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AROMATIC FLUORODERIVATIVES. XCV. THE INVESTIGATION OF THE BEHAVIOUR OF THE POLYFLUOROAROMATIC COMPOUNDS CONTAINING GROUP VA ELEMENTS IN ACID MEDIA

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SUMMARY

The formation of the stable phosphonium ions from polyfluoroaromatic phosphines of $C_6F_5PX_2$ type [$X = H, CH_3, C_6H_5, C_6F_5, Cl, F, NCS, CN, OCH_3, N(C_2H_5)_2$] in HSO_3F-SbF_5 (1:1) at -70 to $-10^\circ C$ has been shown, as well as the transformation of the investigated phosphines in HSO_3F at $20^\circ C$ into the pentavalent phosphorus derivatives. The same processes take place also for the trivalent arsenic and antimony derivatives. The possible routes of the latter reaction together with the determining factors have been discussed. The unusual formation of the protonated form of difluoroanhydride of pentafluorobenzene-phosphonic acid from $C_6F_5P(OCH_3)_2$ and $C_6F_5P(CN)_2$ in HSO_3F has been found. The generation of nitrenium cations from the polyfluorinated nitrosobenzenes in the strong acids at $-60^\circ C$ has been proved. At $20^\circ C$ in the same media these cations undergo oxidation leading to the corresponding nitrobenzenes. The influence of the acidity of media on the reactions of nitrosobenzenes has been investigated.

INTRODUCTION

The electronic structures of polyfluoroaromatic phosphines have been shown by us recently to differ substantially from those of the hydrocarbon analogues of the latter [1]. Thus, the presence of fluorine atoms as substituents in the aromatic rings of aromatic phosphines leads to an increase of the ionization

potential (IP) of highest occupied MO (HOMO) and, as a rule, to the increase of the contribution of $3p(P)$ -AO in it. The positive charge on the phosphorus atom also increases [1], leading to less basicity of polyfluoroaromatic phosphines compared with hydrocarbon analogues [2]. But on the whole the properties of polyfluoroaromatic phosphines (and the analogous derivatives of the other group VA elements) as Lewis bases have been investigated rather poorly [3]. The latter fact makes worthwhile a more detailed examination of the influence of polyfluoroaryl fragments on the reactivity of these compounds towards electrophilic agents. Protonation was the reaction studied: it has been the subject of a number of investigations in the series of the corresponding hydrocarbon derivatives of group VA elements (see, e.g. [4,5]).

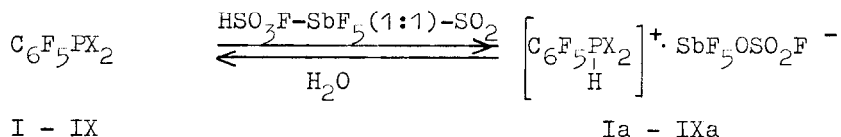
The present work is devoted to the investigation of the behaviour of polyfluoroaromatic compounds containing group VA elements in acid media and the reactivity of generated cationic species. The following compounds have been chosen as the objects of that investigation: $(C_6F_5)_3P$ (I), $(C_6F_5)_2(C_6H_5)P$ (II), $(C_6F_5)(C_6H_5)_2P$ (III), $C_6F_5PH_2$ (IV), $C_6F_5P(CH_3)_2$ (V), $C_6F_5P(OCH_3)_2$ (VI), $C_6F_5PF_2$ (VII), $C_6F_5PCl_2$ (VIII), $C_6F_5P(NCS)_2$ (IX), $C_6F_5P[N(C_2H_5)_2]_2$ (X), $C_6F_5P(CN)_2$ (XI), $(C_6F_5O)_3P$ (XII), $(C_6F_5)_3As$ (XIII), $(C_6F_5)_3Sb$ (XIV), C_6F_5NO (XV), 4- HC_6F_4NO (XVI), $C_6F_5PH(O)(OCH_3)$ (XVII), $(C_6F_5)_3P=O$ (XVIII), $C_6F_5POF_2$ (XIX), $C_6F_5P(O)(OH)_2$ (XX), $(C_6H_5)_3P$ (XXI), $(C_6H_5)_3P=O$ (XXII), $C_6F_5P(O)(OCH_3)_2$ (XXIII), $(C_6F_5)_3As=O$ (XXIV), N-(pentafluorophenyl)piperidine (XXV), N-(pentafluorophenyl)piperidine oxide (XXVI).

