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Abstract

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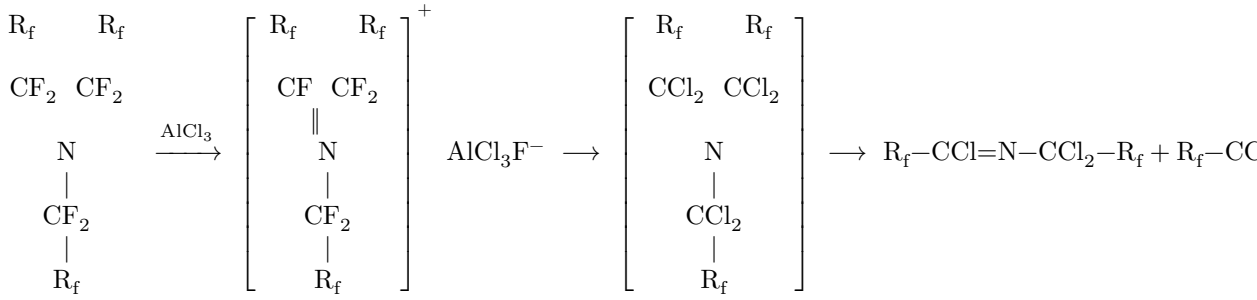
RING OPENING AND REVERSE CYCLIZATION OF PERHALOGENATED AMINES UNDER THE INFLUENCE OF ALUMINUM AND ANTIMONY HALIDES

(Presented by Academician I. L. Knunyants, December 4, 1964)

We have previously shown that tertiary perfluorinated amines can enter into chemical reactions not only at high temperatures under conditions close to pyrolytic ones ([1,2]), but also at low temperatures with suitable reagents ([3]). The present work is devoted to the study of the reaction of tertiary perfluorinated amines with anhydrous aluminum chloride.

Although perfluorinated amines are practically devoid of basicity and do not dissolve even in the strongest concentrated acids, they nevertheless evidently retain the ability to form complex compounds with anhydrous aluminum chloride. The fluorine atoms at the α-carbon atoms in perfluorinated tertiary amines are activated through σ,ρ-conjugation, which is clearly evident in the NMR spectra of these compounds from the shift of the F^{19} resonance absorption lines toward weak fields by 35–45 m.p.p. in comparison with the lines of the groupings $-C-CF_2-C-$. Upon formation of the complex of φ-amines with $AlCl_3$, the activity of the fluorine atoms at the α-carbon atoms increases so much that the structure of the complex approaches the limiting salt-like form. With an increase in temperature and an excess of aluminum chloride, exchange of fluorine atoms for chlorine begins, followed by rearrangement of the α,α',α''-polychloroamines, which are unstable under these conditions, into less sterically hindered iminochlorides, with elimination of ω,ω,ω-trichloroperfluoroalkanes.



We have shown that in this way the reaction proceeds with perfluorodiethylmethylamine and perfluorotriethylamine. This reaction already begins at 60–70° and proceeds vigorously at 100–110°, whereas perfluoro ethers react with $AlCl_3$ only at 170–230° ([4]). This is explained by the greater mobility of the free electron pair at the nitrogen atom in amines as compared with the electron pairs at the oxygen atom in simple ethers. The low temperature at which the reaction proceeds makes it possible to obtain φ-iminochlorides in high yield, since φ-iminochlorides are destructed under the action of anhydrous $AlCl_3$ at a temperature of about 200°, forming polychlorofluoroalkanes. With other Lewis acids: $TiCl_4$, $SbCl_5$, $SnCl_4$, $FeCl_3$, the reaction does not take place at temperatures up to 160°.

When carrying out the reaction of heterocyclic tertiary φ-amines, for example N-perfluoroamylperfluoropiperidine (I), with anhydrous aluminum chloride, rearrangement of the cyclic $\alpha, \alpha', \alpha''$-polychloride can proceed both with cleavage of an exocyclic bond and formation of ω, ω, ω-

trichlorononafluoropentane and α, α, α'-trichlorohexafluoropiperideine, identical to that previously described in the literature ([5]), as well as with cleavage of one of the two ring bonds; in this case a mixture of two isomeric iminochlorides (II) must be formed: N-perfluoro-α, α-dichlorobutyl iminochloride of ω, ω, ω-trichlorohexafluorovaleric acid (IIa) and N-$\alpha, \alpha, \omega, \omega, \omega$-pentachlorohexafluorobutyl iminochloride of perfluorovaleric acid (IIb). The similarity of the structures of IIa and IIb makes their properties practically identical, and the presence in the iminochloride of the two possible isomers IIa and IIb was not detected by the methods available to us (including gas–liquid chromatography).

