Chemistry

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Abstract

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PREPARATION, PYROLYSIS, AND PHOTOLYSIS OF POLYFLUORINATED ALIPHATIC AZO COMPOUNDS

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

A number of methods for preparing polyfluorinated aliphatic azo compounds have been described (^{1}). For a more complete characterization of these little-studied substances, we developed several other methods for the synthesis of polyfluoroazoalkanes and their derivatives. It was found that polyfluorinated azo compounds are formed:

a) by vapor-phase reduction of the corresponding azoxy compounds, in a nitrogen atmosphere, over carbon with vapors of phosphorus trichloride at 100–150°

$$R_{fN} = N(O)R'_f \xrightarrow{\mathrm{PCl_3}} R_{fN} = NR_f + \mathrm{POCl_3};$$

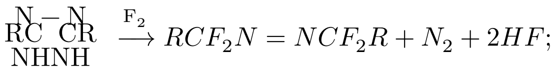
b) by oxidation of the corresponding hydrazo compounds containing the groups R_{fNH} ($R_f = \mathrm{CF_3},\ \mathrm{CF_2}H$, etc.), synthesized by reduction of the corresponding azoxy compounds, for example, with hydrogen iodide:

$$R_fNHNHR'_f \xrightarrow{\mathrm{O}} R_{fN} = NR'_f.$$

As oxidizing agents for the hydrazo derivatives listed, halogens ($\mathrm{Cl_2},\ \mathrm{Br_2}$), nitrogen oxides, chromic acid mixture, potassium permanganate in acetic acid, and others were used.

c) by fluorination of linear or cyclic azines with cobalt trifluoride in a fluorocarbon medium at 90–120°, or with elemental fluorine (diluted with nitrogen) at −10°.

$$R_2C = N - N = CR_2 \xrightarrow{\mathrm{F_2}} R_2CFN = NCFR_2,$$



$$\begin{matrix} N - N \\ RC\ \ CR \\ NHNH \end{matrix} \xrightarrow{F_2} RCF_2N = NCF_2R + N_2 + 2HF;$$

d) by vapor-phase fluorination on CoF_3 at 100–150° of nitriles of polyfluorocarboxylic acids and hydrogen cyanide

$$R_{fC} \equiv N \rightarrow R_fCF_2N = NCF_2R_f.$$

Some derivatives of polyfluoroazoalkanes were synthesized:

e) by halogenation (vapor-phase chlorination under ultraviolet irradiation at 300°, or fluorination on cobalt trifluoride at $50 \div 80°$) of hydrogen-containing azo compounds, for example:

$$R_{fN} = NCH_3 \xrightarrow[\text{u.-v.}]{Cl_2} R_{fN} = NCHCl_2$$

or

$$R_{fN} = NCH_3 \xrightarrow{CoF_3} R_{fN} = NCHF_2 \quad \text{and others;}$$

f) by the usual transformations of functional groups present in them.

in the aliphatic radical of the fluorinated azo compound:

$$R_fN{=}NCH_2CH_2OH \quad \begin{matrix} \xrightarrow{PCl_5} R_fN{=}NCH_2CH_2Cl \\ \xrightarrow{(CH_3CO)_2O} R_fN{=}NCH_2CH_2OCOCH_3, \end{matrix}$$

$$R_fN{=}NCH_2CH{=}CH_2 \xrightarrow{Br_2} R_fN{=}NCH_2CHBrCH_2Br \quad \text{etc.}$$

The starting azo compounds used in reactions (d) and (e) were obtained by condensation of polyfluorinated nitrosoalkanes with the corresponding amines, as described by us earlier (^{1}). The constants of the substances obtained are given in Table 1.

Polyfluorinated azo compounds are yellow-colored liquids (or gases), which explode on heating, od—

