Reports of the Academy of Sciences of the USSR

V. A. GINSBURG, A. Ya. YAKUBOVICH, A. S. FILATOV, G. E. ZELENIN,

1962

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1962, Volume 142, No. 2

CHEMISTRY

V. A. GINSBURG, A. Ya. YAKUBOVICH, A. S. FILATOV, G. E. ZELENIN,
S. P. MAKAROV, V. A. SHPANSKY, G. P. KOTELNIKOVA,
L. F. SERGIENKO, and L. L. MARTYNOVA

HETEROLYTIC TRANSFORMATIONS OF POLYFLUORINATED AZOALKANES

(Presented by Academicians I. L. Knunyants and M. I. Kabachnik on 1 VI 1961)

Previously only homolytic reactions of decomposition and addition of polyfluorinated azoalkanes were known ([1]). In the present work, a series of their heterolytic transformations has been shown for the first time. Polyfluorinated azoalkanes are extremely resistant to the action of oxidizing agents (halogens, hydrogen peroxide, percarbonic acids, hypochlorites). Reducing agents such as HI, H_2S, H_3P, in polar media (ether, methanol) readily react in the cold with the azo compounds studied, converting the azo group into a hydrazo group:

$$CF_3N{=}NCF_3 \rightarrow CF_3NHNHCF_3$$

Hexafluorohydrazomethane has distinctly acidic properties and, like bis(trifluoromethyl)amine, is comparatively stable in the form of solvates (etherate, acetone solvate). When ketene acts on hexafluorohydrazomethane etherate, a normal diacyl derivative is formed. At the same time, the CF_3NH groups in hexafluorohydrazomethane are capable of readily eliminating hydrogen fluoride under the action of bases and alkalis:

$$CF_3NHNHCF_3 \xrightarrow[C_6H_5SH]{C_6H_5NH_2} \begin{matrix}(C_6H_5NH)_2C{=}N{-}N{=}C(NHC_6H_5)_2\\(C_6H_5S)_2C{=}N{-}N{=}C(SC_6H_5)_2\end{matrix}$$

Aluminum trichloride converts hexafluorohydrazomethane into a dimer of tetrafluoroformazine, according to the scheme:

$$CF_3NHNHCF_3 \xrightarrow{AlCl_3} [CF_2ClNHNHCF_2Cl] \xrightarrow{-2HCl} (CF_2N_2CF_2)_2$$

On oxidation of hexafluorohydrazomethane an azo compound is formed; in non-aqueous media ($KMnO_4 + CH_3COOH$) an intensely yellow cis form of hexafluoroazomethane is formed ($\lambda_{max} = 405$ mμ), which readily passes, in light or under the action of alkalis or metals, into the usual almost colorless trans form ($\lambda_{max} = 355$ mμ).

As indicated earlier ([2]), the groups CF_2ClNH or $R_{fCF}2NH$ are considerably less stable than CF_3NH; therefore, on reduction of azoalkanes containing the groups CF_2Cl and $R_{fCF}2$, the corresponding hydrazo compounds are not isolated, but products of their hydrolysis are formed:

$$R_{fCF}2N{=}NR \xrightarrow[H_2O]{HI} R_{fCOOH} + H_2NNHR$$

The hydrazo compound $CF_3NHNHC_6H_5$ can be distilled in vacuo (b.p. 56°/1). On reaction with hydrogen iodide it is converted into indazole:

$$CF_3N{=}N{-} \xrightarrow{HI} [CF_3NHNH{-}\,] \rightarrow CF_2{=}N{-}NH{-} \rightarrow$$

$$\rightarrow [\text{indazole intermediate with NH, N, CF}] \xrightarrow{HI} \text{indazole with NH, N, CH}$$

The action of strong acids on polyfluorinated azoalkanes was previously studied using hexafluoroazomethane as an example by Ruff (3), who established that, upon prolonged heating with hydrochloric acid, this azo compound is unchanged. We have studied the reactions of polyfluoroazoalkanes with acids in greater detail. As it turned out, unsymmetrical azoalkanes are hydrolyzed rather readily by aqueous mineral acids according to the scheme:

$$CF_3N{=}NCH_2R \xrightarrow{H^+} [CF_3NHN^+CH_2R] \xrightarrow{OH^-} CF_3NHN{=}CHR \xrightarrow{H_2O}$$

