N-(POLYFLUOROARYL)-HYDROXYLAMINES. SYNTHESIS AND
PROPERTIES

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SUMMARY

Fluorine–containing N–arylhydroxylamines have been obtained
by the action of hydroxylamine or its N– and O–derivatives on poly-
fluorinated benzenes and pentafluoropyridine. The influence of
fluorine atoms on the reactivity of hydroxylamino group has been
investigated. The reaction of N–polyfluoroarylhydroxylamines with
aldehydes has been shown not to occur, whereas their reaction with
nitrosobenzenes leads to azoxybenzenes and with Lewis acids leads
to corresponding nitrosobenzenes, azoxybenzenes and anilines. The
action of acids on 2,3,5,6–tetrafluorophenylhydroxylamine leads to the
acid–catalyzed rearrangement of the latter into 4–amino–2,3,5,6–tetra-
fluorophenol. C,N–Diarylnitrones have been obtained by the oxidation
with MnO_2 of fluorine–containing arylhydroxylamines possessing the
CH–fragment in an α–position.


INTRODUCTION

The aromatic hydroxylamines play important roles in organic
synthesis, and also in biological investigations [1,2]. These facts
have stimulated the development of synthetic methods and search
for new applications of this class of compounds. Nevertheless, the
fluorohydroxylamines have been insufficiently investigated because of
the lack of convenient methods for their synthesis. Only the isomeric
monofluorosubstituted N–arylhydroxylamines, obtained by reduction of
the corresponding nitrobenzenes [3], and compounds of the
N–(1,1,2–trimethyl)–2–propenyl–N–pentafluorophenylhydroxylamine type,
obtained by interaction of pentafluoronitrosobenzene with ethylene

derivatives [4] , are known. Other authors [5] described an unsuccessful attempt to obtain pentafluorophenylhydroxylamine by the reaction of hydroxylamine with hexafluorobenzene.

   In the present work we have investigated the possibility of the synthesis of polyfluorinated N-arylhydroxylamines and their derivatives, and also the influence of fluorine atoms in the benzene ring on the reactivity of hydroxylamino group.

RESULTS AND DISCUSSION

   The reaction of nucleophilic substitution of various groups by the action of hydroxylamine, together with reduction reactions of substituted nitrobenzenes are known as important methods of synthesis of N-arylhydroxylamines. The reduction of polyfluorinated nitrobenzenes with zinc in presence of NH_4CI at 70-80°C has now been shown by us to lead to the corresponding anilines. At the same time reduction of these nitrobenzenes at 50°C leads to a mixture of corresponding aniline, N-arylhydroxylamine, azoxybenzene and some other products (identified by IR and ^{19}F NMR spectra). The variation of the reaction conditions does not stop the reduction at the stage of N-arylhydroxylamine formation.

$$Ar_F NO_2 \xrightarrow[NH_4CI]{Zn} Ar_F NH_2 \ + \ Ar_F NHOH \ + \ Ar_F - N = N - Ar_F$$
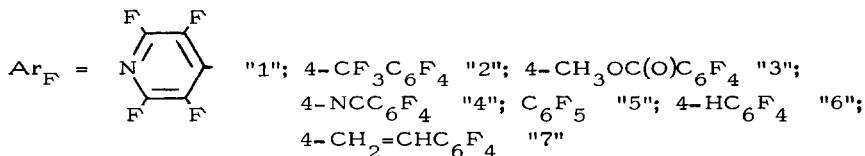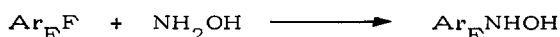
$$Ar_F \ = \ C_6F_5, \ 4-CF_3C_6F_4,$$
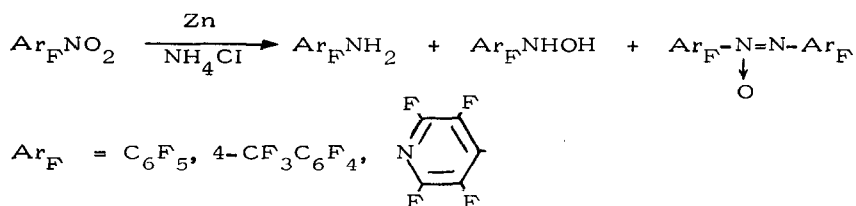
Hence, our data proved the possibility of synthesis of N-polyfluoro-hydroxylamines by this method, but on the whole it seemed to be ineffective because of difficulties in the separation of products. The use of sodium bisulphide is also ineffective because of substitution of the fluorine atoms in the ring by sulfur [6].

   The halogen atom in halobenzenes containing electron-withdrawing substituents is known to be susceptible to substitution by the hydroxylamino group under the action of hydroxylamine [1]. Halobenzenes activated by nitro-groups form, as a rule, the corresponding hydroxylamine with low yield and substantial amounts of by-products [7,8]. By using N- and O-substituted hydroxylamines

the yield of N-arylhydroxylamine increases up to 50-90% [9]. The high activity of halogen atoms in heteroaromatic compounds allows their reaction with hydroxylamine to occur under mild conditions [10].

The molecule of hydroxylamine has two nucleophilic centers. It has been shown [11,12] on the basis of quantum-chemical calculations and the data on the interaction between hydroxylamine and alkyl halides, that hydroxylamine as a base forms mainly N-substituted hydroxylamines, while, in the presence of excess of alcoholates of alkali metals, mainly O-substituted hydroxylamines are obtained. Hence, in the case of hydroxylamine, reaction conditions are of substantial importance.

The interaction of polyfluorinated aromatic compounds containing electron-withdrawing substituents and of pentafluoropyridine with hydroxylamine in boiling THF has been shown by us to lead to substitution of the para-fluorine atom (in respect to a substituent other than fluorine) with formation of the corresponding N-arylhydroxylamines in high yield.

$$Ar_F F \ + \ NH_2OH \ \longrightarrow \ Ar_F NHOH$$

$Ar_F = $

"1"; $4-CF_3C_6F_4$ "2"; $4-CH_3OC(O)C_6F_4$ "3"; $4-NCC_6F_4$ "4"; C_6F_5 "5"; $4-HC_6F_4$ "6"; $4-CH_2=CHC_6F_4$ "7"
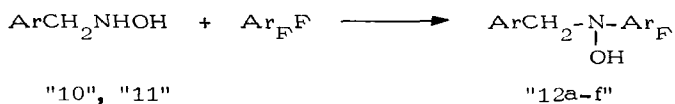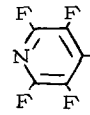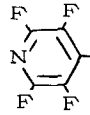
The lack of the formation of the corresponding hydroxamic acid in the reaction of hydroxylamine with methyl pentafluorobenzoate should be noticed. 2,3,4,5,6-Pentafluorobenzohydroxamic acid "8" was obtained by another route - the action of hydroxylamine on pentafluorobenzoyl chloride.

The reaction of hydroxylamine with pentafluoronitrobenzene, as in the case of its reaction with polynitrochlorobenzenes leads to a complex mixture of products. The rate of the reaction of hexafluoro-benzene and pentafluorobenzene with hydroxylamine under the conditions mentioned above is very low, probably, because of the low activity of fluorine atoms in these compounds [6]. Pentafluoro-phenylhydroxylamine "5" and 2,3,5,6-tetrafluorophenylhydroxylamine "6" can be obtained in yields up to 70% by using another solvent - dimethylsulphoxide or sulpholane. 2,3,4,5,6-Pentafluorostyrene reacts
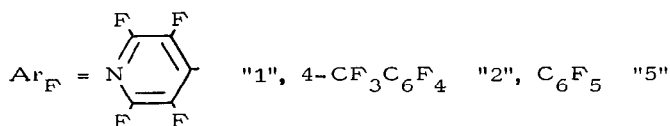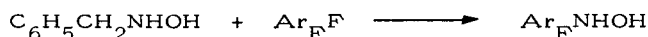
with hydroxylamine under similar conditions to give 4-hydroxylamino-2,3,5,6-tetrafluorostyrene "7". The values of the rate constants for reaction of hydroxylamine with hexafluorobenzene and octafluoro-toluene, determined from kinetical measurements, are $5 \cdot 10^{-5}$ and $1,3 \ 1 \cdot mol^{-1} \cdot sec^{-1}$ (DMSO, 50°C) respectively indicating the substantial difference in their reactivity. Therefore a high temperature is required to realize the reaction of hexafluorobenzene with hydroxylamine in THF. But thermolytic transformation of N-polyfluoroaryl-hydroxylamines can occur at high temperature, as will be shown below.