Table 1

Properties of newly synthesized polyfluoroazoalkanes

No.	Compound	b.p., °C/mm	d_{20}^{20}	n_D^{20}	Found C, %	Found H, %	Found N, %	Found F, %	Found Cl (Br,S), %	Calculated C, %	Calculated H, %	Calculated N, %	Calculated F, %	Calculated Cl (Br,S), %
1	$CF_3N=NCHF_2$	−9	–	–	16.70 [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	16.22	0.68	18.90	64.20	–
2	$CF_3N=NCF_2Cl$	[illegible]	–	–	13.03 [illegible]	–	15.53 [illegible]	[illegible]	[illegible]	13.1	–	15.3	52.2	19.5
3	$CF_2ClN=NCF_2Cl$	40.5	[illegible]	1.3275	–	–	13.70 [illegible]	[illegible]	[illegible]	[illegible]	–	14.1	38.2	35.7
4	$CF_2ClN=NCFCl_2$	78.0	[illegible]	1.3275	12.53 [illegible]	–	14.75 [illegible]	[illegible]	[illegible]	[illegible]	–	13.0	26.5	49.5
5	$CF_3N=NCH_2Cl$	48	[illegible]	1.3780	15.01 [illegible]	[illegible]	[illegible]	[illegible]	–	16.38	1.36	19.1	38.9	–
6	$CF_3N=NCHCl_2$	80	[illegible]	1.3860	14.35 [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	13.30	0.60	15.45	31.42	–
7	$CF_3N=NCCl_3$	55/92	[illegible]	1.4628	10.57 [illegible]	–	7.14 [illegible]	[illegible]	[illegible]	11.17	–	6.50	26.5	–
8	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	21.61	2.73	12.61	34.24	S28.81
9	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	3.60	11.20	22.80	38.40
10	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	4.32	10.40	13.2	S46.16
11	[illegible]	66	[illegible]	[illegible]	–	–	18.57 [illegible]	[illegible]	–	–	–	19.40	52.78	–
12	$CF_3N=NCH_2CHF_2$	45			22.50 [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	22.22	1.85	17.28	58.64	–
13	$CF_3N=NCH_2CF_3$	28	[illegible]	<1.3	21.02 [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.0	1.11	15.56	63.33	–
14	$CF_3N=NCHFCF_3$	17			18.21 [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	18.30	0.50	14.10	68.00	–
15	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	25.35	3.52	19.72	40.14	–
16	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	–	32.60	3.80	15.22	–	–
17	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	25.20	1.68	11.76	47.90	–
18	[illegible]	88	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	2.50	17.45	95.51	22.20
19	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.68	15.80	42.60	19.85
20	[illegible]	48	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.00	14.20	43.50	18.00
21	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.00	14.20	43.50	18.00
22	[illegible]	47	[illegible]	[illegible]	–	–	–	40.40 [illegible]	[illegible]	–	–	–	41.30	–
23	[illegible]	52/7	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	9.40	–	Br53.69
24	$[CF_3N=NCH_2CH_2N(CH_3)_3]Cl$	120				–	–	16.30 [illegible]	[illegible]	–	–	–	–	16.15
		m.p.												
25	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	20.84	0.88	12.18	66.10	–
26	[illegible]	98	[illegible]	[illegible]	[illegible]	[illegible]	8.68	69.30 [illegible]	[illegible]	21.81	0.60	8.50	69.10	–

however, they are appreciably more stable than their analogs containing no fluorine. The pyrolytic decomposition of polyfluorinated azo compounds, as is known, has been studied only with hexafluoroazomethane as an example (^{2}), and the formation of tetrafluoromethane and tetrafluoroethylene was shown. We have investigated these transformations in greater detail. It turned out that hexafluoroazomethane is slowly pyrolyzed at 400° in a copper tube (a mixture with nitrogen containing 9% by volume of hexafluoroazomethane does not explode), decomposing into molecular nitrogen and hexafluoroethane:

$$CF_3N = NCF_3 \rightarrow N_2 + CF_3{-}CF_3.$$

Polyfluorinated analogs of hexafluoroazomethane decompose in a similar way, for example:

$$C_2F_5N = NC_2F_5 \rightarrow N_2 + C_2F_5{-}C_2F_5$$

or

$$CF_3N = NCHF_2 \rightarrow N_2 + CF_3{-}CHF_2,$$

$$CF_2ClN = NCF_2Cl \rightarrow N_2 + CF_2Cl{-}CF_2Cl.$$

As can be seen, the pyrolytic decomposition of polyfluorinated azo compounds may serve as a method for the synthesis of the corresponding polyfluoroalkanes. At higher temperatures (600—700°), decomposition of hexafluoroazomethane gives other products, including tetrafluoromethane, tetrafluoroethylene, and soot, which indicates thermal decomposition of the trifluoromethyl radicals formed as intermediates:

$$CF_3N = NCF_3 \rightarrow 2CF_3 \cdot + N_2,$$

$$CF_3 \cdot \rightarrow CF_2 : + F \rightarrow CF : + F \rightarrow C + F,$$

$$2CF_2 : \rightarrow CF_2 = CF_2,$$

$$CF_3 \cdot + F \rightarrow CF_4.$$

When working with high concentrations of azo compounds, the rate constant of the decomposition reaction of hexafluoroazomethane has a very small temperature coefficient ($E_{\text{act}} \sim 5$ kcal/mol), which indicates the chain radical character of the reaction.