$$\longrightarrow 3HF + CO_2 + NH_2NH_2 + OCHR$$

Trifluoromethylazobenzene in hot hydrochloric acid undergoes conversion into *p*-chlorophenylhydrazine:

$$CF_3N{=}N \xrightarrow{H^+} [CF_3NHN^+\,] \longrightarrow CF_3NHN{=} + \longrightarrow$$

$$Cl^- \longrightarrow CF_3NHNH\ Cl \longrightarrow CO_2 + 3HF + H_2NNH\ Cl$$

These reactions indicate that in strongly acidic media the azo group of polyfluoroazoalkanes is capable of adding a proton directed toward the nitrogen atom adjacent to the electronegative R_f-group. These reactions proceed especially readily in anhydrous hydrogen fluoride; under these conditions polyfluoroazoalkanes dimerize to benzidine derivatives:

$$CF_3N{=}N \xrightarrow{H^+} [CF_3NHN{=}\,] + CF_3N{=}N \longrightarrow$$

$$\longrightarrow [CF_3NHNH - N{=}NCF_3] + H^+ \rightleftharpoons$$

$$\rightleftharpoons CF_3N{=}N - N{=}NCF_3 + [CF_3NHNH\,] \longrightarrow \text{decomposition}$$

Polyfluorinated azo compounds are especially sensitive to the action of nucleophilic reagents (alkalis, amines, compounds of divalent and tetravalent sulfur, phosphines, etc.). In reactions with amines, the rates of interaction of azo compounds increase with increasing basicity of the amine (in the series of azo compounds $CF_3N{=}NR$, the tendency toward reactions with amines decreases correspondingly as $R{=}CF_3 > CF_2H > CH_3$). The most electrophilic of the polyfluorinated azoalkanes studied proved to be hexafluoroazomethane. In reactions with amines containing an NH group, mercaptans, and sulfinic acids, azo compounds behave similarly to azodicarboxylic esters, but they are less active. The primary addition products formed undergo further transformations at the expense of the CF_3NH group. These transformations are represented by the schemes:

$$CF_3N{=}NCF_3 \begin{cases} \xrightarrow{HNR_2} [CF_3NHN(CF_3)NR_2] \xrightarrow{HNR_2} (R_2N)_2C{=}N{-}N(CF_3)NR_2 \\ \xrightarrow{HSR} [CF_3NHN(CF_3)SR] \xrightarrow{HSR} CF_3NHNHCF_3 + RSSR \\ \xrightarrow{C_6H_5SO_2H} [CF_3NHN(CF_3)SO_2C_6H_5] \longrightarrow CF_2{=}NN(CF_3)SO_2C_6H_5 \end{cases}$$

It may be assumed that the indicated transformations begin with the stage of formation of intermediate complexes (of the π-complex type), for example:

$$\begin{array}{c} CF_3N{=}NCF_3 \\ \uparrow \\ HNR_2 \end{array} \quad \text{or} \quad \begin{array}{c} CF_3N{=}NCF_3 \\ \uparrow \\ HSR \end{array}$$

This view is confirmed by the character of the interaction of hexafluoroazomethane with trialkyl phosphites; the resulting complex can be isolated under mild conditions (cooling with solid carbon dioxide):

$$CF_3N{=}NCF_3 + \ddot{P}(OC_2H_5)_3 \longrightarrow CF_3N{=}NCF_3 \cdot P(OC_2H_5)_3$$

Upon heating, this adduct decomposes with formation of nitrogen, tetrafluoroethylene, diethyl ether, ethyl fluoride, diethyl fluorophosphite, and diethyl ethanephosphonate.