   N-Methylhydroxylamine is also an effective nucleophilic reagent and, in its reaction with pentafluoropyridine, N-methyl-N-(2,3,5,6-tetrafluoropyridyl)-hydroxylamine "9" is formed easily. The interaction of N-benzyl- "10" and N-(2,3,4,5,6-pentafluorobenzyl)-"11" hydroxylamines with pentafluorosubstituted derivatives of benzene containing electron-withdrawing substituents (CF_3 and CN) and pentafluoropyridine (DMF or DMSO, 20°C) leads to hydroxyl-amines "12a-f" respectively. Two equivalents of hydroxylamines "10" and "11" should be taken into reaction to neutralize the HF formed.

$$ArCH_2NHOH \ + \ Ar_FF \longrightarrow ArCH_2-\underset{\underset{OH}{|}}{N}-Ar_F$$

   "10", "11"   "12a-f"

Ar_F	(pyridyl)	(pyridyl)	$4\text{-}CF_3C_6F_4$	$4\text{-}CF_3C_6F_4$	$4\text{-}NCC_6F_4$	$4\text{-}NCC_6F_4$
Ar	C_6H_5	C_6F_5	C_6H_5	C_6F_5	C_6H_5	C_6F_5
	a	b	c	d	e	f

   The presence of bases in the reaction can be the determining factor for obtaining products. Thus, the reaction of N-benzylhydroxyl-amine with pentafluoropyridine, octafluorotoluene or hexafluorobenzene in the presence of K_2CO_3 as a base leads to N-polyfluoroaryl-hydroxylamines "1", "2", "5" instead of N-aryl-N-benzylhydroxyl-amines.

$$C_6H_5CH_2NHOH \ + \ Ar_FF \ \longrightarrow \ Ar_FNHOH$$

Ar_F = [structure: pentafluoropyridyl ring with N at position and F substituents: F, F at top; F, F at bottom]   "1", $4-CF_3C_6F_4$ "2", C_6F_5 "5"

Probably the N-benzylhydroxylamine is a source of hydroxylamine under the reaction conditions owing to cleavage of the C-N bond under the action of base. The hydroxylamine "12c" has been found to be stable under these conditions with K_2CO_3; hence it cannot serve as a precursor of the product "2".

At the same time, phenylhydroxylamine is a weaker nucleophile than hydroxylamine and two nucleophilic centers probably can be realized in it. Although it reacts with pentafluoropyridine, that reaction leads to a complex mixture of products. The structure of the latter has not been investigated.

In the case of reaction of O-methylhydroxylamine with pentafluoropyridine, N-(2,3,5,6-tetrafluoropyridyl)-O-methylhydroxylamine "13" is formed. The O-trimethylsilylic ether of hydroxylamine reacts with pentafluoropyridine in the presence of CsF (THF) to yield a mixture of products, with 4-hydroxylamino-2,3,5,6-tetrafluoropyridine "1", 4-amino-2,3,5,6-tetrafluoropyridine "14" and 4-oxy-2,3,5,6-tetrafluoropyridine "15" as the main components in practically equal amounts (from ^{19}F NMR data). The heterolytic cleavage of Si-O bonds in various silicon derivatives is known to take place under the conditions of nucleophilic catalysis by CsF to form the corresponding oxy-anion [13]. Probably, the compound "1" is obtained due to N-substitution of pentafluoropyridine by the O-trimethylsilylic ether of hydroxylamine, with the further elimination of the protecting $Si(CH_3)_3$ group under the condition of nucleophilic catalysis. The compounds "14" and "15" can be suggested to form as products of transformation of intermediate N,O-bis-(2,3,5,6-tetrafluoropyridyl)-hydroxylamine under reaction conditions. As an indirect confirmation of that possibility, the fact of formation of compounds "14" and "15" in practically equal amounts in the reaction of compound "1" with pentafluoropyridine in the presence of triethylamine should be noticed.

One of the typical reactions of N-arylhydroxylamines is their interaction with aldehydes leading to corresponding nitrones. 4-Tri-

fluoromethyl- 2,3,5,6-tetrafluorophenylhydroxylamine "2" and penta-
fluorophenylhydroxylamine "5" have been shown to be inert towards
benzaldehyde and pentafluorobenzaldehyde in ethanol. This fact is
in agreement with the expected decrease of basic and nucleophilic
properties of the hydroxylamino group under the influence of the
fluorine atoms in the aromatic ring [14] . The increase of the
reaction temperature up to $100^{\circ}C$ leads to the thermolytic trans-
formation of the aromatic hydroxylamines into the corresponding
azoxybenzenes and anilines. An attempt to increase the electro-
philicity of the carbon atom in the C=O group of pentafluorobenz-
aldehyde by the use of p-toluene sulphonic acid as catalyst was
also unsuccessful.

Nevertheless, the nucleophilic properties of pentafluorophenyl-
hydroxylamine are not negligible. Thus, it reacts with nitrosobenzene
to form 2,3,4,5,6-pentafluoroazoxybenzene "16" containing the C_6F_5
group at the -N(O)= fragment of the azoxy group.

C_6F_5NHOH + C_6H_5NO

C_6H_5NHOH + C_6F_5NO

$$C_6F_5-N=N-C_6H_5$$
$$O$$

"16"
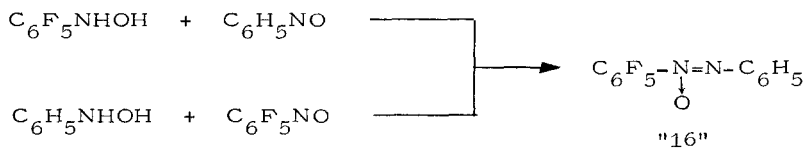
The same azoxybenzene "16" can be obtained by reaction of phenyl-
hydroxylamine with pentafluoronitrosobenzene. Hence, the elimination
of water from the dihydroxy-intermediate occurs in agreement with the
electronic effects of the substituents on the nitrogen atoms.

The oxidation of 2,3,4,5,6-pentafluoroazobenzene with trifluoro-
acetic peracid should be noticed to occur on the nitrogen atom
bonded with the C_6F_5 group.

$$C_6F_5-N=N-C_6H_5 \xrightarrow{CF_3COOOH} C_6F_5-N=N-C_6H_5$$
$$O$$

"16"
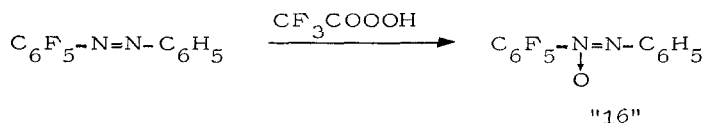
The presence of five fluorine atoms has been suggested earlier to
lead to a decrease in the effectiveness of the interaction between
the lone electron pair of nitrogen and the π-system of the
benzene ring [14]. That fact can probably determine the direction of
the oxidation on the nitrogen atom bonded with C_6F_5 group. This
suggestion corresponds also to the known formation of tetrafluoro-

4-(2,4,6-trimethylphenyl-ONN-azoxy)-pyridine under the action of trifluoroacetic peracid on tetrafluoro-4-(2,4,6-trimethylphenylazo)-pyridine [15]; in the latter compound the effectiveness of the interaction between the lone electron pair of nitrogen and the π-system of the aromatic ring is also decreased because of steric influence of the ortho-CH_3 groups. The final product contains the 2,4,6-trimethylphenyl group at the $-N(O)=$ fragment of the azoxy group.