$$\text{II} \begin{cases} CCl_3 - (CF_2)_3 - CCl{=}N - CCl_2 - C_4F_9 & \text{(IIa)} \\ CCl_3 - (CF_2)_3 - CCl_2 - N{=}CCl - C_4F_9 & \text{(IIb)} \end{cases}$$

$$\text{cyclic structure of (I)} \xrightarrow{AlCl_3} \begin{matrix} \text{cyclic chlorinated imino compound} \\ CCl_3 - C_4F_9 \end{matrix}$$

(I)

In the reaction of I with anhydrous $AlCl_3$ in boiling CCl_4 (without a diluent the reaction proceeds too violently), trichlorononafluoropentane and trichlorohexafluoropiperideine were obtained, along with a small amount of more highly chlorinated products and II, boiling at 255–256° (yield 60–65%). Rearrangement is observed not only for the $\alpha, \alpha', \alpha''$-hexachloroamine, but also for the less chlorinated φ-amine, since in the reaction without solvent it was possible to isolate mono- and dichloroperfluoropentanes. The structure of II was confirmed by elemental analysis, IR and NMR spectra, and also by hydrolysis of it to perfluorovaleric (III) and ω, ω, ω-trichlorohexafluorovaleric (IV) acids. If the

three chlorines located at the α-carbon atoms of II can be quantitatively split off by alcoholic alkali in the cold, then hydrolysis of the trichloromethyl group can be carried out only with oleum in the presence of mercury salts at a temperature of about 100°; in this case, in almost quantitative yield, a mixture of (III) and perfluoroglutaric acid is obtained. II was synthesized by an independent route analogously ([5]), by treating the imide of perfluorovaleric and trichlorohexafluorovaleric acids with phosphorus pentachloride. II reacts with various nucleophilic agents, although it is only slightly hydrolyzed by water. Fluorinating agents of the type CoF_3 at 100–150° replace the three chlorine atoms at the α-carbon atoms of II by fluorine, leading to iminofluorides. Replacement of chlorine atoms by fluorine leads to an increase in the reactivity of the C=N bond and to a shift of the absorption frequency in the IR spectrum from 1676 cm^{-1} for II to 1766 cm^{-1} for the iminofluorides. Anhydrous hydrogen fluoride reacts with II at 100–150°, leading to ω,ω,ω-trichlorooctafluoroamylperfluoroamylamine, which eliminates hydrogen fluoride upon heating, converting into the iminofluoride. In the presence of halides of pentavalent antimony, replacement of chlorines by fluorines with formation of the amine takes place already in the cold. Of particular interest is the reaction of II with antimony pentafluoride or with hydrogen fluoride and antimony pentachloride upon heating. In this case, not only are all six chlorine atoms replaced by fluorine, but a cyclization reaction also occurs, with formation of the starting material for the entire series of compounds –N-perfluoroamylpiperidine (I). Moreover, this reaction is the principal one and proceeds to 70–80%. The obtained I is identical with the product obtained by electrochemical fluorination according to the IR and NMR spectra and

Table 1

Properties of the compounds obtained

Formula of compound	Yield, %	B.p., °C	n_D^{20}	d_4^{20}	I.R., spectrum, cm^{-1}	Gross formula
$C_5F_{10}N-C_5F_{11}$	74	146–147	1.297*	1.870	–	$C_{10}F_{21}N$
$CCl_3-(CF_2)_3-CCl_2-N=CCl-C_4F_9$	60–65	253–256	1.398	1.849	1676	$C_{10}Cl_6F_{15}N$
$CCl_3-(CF_2)_3-CCl_2-N=CCl-C_4F_9$	60–65	253–256	1.398	1.849	1676	$C_{10}Cl_6F_{15}N$
$CCl_3-(CF_2)_3-CF_2-N=CF-C_4F_9$	80–90	188–191	1.332	1.828	1766	$C_{10}Cl_3F_{18}N$
$CCl_3-(CF_2)_4-CF_2-N=CF-C_4F_9$	80–90	188–191	1.332	1.828	1766	$C_{10}Cl_3F_{18}N$
$CCl_3-(CF_2)_4-NH-C_5F_{11}$	95	85–87 (7 mm)	1.339	–	1768; 3414	$C_{10}Cl_3HF_{19}N$

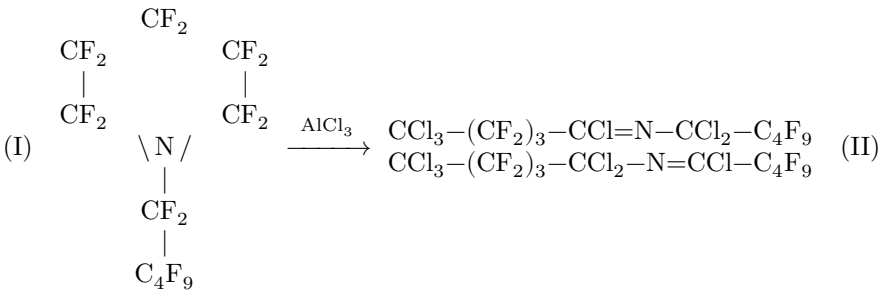
Formula of compound	Yield, %	B.p., °C	n_D^{20}	d_4^{20}	I.R., spectrum, cm^{-1}	Gross formula
$CCl_3-(CF_2)_3-CONH-C_4F_9$	53	230-240; m.p. 136-137	–	–	–	$C_{10}Cl_3HO_2F_{15}N$
$CF_3-CCl_2-N=CCl-C_4F_9$	25	143-146	1.361	–	1680	$C_7Cl_3F_{12}N$
$CF_3-CCl=N-CCl_2-C_4F_9$	25	143-146	1.361	–	1680	$C_7Cl_3F_{12}N$