Table 2

Nos.	Compound	b.p., °C	d_{20}^{20}
1	$CF_3N(CF_2H)N(CF_2H)CF_3$	55	1.520
2	$CF_3N(CF_2H)N(CF_3)N(CF_2H)N(CF_2H)CF_3$	133	1.648
3	$CF_3N(CH_3)N(CH_3)CF_3$	76	1.408
4	$CF_3N(CH_3)N(CF_3)N(CH_3)N(CH_3)CF_3$	75/135	1.570

Experiments on the pyrolysis of hexafluoroazomethane at low concentrations of the azo compound (10—20 mm Hg in a nitrogen atmosphere; at 300—350°) lead to a value of E_{act} for the decomposition reaction of ~ 55 kcal/mol (cf. (3)).

The free-radical character of the decomposition of aliphatic polyfluorinated azo compounds is also clearly manifested in the reactions of their photolysis. In accordance with the data of Desse and Young, as well as Pritchard and Trotman-Dickenson (4,5), we have shown that in ultraviolet light hexafluoroazomethane is destroyed with the formation of perfluorotetramethyl- and perfluorohexamethylhydrazine and tetrazine.

It should be emphasized that polyfluorinated hexaalkyltetrazines have remarkable stability; their thermal decomposition begins only at 350—400°:

$$(CF_3)_2N{\cdot}N(CF_3)N(CF_3){\cdot}N(CF_3)_2 \rightarrow (CF_3)_2N{\cdot}N(CF_3)_2 + CF_3N = NCF_3.$$

Some analogs of hexafluoroazomethane behave similarly. Thus, on photolysis of trifluoro- and pentafluoroazomethane, the corresponding substituted hydrazines and tetrazines were isolated (see Table 2).

The structures of the mixed substituted hydrazines and tetrazines (established with the aid of mass spectra* and a number of chemical transformations) [[unclear: continuation cut off on this page]] showed that, for unsymmetrical azo compounds of the type $CF_3N = NR$, addition of an active free radical occurs preferentially at the nitrogen atom of the azo group adjacent to the less electrophilic group. The free-radical character of the transformations described for polyfluoroazoalkanes is clearly illustrated by the reaction of the latter in ultraviolet light in the presence of free-radical acceptors. Thus, on photolysis in the presence of chlorine, hexafluoroazomethane is converted into trifluorochloromethane; in the presence of nitrogen oxide or methyl nitrite—into trifluoronitromethane. Fatty-aromatic azo compounds of the type $R_{fN} = NC_6H_5$ proved stable to the action of high temperatures and ultraviolet light.

The reactions of polyfluorinated azoalkanes indicate a general tendency of substances of this type toward homolytic dissociation into free polyfluorinated radicals and a nitrogen molecule.

The same tendency is also illustrated by the behavior of the indicated compounds toward electron impact: in the mass spectra a considerable intensity of the ion N_2^+ is observed. In this connection it is of interest to note that the pyrolytic decomposition of hexafluoroazoxymethane (at 250-300°)—a compound in which elimination of molecular nitrogen is hindered—proceeds differently, with predominant cleavage of the molecule at the $N = N$ bond. Among the products

* The mass-spectral study was carried out by S. S. Dubovyi and A. M. Khokhlova.

of this reaction were found trifluoronitromethane, trifluoromethylcarbylamine difluoride, and hexafluoroazomethane, apparently formed according to the scheme

$$CF_3N \xrightarrow{O} NCF_3 \rightarrow CF_3N: + CF_3NO \rightarrow CF_3NO_2 + CF_3N{=}CF_2$$

$$\big| \longrightarrow CF_3N{=}NCF_3$$

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CITED LITERATURE

1. S. P. Makarov, A. Ya. Yakubovich, V. A. Ginsburg, A. S. Filatov, M. A. Englin, N. F. Privezentseva, T. Ya. Nikiforova, DAN, 141, No. 2 (1961).

2. O. Ruff, W. Willenberg, Ber., 73, 724 (1940).

3. D. Clark, H. O. Pritshard, J. Chem. Soc., 1956, 2136.

4. J. R. Dacey, D. M. Young, J. Chem. Phys., 23, 1302 (1955).

5. J. O. Pritshard, H. O. Pritshard, A. F. Trotman-Dickenson, Chem. and Ind., 1955, 564; Trans. Farad. Soc., 52, No. 6, 849 (1956).