N-Arylhydroxylamines are thermally unstable and undergo decomposition into anilines and nitrosobenzenes at high temperatures [16]. The polyfluorinated N-arylhydroxylamines show similar behaviour. Thus, heating compound "2" up to 110–115°C leads to 4,4'-bis-(trifluoromethyl)-octafluoroazoxybenzene "17" and 4-trifluoromethyl-2,3,5,6-tetrafluoroaniline "18". The thermolysis of 4-hydroxy-amino-2,3,5,6-tetrafluoropyridine occurs similarly. Nitrosobenzene is known to be able to react with aniline to form azobenzene [17]. The yield of azobenzene depends on the nucleophilic properties of the corresponding aniline and in the case of 2,3,4,5,6-pentafluoroaniline is equal to only 15% [14]. We did not observe the formation of the corresponding azobenzenes during thermolysis of the hydroxylamines "1" and "2".

The action of acids on phenylhydroxylamines leads to their rearrangement into 2- and 4-aminoderivatives of phenols, ethers etc. [1]. The presence of four fluorine atoms in the benzene ring has been shown by us to require more forcing conditions for the occurence of the Bamberger rearrangement. Thus, 4-amino-2,3,5,6-tetra-fluorophenol "19" can be obtained by the action of H_2SO_4 (conc.) on compound "6" :
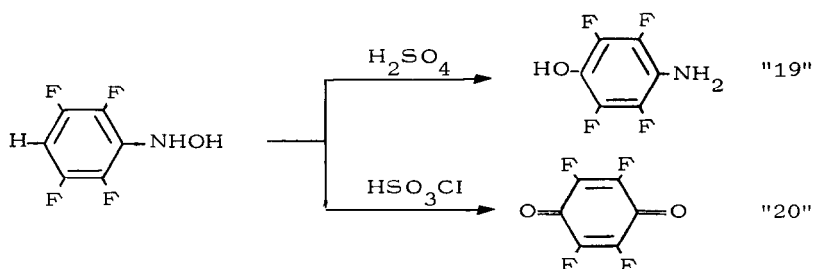
At the same time the action of chlorosulfonic acid on compound "6" leads to fluoroanil "20". In the case of pentafluorophenylhydroxylamine the stabilization of the initially generated cation is possible by interaction with the anion of the acid medium. Thus, the solvation of

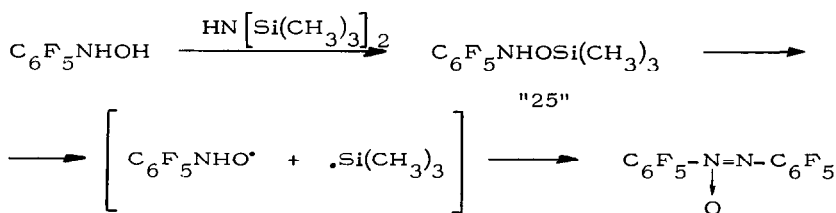compound "5" in HSO_3Cl leads to the elimination of water from an intermediate "21" to give the cation "22". The positive charge in the latter is localized mainly on the carbon atom in the 4-position [18]. The cation "22" is highly reactive and forms imino- 2,3,4,5,6-penta-fluoro- 4- chlorosulfonate- cyclohexadiene- 2,5 as a result of interaction with the anion of the medium. That compound is attacked further by protons to give 4-aminopolyfluorobenzolonium ion "23". The analogous formation of 4-aminopolyfluorobenzolonium ion has been shown to take place during solvation of N- chloroimino- 2,3,4,5,6-pentafluoro- 4- chlorocyclohexadiene- 2,5 in HSO_3Cl [19]. The ion "23" can undergo fast transformation in HSO_3Cl at $20^{\circ}C$ into polyfluorocyclo-hexadienone "24" with elimination of NH_3 and subsequent hydrolysis of the latter affords fluoroanil "20".

$$C_6F_5NHOH \xrightarrow{HSO_3Cl} \left[C_6F_5\overset{+}{N}\underset{H}{H}OH \xrightarrow{-H_2O} C_6F_5\overset{+}{N}H \longrightarrow \right.$$

"21" "22"

"23" "24" "20"
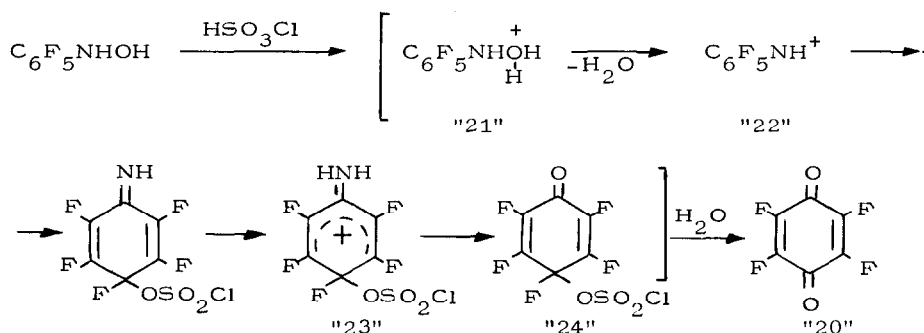
The formation of 2,3,4,5,6-pentafluoro- 4- chlorocyclohexadienone from N- chlorimino- 2,3,4,5,6-pentafluoro- 1- chlorohexadiene- 2,5 in HSO_3Cl [19] and hydrolysis of iminocyclodienoles [20] can be mentioned as evidence of the possibility of the realization of this reaction route. It is interesting that the action of trifluoroacetic acid on the pentafluoro-phenylhydroxylamine in CCl_4 leads to decafluoroazoxybenzene. The formation of azoxybenzenes is known to take place also under the action of acids on phenylhydroxylamines [21].

N-Arylhydroxylamines can be silylated by the action of silylic agents [22]. Initially the hydrogen atom of the OH group of hydroxyl-amines can be replaced. In fact, the silylation of pentafluorophenyl-hydroxylamine has been shown by us to occur with formation of the O-trimethylsilylic ether of pentafluorophenylhydroxylamine "25". The ether "25" has been found to be thermally unstable : at $20^{\circ}C$ (two months) the complete decomposition of it to yield decafluoroazoxyben-zene has been observed.

$$C_6F_5NHOH \xrightarrow{\text{HN}\left[Si(CH_3)_3\right]_2} C_6F_5NHOSi(CH_3)_3 \longrightarrow$$

"25"

$$\longrightarrow \left[C_6F_5NHO^\bullet + {}^\bullet Si(CH_3)_3 \right] \longrightarrow C_6F_5-\underset{\underset{O}{\downarrow}}{N}=N-C_6F_5$$