(continued)

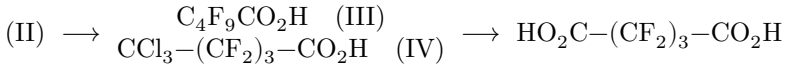
Formula of compound	Found, % N	Found, % F	Found, % Cl	Calculated, % N	Calculated, % F	Calculated, % Cl
$C_5F_{10}N-C_5F_{11}$	2.81	74.51	–	2.63	74.86	–
$CCl_3-(CF_2)_3-CCl=N-CCl_2-C_4F_9$	2.43	44.93	33.93	2.21	45.09	33.64
$CCl_3-(CF_2)_3-CCl_2-N=CCl-C_4F_9$	–	–	16.43**	–	–	16.80**
$CCl_3-(CF_2)_3-CH=N-C_5F_{11}$	2.69	58.56	18.40	2.40	58.76	18.29
$CCl_3-(CF_2)_4-N=CF-C_4F_9$	3.41**	8.41**	0.57**	–	9.79**	0.00**
$CCl_3-(CF_2)_4-NH-C_5F_{11}$	2.38	58.99	18.57	2.32	59.97	17.69
$CCl_3-(CF_2)_4-NH-C_5F_{11}$	1.44**	12.62**	0.63**	–	12.62**	0.00**
$CCl_3-(CF_2)_3-CO-NH-CO-C_4F_9$	2.90	44.93	19.44	2.51	–	19.08
$CF_3-CCl_2-N=CCl-C_4F_9$	3.00	52.34	24.49	3.25	52.78	24.63
$CF_3-CCl=N-CCl_2-C_4F_9$	–	–	23.93**	–	–	–

* Determined on a refractometer having a measurement range of 1.300-1.750.
** Amount of ionic halide obtained by treatment of the substance with alcoholic alkali.

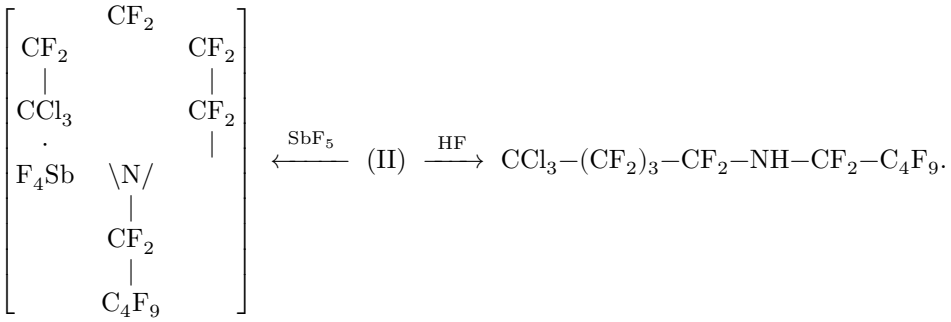
chemical properties. This unusual reaction can be explained only by taking into account the initial formation of an intramolecular complex–



$$CCl_3{-}(CF_2)_3{-}CO{-}NH{-}CO{-}C_4F_9 \xrightarrow{PCl_5} (II)$$



$$(II) \xrightarrow{CoF_3} \begin{matrix} CCl_3{-}(CF_2)_3{-}CF{=}N{-}CF_2{-}C_4F_9 \\ CCl_3{-}(CF_2)_3{-}CF_2{-}N{=}CF{-}C_4F_9 \end{matrix} \underset{-HF}{\overset{+HF}{\rightleftharpoons}} CCl_3{-}(CF_2)_3{-}CF_2{-}NH{-}CF_2{-}C_4F_9$$



of the complex of the terminal trichloromethyl group with the residue $-SbF_4$, bonded to the nitrogen atom. Spatial proximity within a single molecule is apparently a necessary condition for this reaction, since so far we have not succeeded in carrying out any analogous reaction for the formation of a tertiary perfluorinated amine from imino chlorides that do not contain trichloromethyl groups, with perfluoroalkyl derivatives of trichloromethane. The properties of the principal compounds are summarized in the table.

The indicated reactions are represented by the scheme.

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