RESULTS AND DISCUSSION

The first stage of the protonation of phosphines in acids has been widely examined [4-10]. The solvation of aromatic phosphines [5], alkylated phosphites and thiophosphites [6,7] in HSO_3F has been shown to lead to protonation on phosphorus, and formation of the corresponding phosphonium ions. Comparison of the electronic structures of aromatic and polyfluoroaromatic derivatives of trivalent phosphorus [1] does not lead to a

conclusion about the possibilities of their different chemical behaviour at that stage, though the lower basicity of polyfluoroaromatic phosphines requires stronger acids for their protonation.

The solvation of polyfluoroaromatic phosphines of $C_6F_5PX_2$ type (I)-(IX) in superacid HSO_3F-SbF_5 (1:1)- SO_2 at -70 to $-10^\circ C$ has been shown by us to lead to the formation of species protonated on the phosphorus atom.



The ^{19}F NMR spectra of the cations (Ia) - (IXa) (Table 1) show the typical downfield shift of fluorine atom signals with respect to the precursors being the largest in the cases of para-fluorine atoms. The 1H NMR spectra of these solutions show a doublet (because of the interaction with phosphorus atoms). The ^{31}P signals in the corresponding spectra also have doublet structure (P-H interaction), but each component is split into multiplets because of interaction with ortho-fluorine atoms of the polyfluoroaromatic ring. The ^{31}P signals of the ions (Ia) - (Va) are shifted downfield with respect to their precursors. That situation is typical for phosphonium ions [5,11,12]. But at the same time the ^{31}P signals of the phosphonium cations (VIa) - (IXa) and also (XIIa), generated from compound (XII) under similar conditions, are shifted upfield with respect to their precursors (Table 1). That direction of signal shifts on protonation has been noted earlier for trialkyl- and triarylphosphites [6,13], thiophosphites [7] and phenyldichlorophosphine [10].

The upfield shift of the ^{31}P signal on the protonation of the compounds (VI) - (IX), (XII) being rather unusual for phosphonium ions, together with doublet splitting because of P-H interaction, lead to the possible assignment of the shifted ^{31}P signal to the phosphonium ion (VIa) - (IXa), (XIIa) or to a phosphorane formed as a result of the interaction of the former with the medium anion.

TABLE 1

^1H , ^{19}F and ^{31}P NMR data for the solutions of polyfluoroaromatic phosphines in various solvents

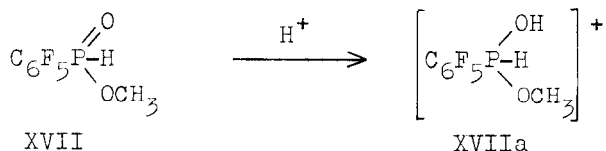
Compd	Medium (temperature, °C)	Chemical shift p.p.m. (spin-spin coupling constants, Hz) from						^{31}P * { relative intensity } ($^1\text{J}(\text{P-H})$)
		^1H (CH_2) ₄ Si ($^1\text{J}(\text{H-P})$)	^{19}F		^{31}P			
			F at P	F ^{2,6}	F ^{3,5}	F ⁴	C ₆ F ₆	
I	CH ₃ CN (20)			-33.2	-2.3	-14.4	74.9	
	HSO ₃ F (30)			-39.0	-10.1	-33.2	-30.1	
	HSO ₃ F-SbF ₅ (1:1) (-60)	9.65(594)		-38.5	-10.4	-32.3	47.1(594)	
	HSO ₃ F-SbF ₅ (1:1) (30)	9.68(594)		-38.5	-11.0	-34.4	47.6(594)	
II	CH ₃ CN (30)			-33.7	-1.8	-12.2	42.5	
	HSO ₃ F-SbF ₅ (30)	9.23(560)		-38.1	-9.1	-30.0	31.4(560)	
III	CH ₃ CN (30)			-35.2	-1.6	-11.5	25.1	
	HSO ₃ F-SbF ₅ (1:1) (30)	8.98(534)		-34.4	-5.7	-24.3	11.5(534)	
IV	CH ₂ Cl ₂ (30)	3.76(208)		-34.6	0.7	-8.5	183.1(208)	
	HSO ₃ F-SbF ₅ (1:1) (30)	7.33(544)		-38.5	-8.0	-28.9	86.9(544)	
V	CH ₃ CN (30)			-31.2	-0.5	-8.9	47.3	
	HSO ₃ F (30)	7.35(534)		-34.8	-5.9	-24.3	12.4(534)	
	HSO ₃ F-SbF ₅ (1:1) (30)	7.39(534)		-35.0	-7.1	-25.7	12.4(534)	