The action of Lewis acids on benzohydroxamic acids is known to lead to aryl isocyanates as a result of Lossen rearrangement. 2,3,4,5,6-Pentafluorobenzohydroxamic acid also has been shown by us to form pentafluorophenyl isocyanate "26" under the action of $SOCl_2$ or PCl_5. The compound "26" has been synthesized by us independently with high yield by heating of bis-(trimethylsilyl)-2,3,4,5,6-pentafluorobenzohydroxamic acid "27" in a flow system ($300^\circ C$) under argon.
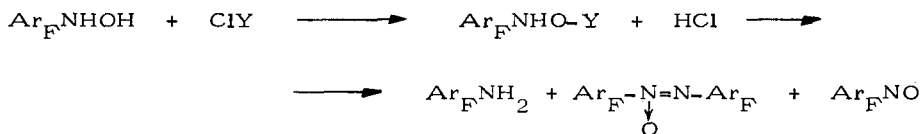
The mechanism of the Lossen rearrangement is known to include the generation of nitrenes as intermediates. The problem to solve in the case of reactions of polyfluoroarylhydroxylamines with Lewis acids was the possibility of the formation of arylnitrenes as in the cases of reactions of polyfluoronitrosobenzenes and polyfluorophenyl-azides [14]. The interaction of 4-trifluoromethyl-2,3,5,6-tetrafluoro-phenylhydroxylamine "2" with $SOCl_2$ has been found to lead to 4,4'-bis-(trifluoromethyl)-octafluoroazoxybenzene "17", 4-trifluoromethyl-2,3,5,6-tetrafluoroaniline "18" and 4-trifluoromethyl-2,3,5,6-tetrafluoro-nitrosobenzene "28" (see Table 1). The formation of 4,4'-bis-(tri-fluoromethyl)-octafluoroazobenzene "29" has not been observed. That fact indicates a reaction route of $SOCl_2$ and other Lewis acids with N-arylhydroxylamines excluding the formation of phenylnitrenes. The nature of the Lewis acid determines the ratio of the products and their structure (see Table 1). Thus, the reaction of hydroxylamine "2" with PCl_5 leads to the compounds "28" and trichlorophosphazo-(4-trifluoromethyl)-2,3,5,6-tetrafluorophenyl "30", the latter being the final product of reaction between compound "18" and PCl_5 with high yield [20]. The use of $FeCl_3$ as Lewis acid leads to equal amounts of compounds "18" and "28", whereas $SbCl_5$ leads to the same products with substantial admixture of compound "17". The formation of azo-compound "29" ($\approx 25\%$) was observed only with PCl_3. These data lead us to suppose that the reaction of polyfluoroaromatic hydroxylamines with Lewis acids occurs through the initial product of

TABLE 1

The composition of the reaction mixture of the interaction of 4-trifluoromethyl-2,3,5,6-tetrafluorophenylhydroxylamine with Lewis acids (^{19}F NMR data)

Lewis	Composition (%)				
acids	"17"	"18"	"28"	"29"	"30"
PCl$_5$			30		70
PCl$_3$	25	50		25	
SO$_2$Cl$_2$	25		75		
SOCl$_2$	40	40	20		
SbCl$_5$	45	10	45		
FeCl$_3$		50	50		

substitution of the proton of the OH group ; further transformation of that intermediate leads to the observed reaction products.

$$Ar_F NHOH + ClY \longrightarrow Ar_F NHO\text{-}Y + HCl \longrightarrow$$

$$\longrightarrow Ar_F NH_2 + Ar_F\text{-}\underset{\underset{O}{\downarrow}}{N}=N\text{-}Ar_F + Ar_F NO$$
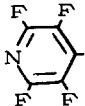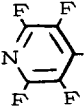
The polyfluorinated N-arylhydroxylamines can be oxidized similarly to their hydrocarbon analogues. The products of oxidation depend on the oxidant used. E.g. the oxidation of 4-hydroxylamino-2,3,5,6-tetrafluoropyridine by CF$_3$COOOH leads to 4-nitro-2,3,5,6-tetra-fluoropyridine "31". The action of MnO$_2$/CH$_2$Cl$_2$ on hydroxylamine "2" leads to the corresponding nitroso- "28" and azoxy- "17" compounds in 1:1 ratio. The oxidation of hydroxylamine "2" by aqueous FeCl$_3$ at 0°C gives mainly 4-trifluoromethyl-2,3,5,6-tetrafluoronitrosobenzene "28".

4-CF$_3$C$_6$F$_4$NHOH

$\xrightarrow[\text{CH}_2\text{Cl}_2,20°\text{C}]{\text{MnO}_2}$ 4-CF$_3$C$_6$F$_4$-$\underset{\underset{O}{\downarrow}}{N}$=N-C$_6F_4CF_3$-4 + "17"

+ 4-CF$_3$C$_6$F$_4$NO "28"

$\xrightarrow[\text{H}_2\text{O, 0°C}]{\text{FeCl}_3}$ "28"
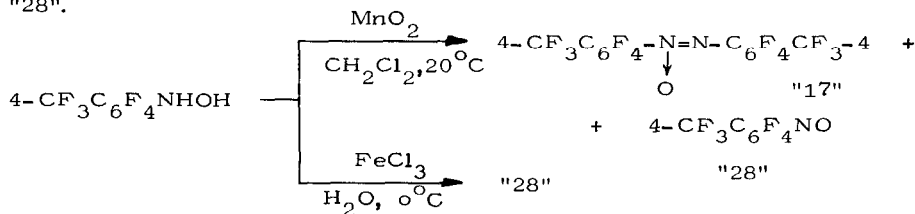
The oxidation of aromatic hydroxylamines, containing a CH fragment in the α -position to the nitrogen atom of the hydroxylamino group is known to be a method of synthesis of C,N-diphenylnitrones in case of non-fluorinated compounds [23]. The oxidation of poly-fluorinated hydroxylamines also has been found by us to lead to nitrones. Thus, N-polyfluoroaryl-N-benzylhydroxylamines and N-poly-fluoroaryl-N- 2,3,4,5,6-pentafluorobenzylhydroxylamines, can be easily oxidized to corresponding nitrones "32a-f" by the action of MnO_2 in benzene at $20°C$.

$$Ar_F\text{-}\underset{\underset{OH}{|}}{N}\text{-}CH_2Ar' \quad \xrightarrow{MnO_2} \quad Ar_F\text{-}\underset{\underset{O}{\downarrow}}{N}\text{=}CH\text{-}Ar'$$

$$\text{"12a-f"} \qquad\qquad\qquad \text{"32a-f"}$$

Ar_F	![F,F ring with N]	![F,F ring with N]	$4\text{-}CF_3C_6F_4$	$4\text{-}CF_3C_6F_4$	$4\text{-}NCC_6F_4$	$4\text{-}NCC_6F_4$
Ar'	C_6H_5	C_6F_5	C_6H_5	C_6F_5	C_6H_5	C_6F_5
	a	b	c	d	e	f

N-Benzyl-N- 2,3,4,5,6-pentafluorobenzylhydroxylamine "32" and N,N-bis-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine "34" obtained by action of 2,3,4,5,6-pentafluorobenzyl chloride on ben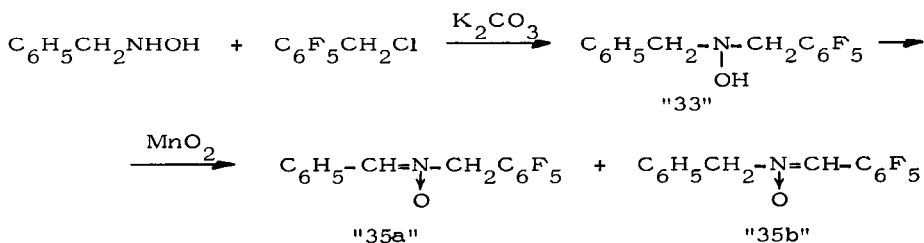zylhydroxylamine and 2,3,4,5,6-pentafluorobenzylhydroxylamine also oxidize easily by that oxidant to form nitrones "35a,b" and "36" respectively.

