegible]	31.49	–		33.14	3.32	23.10	31.40	–	–
12	[illegible]	79	[illegible]	[illegible]	29.12	[illegible]	[illegible]	45.23	–		29.06	2.40	22.51	46.00	–	–
13	$CF_3N = CFN(CF_3)_2$	37	[illegible]	[illegible]	18.79	–	9.30	[illegible]	–		18.00	–	10.50	71.50	–	–
14	[illegible]	30	[illegible]	1.556	–	–	8.57	[illegible]	[illegible]		–		8.30	56.00	Cl21.0	–
15	[illegible]	45	1.469	[illegible]	[illegible]	–	[illegible]	[illegible]	[illegible]		[illegible]	–	8.50	34.40	Cl42.80	–

* Non-distillable yellow oil.

** Molecular weight (in acetic acid): found 580; calculated for the pentamer 565.

···is converted into an anilide identical with the anilide of the monomer; on pyrolysis, the dimer $C_4N_2F_{10}$ dissociates into the monomeric compound:

$$2CF_3N{=}CF_2 \rightarrow CF_3N{=}CFN(CF_3)_2 \begin{cases} \xrightarrow{>500^\circ} 2CF_3N{=}CF_2 \\ \xrightarrow{C_6H_5NH_2} 2C_6H_5NHNHC(NHC_6H_5)_3 \end{cases}$$

Unlike polyfluorocarbylamine fluorides, difluoroformimine $CF_2{=}NH$ readily adds to diphenylketene, forming the adduct $(C_6H_5)_2CCO \cdot 2CF_2NH$. At the same time, addition reactions of hydrogen fluoride and hydrogen chloride and of mercuric fluoride according to the scheme proved very characteristic for the polyfluorinated azomethines studied, as has already been reported in part ([2,3,12])

$$CF_3N{=}CF_2 \begin{cases} \xrightarrow{HF} (CF_3)_2NH \\ \xrightarrow{HCl} (CF_3)CF_2ClNH \\ \xrightarrow{HgF_2} [(CF_3)_2N]_2Hg \begin{cases} \xrightarrow{ClNO} (CF_3)_2NNO \text{ (b.p. } -3^\circ) \\ \xrightarrow{ClNO_2} (CF_3)_2NNO_2 \text{ (b.p. } +17^\circ) \end{cases} \end{cases}$$

Thus, in polyfluorinated substances with multiple bonds, the ease of addition reactions to olefins decreases in the series:

$$N{=}O > N{=}N > N{=}C.$$

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