XVII	CH ₂ Cl ₂ (30)	3.16, 7.00 (652)							8.8 (652)
	HSO ₃ F (-30)	3.86, 8.00 (725)							-38 (725)
	HSO ₃ F-SbF ₅ (1:1) -	3.86, 8.00 (725)							-38 (725)
	SO ₂ ClF (-60)	8.51 (0-H)							
	HSO ₃ F (30)		-107.8 (1100)						2.3 (1100**)
XIX	HSO ₃ F-SO ₂ (-70)								
	CH ₂ Cl ₂ (30)								2.1 (1100**)
	HSO ₃ F (30)								5.5 (1140**)
	HSO ₃ F-SbF ₅ (1:1) (30)								2.1 (1100**)
									2.1 (1100**)
XXI	CH ₃ CN (30)								5.9
	HSO ₃ F-SbF ₅ (1:1) (30)	8.48 (510)							-7.3 (510)
	HSO ₃ F (30)	8.48 (510)							-7.3 (510)
	HSO ₃ F (30)								-55.7 ***
									-26.5
XXII	CH ₃ CN (30)								
	HSO ₃ F (30)								-57.3
	HSO ₃ F-SbF ₅ (1:1) (30)								-55.6
XXIII	CH ₂ Cl ₂ (30)								-6.5 {3}, -4.9 {2}
	HSO ₃ F (30)								-19.5 {3}, -17.1 {2}

* The upfield values of the ³¹P chemical shifts from 85% H₃PO₄ have been taken as positive;

** ¹J (³¹P-¹⁹F); *** After 10 hrs at 30°C.

The allocation of the assignment has been made by us taking compound (VI) as an example. We have studied the protonation of a model compound - the methyl ester of pentafluorobenzenephosphonous acid (XVII), occurring on the oxygen atom of the phosphoryl group (at -40°C in $\text{HSO}_3\text{F}-\text{SbF}_5$ (1:1) and HSO_3F , cf. [14]). The ion generated in this way (XVIIa) can be taken as a model for the ion (VIa) , differing from the latter by having a hydrogen atom at oxygen instead of a methyl group.



The structure of the ion (XVIIa) has been proved by ^1H , ^{19}F and ^{31}P NMR data (Table 1). The proximity of ^{31}P chemical shifts and the structure of corresponding ^{31}P signals for the cations (VIa) and (XVIIa) supports the assignment of the doublet at $-44,3$ p.p.m. in the ^{31}P spectrum of the solution of compound (VI) in $\text{HSO}_3\text{F}-\text{SbF}_5$ (1:1)- SO_2 (Table 1) to the cation (VIa) and not to the corresponding phosphorane.

In the cases of the phosphines (X) and (XI) the protonation occurs on the nitrogen atoms. The corresponding ^{31}P signals ($\text{HSO}_3\text{F}-\text{SbF}_5$ (1:1)- SO_2 at -70°C) are shifted downfield, but splitting by the hydrogen atom has not been observed (Table 1) and the ^1H NMR spectra contain the broad signal at 6.63 and 6.78 p.p.m. (N-H protons).

Hydrolysis of the solutions of the investigated phosphines in $\text{HSO}_3\text{F}-\text{SbF}_5$ (1:1) leads to recovery of the initial compounds in practically quantitative yield, and in the case of compounds (VII) and (VIII), because of their further hydrolysis, the pentafluorobenzenephosphonous acid has been obtained.