$$C_6H_5CH_2NHOH \quad + \quad C_6F_5CH_2Cl \quad \xrightarrow{K_2CO_3} \quad C_6H_5CH_2\text{-}\underset{\underset{OH}{|}}{N}\text{-}CH_2C_6F_5 \quad \longrightarrow$$

$$\text{"33"}$$

$$\xrightarrow{MnO_2} \quad C_6H_5\text{-}CH\text{=}\underset{\underset{O}{\downarrow}}{N}\text{-}CH_2C_6F_5 \quad + \quad C_6H_5CH_2\text{-}\underset{\underset{O}{\downarrow}}{N}\text{=}CH\text{-}C_6F_5$$

$$\text{"35a"} \qquad\qquad\qquad\qquad \text{"35b"}$$

The presence of two different CH_2-fragments in N-benzyl-N- 2,3,4,5,6-pentafluorobenzylhydroxylamine leads to two nitrones : C-phenyl-N- 2,3,4,5,6-pentafluorobenzylnitrone "35a" and C-pentafluoro-

phenyl-N-benzylnitrone "35b" in 5:1 ratio (from ^{19}F NMR data). The structures of the nitrones have been proved by ^{1}H and ^{19}F NMR spectra and their independent synthesis by condensation of penta-fluorobenzaldehyde with benzylhydroxylamine and 2,3,4,5,6-penta-fluorobenzylhydroxylamine and also benzaldehyde with 2,3,4,5,6-penta-fluorobenzylhydroxylamine.

The structures of the hydroxylamines and nitrones obtained have been proved by their spectral characteristics (see Table 2). The ^{17}O NMR spectrum of hydroxylamine "12a" contains a signal at 119 ppm, whereas that of the nitrone "32a" contains a signal at 386 ppm being typical for the resonance of the oxygen atom of the nitrone group [24]. The hydroxylamines "1", "12a–f", "33", "34" possess the characteristic absorption bands in their IR spectra at 3530–3570 sm^{-1} assigned to the valence vibration of the free OH groups. The nitrones "32a,c,e", "35a,b" have a long-wave band in their UV spectra at 300–320 nm, being characteristic for aromatic nitrones [25]. The nitrones "32b,d", "35b" and "36" have that band at 275–285 nm ; the observed shift is connected with the influence of a C_6F_5 group. The ^{1}H NMR spectra of hydroxylamines "12a–f", "11", "33" and "34" contain a signal at 4.4–4.8 ppm (CH_2–protons), and nitrones "32a–f", "35a,b" and "36" one at 7.8–8.1 ppm (=CH–proton) (see [25]).

EXPERIMENTAL

The ^{1}H and ^{19}F NMR spectra were measured on a Varian A56/60A instrument at 60 and 56.4 MHz respectively (solvent – CH_3CN ; internal standard HMDS and C_6F_6). The UV spectra were measured for ethanolic solution on Specord UV–VIS spectrophotometer; the IR spectra – for KBr (0.25%) and $CHCl_3$ (1%) solution on Specord 75IR spectrometer.

The kinetic measurements were made according to [26].

N–Benzylhydroxylamine was obtained by [1], O–trimethylsilylic ether of hydroxylamine – by [27].

The reduction of polyfluorinated nitrobenzenes

a) 6 G of 90% zinc powder was added stepwise during 15–20 minutes to a mixture of 4 g of NH_4Cl and 5 g of $C_6F_5NO_2$ in 100 ml of water. An exothermic effect was observed; the temperature rising up to 70°C. After the addition of zinc the reaction mixture was

maintained at 70–80°C during 20 minutes; the hot solution was then filtered. The solid residue was washed with the hot water and extracted with ether. The extract was dried over $MgSO_4$ and evaporated on a rotary vacuum–evaporator to give 3.5 g of $C_6F_5NH_2$ (b.p. 153–154°C), identified by IR and ^{19}F NMR spectra (see [28]).

b) Similarly, the $C_6F_5NO_2$ was reduced at a temperature of 50°C. A mixture of pentafluoroaniline, pentafluorophenylhydroxylamine, pentafluoronitrobenzene and decafluoroazoxybenzene was obtained (the ratio was 3:4:2:1 respectively – from ^{19}F NMR data).

c) Similarly, the reaction of 4–nitroheptafluorotoluene (5 g), NH_4Cl (2 g), Zn (3.5 g), EtOH (5 ml) in 50 ml of water at 50–60°C yielded 4 g of reaction mixture containing 4–aminoheptafluorotoluene, 4–trifluoromethyl–2,3,5,6–tetrafluorophenylhydroxylamine, 4–nitroheptafluorotoluene and 4,4'–bis–(trifluoromethyl)–octafluoroazoxybenzene (5:3:1:1 ratio from ^{19}F NMR data).

d) Similarly, the reaction of 4–nitro–2,3,5,6–tetrafluoropyridine (5 g), NH_4Cl (3 g), EtOH (5 ml) in 50 ml of water at 50–60°C yielded 4 g of reaction mixture containing 4–amino–2,3,5,6–tetrafluoropyridine, 4–hydroxylamino–2,3,5,6–tetrafluoropyridine, 4–nitro–2,3,5,6–tetrafluoro–pyridine and 2,2',3,3',5,5',6,6'–octafluoro–4,4'–azoxypyridine (4:3:1:2 ratio from ^{19}F NMR data).

The interaction of polyfluorinated benzenes with hydroxylamine and its derivatives

a) $NH_2OH·HCl$ (0.1 mol) and triethylamine (0.1 mol) in dioxane (100 ml) were maintained under stirring and bath temperature 110°C during 2 h. After that, 2,3,4,5,6–pentafluorobenzyl chloride (0.02 mol) was added and the reaction mixture was stirred during 5 h, poured into water and extracted with ether. The extract was dried over $CaCl_2$, the solvent was evaporated on a rotary vacuum–evaporator and the residue was recrystallized from petroleum ether (40–70°C). The yield and the characteristics of N–(2,3,4,5,6–pentafluorobenzyl)–hydroxylamine "11" are given in Tables 2 and 4.

TABLE 2

The spectral characteristics of polyfluoroaromatic compounds

| Compound | δ ppm from C_6F_6 | | | | | | UV spectrum | IR spectrum |
| | Ar | | | Ar_F | | | λ max, nm | ν sm^{-1} |
	$F^{2,6}$	$F^{3,5}$	F^4	$F^{2,6}$	$F^{3,5}$	$F^4(CF_3)$	(lg ϵ)	OH (NH)
"8"	20.5	-0.8	6.5	22.2	1.9	11.4	210 (3.92), 264sh(3.10)	
"11"							256 (3.08), 328 (2.65)	3570
"12a"				70.0	12.4		268 (4.12)	3540
"12b"			8.7	71.2	14.3		265 (4.09)	3530
"12c"				18.3	21.1	(109.1)	275 (3.99)	3540
"12d"	21.8	0.0	8.5	18.6	21.6	(108.7)	265 (4.01)	3540
"12e"				18.4	28.9		299 (4.19)	3540
"12f"	21.5	0.0	8.5	18.7	29.0		290 (4.37)	3540
"16"				20.6	0.0	6.3	220 (3.98), 269 (4.06), 310sh(3.93)	
"25"				10.7	-0.9	0.6		(3300)
"27"				23.8	0.0	8.6		
"32a"				75.7	14.2		312 (4.17)	
"32b"	32.1	1.0	13.1	77.3	14.8		279 (4.03)	
"32c"				16.3	24.8	(109.1)	313 (4.29)	
"32d"	31.9	0.9	12.6	16.5	25.4	(108.5)	284 (4.15)	
"32e"				17.0	32.6		301 (4.27), 313sh(4.25)	
"32f"	31.8	1.0	12.9	17.3	33.3		291 (4.18)	
"33"				22.0	-1.1		258 (3.08), 264sh(3.04)	3560