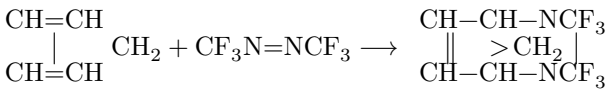
Table 1

Compounds synthesized for the first time

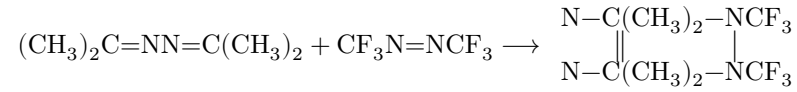
No.	Compound	b.p., °C	d_{20}^{20}	n_D^{20}
1		40/7	0.804	1.3780
2		50–55/15	0.7867	1.6818
3		–	–	1.4220
4		1/1	1.136	–
5		–	1.547	–
6	$CF_3NH{-}NHCF_3$	(C$_2$H$_5$)$_2$O	1.20	–
7	$CF_3N(COCH_3)N(COCH_3)CF_3$	45/90	–	–
8	$(C_6H_5NH)_2C{=}N{-}N{=}C(NHC_6H_5)_2$	m.p. 238	–	–
9	$(C_6H_5S)_2C{=}N{-}N{=}C(SC_6H_5)_2$	Does not boil up to 300	–	–
10	$(CF_2{=}N{-}N{=}CF_2)_2$	m.p. +30	–	–
11	$CF_2{=}N{-}N(CF_3)N(C_2H_5)_2 \cdot \frac{1}{2}(C_2H_5)_2O$	–	–	–
12	$(C_6H_5NH)_2C{=}N{-}N(CF_3)N(C_2H_5)_2$	–	1.015	1.6485
13	$CF_3N(CH_3)NHCOF$	m.p. 51	–	–
14	$CF_3N(CH_3)NHCOC_2H_5$	b.p. 51–52/2 mm; m.p. 32	–	–
15	$CF_3N(CH_3)NHCONHC_6H_5$	m.p. 115	–	–
16	$CF_3N(C_4H_9)NHCOF$	b.p. 45–56/1	1.195	–

No.	Compound	b.p., °C	d_{20}^{20}	n_D^{20}
17	$CF_3N(C_6H_5)NHCOF$	135; b.p. 95/2 mm	–	–
18	$CF_3N(C_6H_5)NHCONH_2$	m.p. 162	–	–
19	$CF_2{=}N{-}N(CF_3)SO_2C_6H_5$	m.p. 67	–	–
20	$(C_6H_5NH_2)C{=}N{-}N(CF_3)SO_2C_6H_5$	m.p. 130	–	–
21	$CF_3N{=}NCF_3 \cdot P(OC_2H_5)_3$	–	1.263	1.3990
22	$CF_3N{=}N{-}C_6H_4{-}C_6H_4{-}N{=}NCF_3$	m.p. 196	–	–
23	$CF_3N{=}N{-}C_6H_3(CH_3){-}C_6H_3(CH_3){-}N{=}NCF_3$	m.p. 125	–	–

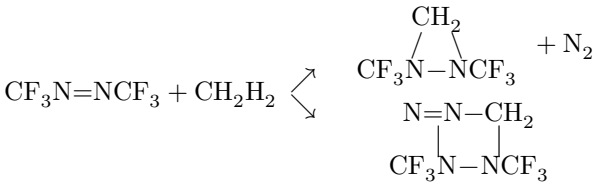
Like esters of azodicarboxylic acid, hexafluoroazomethane readily reacts with dienes (cyclopentadiene, isoprene, etc.):



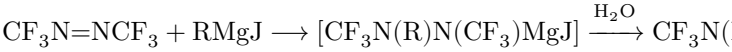
and also with azines:



and with diazomethane. In the latter case two products can be isolated in the form of ethers:



In reaction with Mg-organic compounds (in the cold), hexafluoroazomethane is smoothly converted into previously unknown fluoroanhydrides of polyfluoroalkyl-(aryl)-hydrazinecarboxylic acids, for example:



From the latter, a series of derivatives can be obtained by ordinary methods:

$$\mathrm{CF_3N(R)NHCOF} \xrightarrow{\mathrm{NH_3}} \mathrm{CF_3N(R)NHCONH_2}$$
$$\xrightarrow{\mathrm{C_6H_5NH_2}} \mathrm{CF_3N(R)NHCONHC_6H_5}$$
$$\xrightarrow{\mathrm{NaOCH_3}} \mathrm{CF_3N(R)NHCO_2CH_3}$$
$$\xrightarrow{\mathrm{HCl,\ H_2O}} \mathrm{RNHNH_2 + 2CO_2 + 4HF}$$

It follows from the foregoing that fluorinated azo compounds are substances capable of undergoing a large number of diverse heterolytic transformations. (The properties of the compounds synthesized for the first time are given in Table 1.)

Received
1 VI 1961

CITED LITERATURE

[1] V. A. Ginsburg, A. Ya. Yakubovich, S. P. Makarov et al., DAN, **142**, No. 1 (1962). [2] A. Ya. Yakubovich, V. A. Ginsburg, S. P. Makarov et al., DAN, **140**, No. 6 (1961). [3] O. Ruff, W. Willenberg, Ber., **73**, 724 (1940).

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