The analysis of ^1J (P-H) coupling constants in phosphonium ions shows their dependence on the nature of substituents at the phosphorus atom. The ^1J (P-H) value has been noticed earlier to characterize the availability of the phosphorus lone electron pair towards proton attack [15] and has been connected with the

change of $3s(P)$ -AO character of the P-H bond in phosphonium ions [15,16] and also with the electronegativities of the substituents at phosphorus atom [15]. A linear correlation has been found to exist between 1J (P-H) values and the sum of cubes of charges (calculated by CNDO/2 method) on phosphorus and hydrogen atoms in the corresponding phosphonium ions [17,18].

As follows from the data of Table 1, the 1J (P-H) values for protonated forms of investigated phosphines increase with the increase of positive charge on the phosphorus atom in precursors, the latter being characterized by X-ray $PK\alpha$ -shift value measured by us in [1]. In this case the corresponding dependence is linear.

$$^1J ({}^{31}P-^1H) = 1057 \Delta PK\alpha + 485 \quad (1)$$

$$r = 0.987, s = 31, n = 11$$

As the value of $PK\alpha$ -shift can be directly connected with the basicity of corresponding phosphines [2], the equation (1) together with the data presented in [2] leads to the conclusion that the 1J (P-H) for the protonated form of the phosphine can be used as at least a qualitative measure of the basicity of the latter.

The ions (Ia) - (IXa) have been found to be stable and to remain unchanged when the corresponding solutions in HSO_3F-SbF_5 (1:1) are kept at room temperature during a few months. This probably can be connected with the relatively small reactivity of the complex fluoroantimonate anion. The change of the anion of the medium to a more nucleophilic one (with sufficient acidity of corresponding medium) can be expected to lead to the second stage of the investigated reaction, namely the interaction of the phosphonium ion formed with the anion of the medium, to give a phosphorane or the products of the transformations of the latter under the reaction conditions. Such interaction has been realized for polyfluoroaromatic phosphines in fluorosulphonic acid because of sufficient acidity of the latter and the relatively high nucleophilicity of the fluorosulphate-anion.

The solvation of investigated phosphines (I) - (IX) in HSO_3F at -70°C has been found to lead initially to phosphonium ions (Ia) - (IXa). But the raising of the temperature to 20°C causes irreversible transformations of the latter. Thus, the doublet signal at 47.6 p.p.m. in the ^{31}P NMR spectrum of the solution of compound (I) in HSO_3F at 20°C disappears and a new signal (singlet) at -30.1 p.p.m. is observed; the proton signal at 9.68 p.p.m. in the corresponding ^1H NMR also disappears, while the shifts of fluorine atoms in the ^{19}F NMR spectrum remain practically unchanged (Table 1). Subsequent cooling of the solution to -70°C does not lead to the reverse transformation. Hydrolysis of the solution leads to tris(pentafluorophenyl)phosphine oxide (XVIII).

The presence of electron-acceptor substituents on the phosphorus atom must be expected to facilitate the second stage of the reaction - the interaction with medium anion - but the occurrence of the first stage - the protonation - becomes unfavourable because of the increase of positive charge on phosphorus. Thus, phosphorus trifluoride does not protonate in HSO_3F at -60°C [19]. But in spite of the relatively high positive charge on phosphorus, compound (VII) forms under these conditions the phosphonium ion (VIIa) (see ^1H , ^{19}F and ^{31}P NMR data in Table 1). The raising of the temperature to 20°C leads to the evolution of HF and SO_2 and the formation of the protonated form $[\text{C}_6\text{F}_5\text{PF}_2\text{-OH}]^+$ (XIXa) of pentafluorophenylphosphonic acid difluoroanhydride (XIX). Indirect evidence for the structure of the cation (XIXa) can be obtained from the identity of chemical shifts of phosphorus and fluorine between the possible cation (XIXa) formed as mentioned above and the cation obtained by the solvation of the compound (XIX) in HSO_3F at 20°C (Table 1). The action of HSO_3F (equimolar amount) on compound (VII) in 1,1,2-trichloro-1,2,2-trifluoroethane solution at 20°C is accompanied by the evolution of HF and SO_2 and leads to compound (XIX) with almost quantitative yield. The hydrolysis of this solution gives pentafluorophenylphosphonic acid (XX).