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"34"	21.7	-1.0	6.9	6.9	21.7	-1.0	6.9	259 (3.23), 285sh(2.75)	3560
"35a"					22.0	0.2	9.6	297 (4.33)	
"35b"					29.6	0.2	9.6	279 (4.09)	
"36"	30.0	0.2	10.4	10.4	21.7	0.2	10.4	275 (4.11)	

TABLE 3

The spectral characteristics of polyfluorinated N-arylhydroxylamines

Compound	δ ppm from HMDS		δ ppm from C_6F_6		UV spectrum λ max., nm.	IR spectrum ν sm^{-1}	
	NH	OH	$F^{2,6}$	$F^{3,5}$	(lg ε)	NH	OH
"1"	7.97	7.55	68.5	4.5	251 (4.27)	3350	3560
"2"*	7.66	7.47	8.9	19.2	237 (4.34)	3340	3570
"3"	7.60	7.46	8.1	22.1	280 (4.15)	3350	3570
"4"	7.87	7.38	8.9	27.1	295 (4.39)	3330	3550
"5"**	7.14	7.14	9.7	-1.1	260 (4.14)	3360	3570
"6"	7.33	7.14	9.2	22.4	231 (3.81)	3330	3570
"7"	7.32	7.13	9.6	17.4	273 (4.18)	3330	3570
"9"		7.37	69.2	10.2	267 (4.03)		3560
"13"	8.59		69.7	4.7	247 (4.18)	3330	

* Chemical shift of fluorine atoms of CF$_3$ group - 108.1.

** Chemical shift of F^1 - -1.2.

TABLE 4

The yields and analytical characteristics of polyfluoroaromatic compounds

Compound (formula)	Yield %	M.p., °C	Found,%				Calculated,%			
			C	H	F	N	C	H	F	N
"1" ($C_5H_2F_4N_2O$)	93	80–81	32.36	1.00	41.90	15.25	32.97	1.10	41.76	15.38
			32.11	0.99	42.17					
"2" ($C_7H_2F_7NO$)	90	112.5–113	33.95	0.63	53.35	5.26	33.73	0.80	53.41	5.62
			33.74	0.55	53.03					
"3" ($C_8H_5F_4NO_3$)	80	113–115	39.57	2.13	31.96	5.53	40.17	2.09	31.80	5.86
			39.34	2.09	32.00					
"4" ($C_7H_2F_4N_2O$)	75	88.5–90.5	40.65	0.92	37.03	13.33	40.78	0.97	36.89	13.59
			40.32	1.03	36.80					
"5" ($C_6H_2F_5NO$)	70	101–102	36.18	1.16	47.90	7.31	36.18	1.00	47.74	7.04
			35.96	1.17	48.00					
"6" ($C_6H_3F_4NO$)	70	134–135	39.81	1.83	42.15	7.89	39.78	1.66	41.99	7.73
			39.85	1.72	41.80					
"7" ($C_8H_5F_4NO$)	80	124–126	45.74	2.35	36.26	6.76	46.38	2.41	36.71	6.76
			46.03	2.46	37.00					
"8" ($C_7H_2F_5NO_2$)	69	143–144	36.61	1.02	42.07	6.09	37.00	0.88	41.83	6.17
			36.82	0.83	42.16					
"9" ($C_6H_4F_4N_2O$)	90	41–42	36.96	1.86	38.47	14.39	36.73	2.04	38.77	14.29
			36.69	1.88	38.55					

Compound	Formula	Yield (%)	mp (°C)	Found C	Found H	Found F	Found N	Calc C	Calc H	Calc F	Calc N
"11"		80	110–111	39.75	1.98	44.51	6.87	39.44	1.88	44.60	6.57
	(C₇H₄F₅NO)			39.45	2.15	44.63					
"12a"		60	126–128	52.92	3.14	27.76	10.34	52.94	2.94	27.94	10.29
	(C₁₂H₈F₄N₂O)			53.17	3.21	27.53					
"12b"		55	102–103	39.52	0.84	47.40	7.69	39.78	0.83	47.24	7.73
	(C₁₂H₃F₉N₂O)			39.72	1.02	47.62					
"12c"		65	154–155	49.61	2.23	39.38	4.16	49.56	2.36	39.23	4.13
	(C₁₄H₈F₇NO)			49.95	2.34	38.44					
"12d"		60	152–154	39.25	0.68	53.46	3.46	39.16	0.70	53.15	3.26
	(C₁₄H₃F₁₂NO)			39.32	0.75	53.39					
"12e"		50	156–158	56.87	2.67	25.25	9.56	56.76	2.70	25.63	9.46
	(C₁₄H₈F₄N₂O)			56.99	2.78	25.40					
"12f"		50	125–127	43.48	0.81	44.51	7.14	43.52	0.78	44.30	7.25
	(C₁₄H₃F₉N₂O)			43.64	0.90	44.40					
"13"		85	68.5–69.5	36.82	1.99	38.40	14.06	36.73	2.04	38.77	14.29
	(C₆H₄F₄N₂O)			36.64	1.80	38.60					
"16"		70	51–52	50.68	1.68	33.30	9.72	50.00	1.74	32.99	9.72
	(C₁₂H₅F₅N₂O)			50.43	1.72	33.17					
"25"		49		39.69	3.84	35.50	4.94	39.85	3.72	35.02	5.16
	(C₉H₁₀F₅NOSi)			39.78	3.71	35.30					
"27"		80		43.34	5.14	26.55	4.12	43.97	5.07	26.75	3.95
	(C₁₈H₁₈F₅NOSi₂)			43.47	5.08	26.43					
"32a"		90	163–164	53.17	2.39	27.90	10.34	53.33	2.22	28.15	10.37
	(C₁₂H₆F₄N₂O)			53.41	2.15	27.68					

(continued)

TABLE 4 (cont.)

Compound (formula)	Yield %	M.p., °C	Found,% C	H	F	N	Calculated,% C	H	F	N
"32b" ($C_{12}HF_9N_2O$)	60	118–120	39.79 / 39.78	0.27 / 0.21	48.15 / 48.20	7.57	40.00	0.28	47.50	7.78
"32c" ($C_{14}H_6F_7NO$)	95	212–213	49.90 / 49.66	1.78 / 1.68	39.17 / 39.40	4.13	49.85	1.78	39.47	4.15
"32d" ($C_{14}HF_{12}NO$)	70	136–137	39.22 / 39.16	0.22 / 0.21	53.51 / 53.32	3.18	39.34	0.23	53.40	3.28
"32e" ($C_{14}H_6F_4N_2O$)	90	181–182	57.21 / 57.15	1.82 / 2.07	26.13 / 26.23	9.39	57.14	2.04	25.85	9.52
"32f" ($C_{14}HF_9N_2O$)	80	143–144	43.66 / 43.58	0.23 / 0.25	44.77 / 44.59	7.32	43.75	0.26	44.53	7.29
"33" ($C_{14}H_{10}F_5NO$)	90	120–121	55.63 / 55.74	3.24 / 3.23	31.20 / 31.54	4.76	55.45	3.30	31.35	4.62
"34" ($C_{14}H_5F_{10}NO$)	80	149–151	42.93 / 42.78	1.24 / 1.36	48.07 / 48.12	3.55	42.75	1.27	48.35	3.56
"35a" ($C_{14}H_8F_5NO$)	62	160–162	55.60 / 55.72	2.43 / 2.60	31.62 / 31.45	4.40	55.81	2.66	31.56	4.65
"35b" ($C_{14}H_8F_5NO$)	12	138–139.5	55.70 / 55.89	2.72 / 2.51	31.44 / 31.40	4.59	55.81	2.66	31.56	4.65
"36" ($C_{14}H_3F_{10}NO$)	80	156–158	42.88 / 42.76	0.80 / 0.82	48.78 / 48.66	3.49	42.97	0.77	48.59	3.58

b) K_2CO_3 (0.1 mol) was added under stirring at 20^oC to a solution of $NH_2OH \cdot HCl$ (or $CH_3NHOH \cdot HCl$, $CH_3ONH_2 \cdot HCl$, C_6H_5NHOH) in 40 ml THF (for C_6F_6, C_6HF_5 and $C_6F_5CH=CH_2$ – DMSO). After that the polyfluorinated compound (0.1 mol) was added dropwise and the reaction mixture was stirred during 3 h at 70^oC (or THF – boiling), poured into water and extracted with ether. The extract was dried over $MgSO_4$, the ether was removed on the rotary vacuum-evaporator and residue was recrystallized from CCl_4. The yields and characteristics of products "1" – "7" are given in Tables 3 and 4.

c) 0.02 Mol of pentafluoropyridine (or octafluorotoluene, penta-fluorobenzonitrile) were added to a solution of compound "10" (0.04 mol) in DMF (50 ml) (or in case of compound "11" – DMSO), stirred at 20^oC during 5 h (for compound "11" – 20 h). After that the mixture was poured into water, acidified with HCl and extracted with ether. The extract was dried over $MgSO_4$. After distilling of the solvent the residue was recrystallized from CCl_4. The yields and characteristics of products "12a-f" are given in Tables 2 and 4.

d) 0.02 Mol of pentafluoropyridine (or octafluorotoluene, hexafluo-robenzene) were added to a mixture of compound "10" (0.03 mol) and K_2CO_3 (0.01 mol) in THF. The mixture was stirred during 3 h at bath temperature 80^oC (the reaction conditions with C_6F_6 : DMSO, 6 h, 80^oC), poured into water, acidified with HCl and extracted with ether. The extract was dried over $CaCl_2$. After distilling of the solvent the residue was recrystallized from CCl_4. The compounds "1", "2" and "5" were obtained with yields 55, 70 and 65% respectively.

e) 0.01 Mol of compound "12c" and K_2CO_3 (0.01 mol) in THF (30 ml) were treated under the conditions described above. The compounds "12c" remained unchanged.

f) 0.1 g of CsF were added to a solution of 0.8 g of pentafluoro-pyridine and 0.5 g of O-trimethylsilylic ether of hydroxylamine in 15 ml of THF and stirred at 20^oC for 1.5 h. After that the mixture was poured into water and extracted with ether. A mixture of compounds "1", "14" and "15" was obtained (1:1:1 ratio from ^{19}F NMR data). The pure compounds "1", "14" and "15" were separated and identified by comparison of IR data with authentic samples.

g) Pentafluoropyridine (0.46 g) was added to a solution of 0.5 g of compound "1" and 3 g of triethylamine in 20 ml of THF. An exothermic effect was observed. The solution was stirred during 2 h, poured into water and extracted with ether. The extract was dried over $CaCl_2$ and evaporated on a rotary vacuum-evaporator. A mixture of compounds "14" and "15" was obtained (1:1 ratio from ^{19}F NMR data). The pure compounds "14" and "15" were separated and identified by comparison of IR data with authentic samples.

h) A mixture of 0.01 mol of compound "10" (or "11"), 0.01 mol of 2,3,4,5,6-pentafluorobenzyl chloride and 0.005 mol of K_2CO_3 in 20 ml of DMF was stirred at $20^{\circ}C$ for 5 h (for compound "11" : DMSO, $20^{\circ}C$, 10 h), poured into water, acidified with HCl and extracted with ether. The extract was dried over $CaCl_2$. After evaporation of the solvent on a rotary vacuum-evaporator the residue was recrystallized from petroleum ether ($40-70^{\circ}C$). The yields and characteristics of products "33" and "34" are given in Tables 2 and 4.

The interaction of N-arylhydroxylamines with aromatic aldehydes and nitrosobenzenes

a) A mixture of 0.5 g of compound "2" and 0.21 g of benzaldehyde in 5 ml of EtOH was heated at $70^{\circ}C$ for 10 h. The solution was concentrated on a rotary vacuum-evaporator and its ^{19}F and ^1H NMR spectra were recorded. As indicated by the spectra the mixture contained only initial compounds.

b) A mixture of 0.64 g of compound "2" and 0.5 g of pentafluorobenzaldehyde was heated at $100^{\circ}C$ for 5 h. As followed from ^{19}F NMR spectrum, the mixture contained compounds "2", "17", "18" and pentafluorobenzaldehyde (1:3:3:10 ratio).

c) A mixture of 0.5 g compound "5" and 0.49 g of pentafluorobenzaldehyde in 5 ml of EtOH was heated at $70^{\circ}C$ for 5 h. The solution was concentrated on a rotary vacuum-evaporator and its ^{19}F NMR spectrum was recorded. As followed from the spectrum, the mixture contained compound "5", decafluoroazoxybenzene, pentafluoroaniline and pentafluorobenzaldehyde (1:10:10:30 ratio).

d) A mixture of 1 g of compound "2", 0.79 g of pentafluorobenzaldehyde and 0.05 g of 4-toluenesulphonic acid in 50 ml of benzene

was boiled for 4 h. The solution was concentrated on a rotary vacuum-evaporator and its ^{19}F NMR spectrum was recorded. As followed from the spectrum, the mixture contained pentafluorobenzalde-hyde, compound "2" (3:1 ratio) and non-identified products.

e) A solution of 0.5 g of nitrosobenzene and 1 g of compound "5" in 10 ml of EtOH was maintained at $20^{\circ}C$ for 24 h. After evapo-ration of solvent on a rotary vacuum-evaporator the residue was recrystallized from EtOH to give 0.8 g of compound "16". The yield and characteristics of compound "16" are given in Tables 2 and 4.

f) A solution of 1 g of pentafluoronitrosobenzene and 0.5 g of phenylhydroxylamine in 10 ml of EtOH was maintained at $20^{\circ}C$ for 1 h. After evaporation of solvent on a rotary vacuum-evaporator the residue was recrystallized from EtOH to give 0.5 g (34%) of compound "16" identical with the sample from the previous experiment.

Oxidation of 2,3,4,5,6-pentafluoroazobenzene

2,3,4,5,6-Pentafluoroazobenzene (0.54 g) was added to a solution of trifluoroacetic peracid obtained by addition of 1 ml of 80% hydrogen peroxide to 2 ml of trifluoroacetic anhydride in 20 ml of CH_2Cl_2, and the mixture was boiled under stirring for 5 h. Then the reaction mixture was washed with water, the organic layer was separated and dried over $MgSO_4$. After evaporation of solvent on a rotary vacuum-evaporator the residue was recrystallized from EtOH to give 0.5 g (87%) of compound "16" identical with samples from the previous two experiments. Mixing of this sample with those from the previous two experiments did not result in m.p. depression.

Thermolysis of compounds "1" and "2"

a) Compound "1" was heated for 10 h in a sealed tube at $120-125^{\circ}C$, and the ^{19}F NMR spectrum was recorded. As followed from the spectrum, the mixture contained compounds "1", "14" and 2,2',3,3',5,5',6,6'-octafluoro-4,4'-azoxypyridine (1:3:3 ratio). The latter product was obtained with analytical purity by crystallization from petroleum ether ($40-70^{\circ}C$) with yield 1 g (70%). M.p. $96-97^{\circ}C$. Analy-sis : Found : C, 34.83, 35.06; F, 44.26, 44.38; N, 16.17%. $C_{10}F_8N_4O$ requires C, 34.88; F, 44.19; N, 16.28%. ^{19}F NMR spectrum (δ ppm) :

16.1 ($F^{3,5}$), 21.1 ($F^{3',5'}$), 73.7 ($F^{2,6}$), 78.1 ($F^{2',6'}$). UV spectrum , λ_{max} (lg ε) : 238 (4.21), 278 (3.72).

b) Compound "2" was heated for 15 h in a sealed tube at 110–115°C, and the ^{19}F NMR spectrum was recorded. As followed from the spectrum, the mixture contained compounds "2", "17" and "18' (1:2:2 ratio).