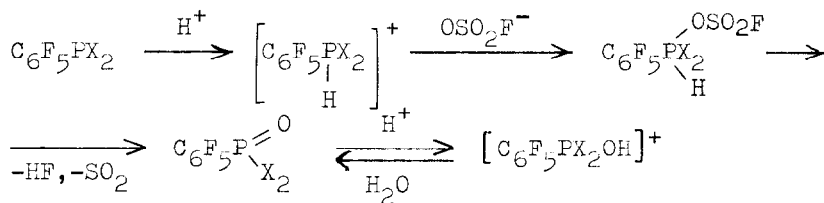
The cations (IVa) and (Va) remain unchanged in HSO_3F , possibly because of their lower electrophilicity because of the donor effect of hydrogen and methyl substituents towards positively charged tetracoordinated phosphorus atom. Taking into account that the charge on phosphorus (and the electrophilicity of the corresponding cation) is mainly determined by the inductive effect of substituents bound to it [2] the phenyl group could be expected to be an intermediate case between these substituents and pentafluorophenyl, indicating that the second stage of the investigated reaction leading to phosphine oxide can occur, e.g. for triphenylphosphine (XXI), but with substantially reduced rate. Thus, Olah and co-workers [5] has not found on the protonation of compound (XXI) in HSO_3F at -60°C any phosphonium ions except the protonated form $[(\text{C}_6\text{H}_5)_3\text{P}-\text{OH}]^+$ (XXIa). But the raising of the temperature of this solution has been shown by us to lead to the slow irreversible transformations of the cation (XXIa). In the ^{31}P NMR spectrum a new signal at -55.7 p.p.m. has been observed, and its intensity has increased with time. After 4 hrs it is equal to 27 %, after 50 hrs to 43 % with respect to the intensity of the signal of the cation (XXIa) at -7.3 p.p.m. (Table 1). The intensity of the signal of proton on phosphorus in the ^1H NMR spectrum (8.48 p.p.m.) decreases, while for the analogous solution in $\text{HSO}_3\text{F}-\text{SbF}_5$ (1:1) it remains constant with time. Hydrolysis of the solution of compound (XXI) in HSO_3F maintained during 150 hrs at 20°C leads to triphenylphosphine oxide (XXII) in 89 % yield. The characteristics of the ^1H and ^{31}P NMR spectra of the solution after the reaction are identical to those for the solution of compound (XXII) in HSO_3F at 20°C (Table 1).

Thus, a quantitative difference in the reactivity of phosphonium ions has been observed depending on the influence of the substituents at phosphorus (particularly, the pentafluorophenyl group) on the charge on phosphorus connected with the electrophilicity of the corresponding phosphonium ions. E.g. because of the high electron-acceptor properties of the CH_2O -group towards phosphorus bonded with it leading to the high positive charge in methoxy-substituted phosphines (see [1]) the occurrence of the irreversible transformation would be

expected for the compound (VI) in solution in HSO_3F . In fact, in this case the reaction takes place, but the formation of the ion $[\text{C}_6\text{F}_5\text{PF}_2\text{-OH}]^+$ (XIXa) instead of the protonated form $[\text{C}_6\text{F}_5\text{P}(\text{OCH}_3)_2\text{OH}]^+$ (XXIIIa) of the dimethyl ester of pentafluorophenylphosphonic acid (XXIII) has been found.

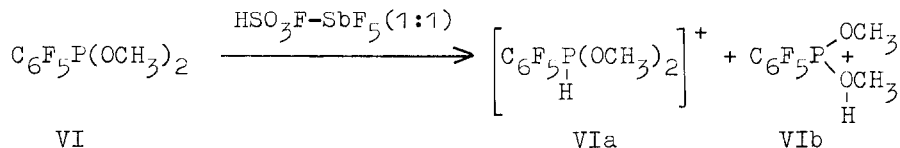
The formation of tertiary phosphine oxide in acid media has been observed earlier in the case of diphenyl(4-diphenylmethanol)phosphine [20], but the protonation of this compound occurs at the oxygen atom of the oxy-group not bonded to phosphorus. It should be noticed that the fact of phosphine oxide formation did not attract the authors attention in the latter work.