Reaction of compounds "5" and "6" with acids

a) Compound "6" was added stepwise during an hour to 10 ml of H_2SO_4 (d = 1.89) at -40°C. Then the mixture was maintained at 20°C for 72 h, poured into water, extracted with ether and dried over $MgSO_4$. After evaporation of the solvent on a rotary vacuum–evaporator the residue was recrystallized from water to give 0.45 g (90%) of compound "19", m.p. 177–178°C (m.p. 177.5–178°C [29]). ^{19}F NMR spectrum (δ ppm) : -1.1 ($F^{3,5}$), 0.2 ($F^{2,6}$).

b) Similarly, compound "5" (or "6") reacted with HSO_3Cl to give fluoroanil, identified by the IR and ^{19}F NMR spectra.

c) Trifluoroacetic acid (5 ml) was added to solution of compound "5" in 20 ml of CCl_4 at 20°C. The mixture was stirred for 1 h, washed with water, dried over $MgSO_4$. After evaporation of solvent on a rotary vacuum–evaporator the ^{19}F NMR spectrum was recorded to show the residue to contain only the decafluoroazoxybenzene.

The silylic derivatives of compounds "5" and "8"

a) Hexamethyldisilazane (5 g) was added to solution of 3 g of compound "5" and maintained at 20°C for 48 h. After vacuum distillation 2 g of compound "25" were obtained (b.p. 50°C/3·10^{-2} Torr). The yield and characteristics of compound "25" are given in Tables 2 and 4.

b) Compound "25" was maintained for 2 months in a sealed tube at 20°C. As followed from the ^{19}F NMR spectrum, decafluoroazoxy-benzene was the main product present in the mixture.

c) A mixture of $NH_2OH \cdot HCl$ (5 g) and K_2CO_3 (10 g) in dioxane (50 ml) was stirred at bath temperature 110°C for 3 h. After that, pentafluorobenzoyl chloride (10 g) was added to the mixture at 20°C

The mixture was stirred for 0.5 h, poured into water, extracted with ether and dried over $MgSO_4$. After evaporation of solvent the residue was recrystallized from benzene to give 7 g of compound "8", m.p. 143–144°C (see [30]). The yield and characteristics of compound "8" are given in Tables 2 and 4.

d) Hexamethyldisilazane (8.4 g) was added to a solution of 3.9 g of compound "8" and maintained at 20°C for 48 h. After vacuum distillation 4.9 g of compound "27" were obtained (b.p. 75°C/3·10^{-2} Torr). The yield and characteristics of compound "27" are given in Tables 2 and 4.

e) Compound "27" was passed through a quartz tube (l = 30 sm, d = 1 sm) at 300°C. The vapour was condensed in a cooled trap (T = −50°C). The liquid obtained was distilled and the fraction boiling at 147–150°C (see [31]) collected. Yield of compound "26" was 5 g (85%). ^{19}F NMR spectrum (δ ppm) : 0.4 ($F^{3,5}$), 3.7 (F^4), 14.3 ($F^{2,6}$).

The reactions of compounds "2" and "8" with PCl_5, PCl_3, SO_2Cl_2, $SOCl_2$, $SbCl_5$ and $FeCl_3$

0.02 Mol of PCl_5 (or PCl_3, SO_2Cl_2, $SOCl_2$, $SbCl_5$, $FeCl_3$) were added to a solution of compound "2" (0.01 mol) (or 0.01 mol of compound "8" in case of PCl_5 and $SOCl_2$) in CH_2Cl_2 (100 ml). The mixture was maintained at 20°C for 20 h. The solvent was evaporated under reduced pressure. In the cases of $SbCl_5$ and $FeCl_3$ the mixture previously was washed with water and dried over $MgSO_4$. The composition of reaction mixtures are given in Table 1.

Compounds "28" and "30" were obtained from vacuum distillation of a reaction mixture of compound "2" with PCl_5. Compound "28" – b.p. 50°C/2·10^{-2} Torr, m.p. 63°C (from EtOH). Analysis : Found : C, 34.42, 34.46; F, 53.15, 53.46; N, 5.53%. C_7F_7NO requires C, 34.04; F, 53.85; N, 5.67%. ^{19}F NMR spectrum (δ ppm) : 3.7 ($F^{2,6}$), 24.2 ($F^{3,5}$), 106.8 (CF_3). UV spectrum, λ_{max} (lg ϵ) : 266 (3.95), 273sh (3.91), 345 (3.19). Compound "30" – b.p. 70°C/2·10^{-2} Torr. Spectral characteristics of compound "30" are identical with those described in [20].

Oxidation of polyfluorinated N-arylhydroxylamines

a) A solution of 10 g of compound "2" in 20 ml of EtOH was added to a solution of 20 g of $FeCl_3$ in 1000 ml of water at $0^{\circ}C$ and vigorously stirred for 5-10 min. After that the mixture was extracted with CH_2Cl_2 and dried over $MgSO_4$. After evaporation of solvent on a rotary vacuum-evaporator the residue consisted of compounds "17" and "28" (1:4 ratio from ^{19}F NMR data). Compound "28" (5.1 g (51%)) was obtained by vacuum distillation ($80^{\circ}C/2$ Torr). Its m.p., analytical and spectral characteristics are identical with those from the previous experiment.

b) A mixture of compound "2" (1 g) in CH_2Cl_2 (50 ml) and MnO_2 (1 g) was stirred at $20^{\circ}C$ for 3 h and was filtered. After evaporation of solvent on a rotary vacuum-evaporator the residue consisted of compounds "17" and "28" (1:1 ratio from ^{19}F NMR data).

c) Compound "1" (1 g) was added to a solution of trifluoro-acetic peracid obtained by addition of 1.2 ml of 80% hydrogen peroxide to 2 ml of trifluoroacetic anhydride in 30 ml of $CHCl_3$ and the mixture was boiled under stirring for 5 h. Then the reaction mixture was washed with water, the organic layer was separated and dried over $MgSO_4$. After distillation 0.6 g (56%) of compound "31" were obtained (b.p. 152-154$^{\circ}C$ (see [32]).

d) A mixture of 0.01 mol of compound "12a" (or "12b-f", "33", "34") in benzene (50 ml) and 0.03 mol of MnO_2 was stirred at $20^{\circ}C$ for 2 h and filtered. After evaporation of solvent on a rotary vacuum-evaporator the residue was recrystallized from CCl_4. Yields and characteristics of products "32a-f", "35a,b" and "36" are given in Tables 2 and 4.

The oxidation of compound "33" leads to a mixture of two nitrones. Its ^{19}F NMR spectrum contains 4 signals (δ ppm) : 29.6, 22.0, 9.6 and 0.2 (1:5:3:6 ratio). Signals at 22.0, 9.6 and 0.2 ppm belong to nitrone "35a", isolated from the reaction mixture by crystalli-zation from CCl_4. Signals at 29.6, 9.6 and 0.2 ppm belong to nitrone "35b".

Synthesis of nitrones "35a,b" and "36"

A solution of 0.01 mol of benzaldehyde (or pentafluorobenzalde-hyde) and 0.01 mol of compound "11" (or "10" in the case of penta-

fluorobenzaldehyde) was maintained at $20^{\circ}C$ for 24 h. The crystals obtained were filtered off and recrystallized from CCl_4. Yields of nitrones "35a", "35b" and "36" were 70, 80 and 60% respectively. Their characteristics are in accordance with those given in Tables 2 and 4.

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