A possible route for the observed transformation involves interaction between the initially formed phosphonium ion and the medium anion leading to corresponding phosphorane. The formation of monohydrophosphoranes has been shown earlier, e.g., in the reaction of aryl dichlorophosphines with HF [21] and in the reaction of the alcohols with phenyldifluorophosphine [22]. Solvation of compound (VI) in HF-SbF_5 (10:1) has been found by us to lead to the phosphorane $\text{C}_6\text{F}_5\text{PF}_3\text{OCH}_3$. The ^{31}P NMR spectrum of this solution contains a signal at 29.3 p.p.m. with quartet structure ($^1J(^{31}\text{P-}^{19}\text{F}) = 917 \text{ Hz}$; cf. ^{31}P NMR spectrum of phosphorane $\text{C}_6\text{F}_5\text{PF}_3\text{OC}_6\text{F}_5$: quartet at 57.1 p.p.m. with $^1J(^{31}\text{P-}^{19}\text{F}) = 925 \text{ Hz}$ [23]). The detailed mechanism of the further transformations of phosphorane has not been established reliably. As a possible route, in our reactions the elimination of HF and SO_2 from phosphoranes leading to phosphine oxides (intermolecular oxidation - reduction) can be taken into account. In that case the final products of transformations must represent the protonated forms of phosphine oxides observed in the ^1H , ^{19}F and ^{31}P NMR spectra. IR spectral data obtained by us indicate that the gas evolved from the phosphine solutions in HSO_3F is a mixture of HF and SO_2 . The ^{19}F and ^{31}P NMR spectral data, e.g., for compound (I) solution in HSO_3F maintained at 20°C during 30 min. have been found to be identical to those for compound (XVIII) in solution in that acid. Overall the observed reaction can be presented in following way :



The possibility of delocalization of the positive charge in the oxygen-containing phosphonium ion $[\text{C}_6\text{F}_5\text{PX}_2\text{OH}]^+$ compared with the initial ion $[\text{C}_6\text{F}_5\text{PX}_2\text{H}]^+$ because of $d_{\pi}-p_{\pi}$ -interaction between phosphorus and oxygen can facilitate this process.

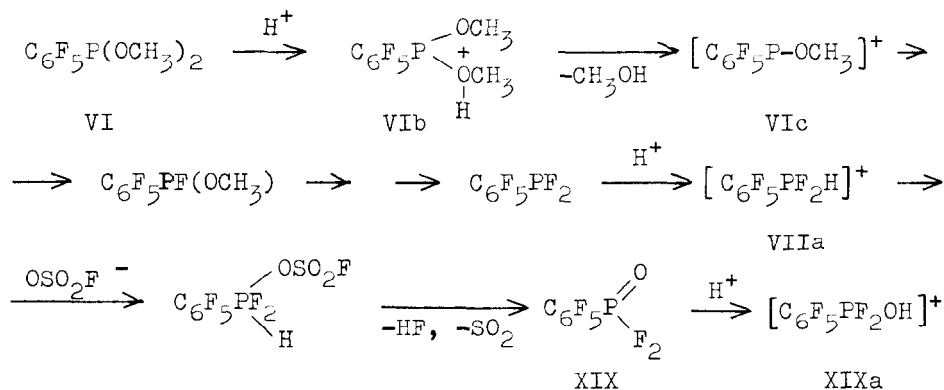
In the previous work [1] we have shown that the substituents bonded to phosphorus by the oxygen and nitrogen atoms act as effective acceptors towards phosphorus. In the cases of such compounds the possibility for competitive protonation on phosphorus and heteroatom exists. E.g. the solvation of compound (VI) in acids can lead to proton attack directed on phosphorus or on oxygen. The ^{31}P NMR spectrum of the solution of the compound (VI) in $\text{HSO}_3\text{F}-\text{SbF}_5$ (1:1) at -70°C contains a singlet of relatively low intensity at -67.6 p.p.m. and an intense doublet at -44.3 p.p.m. with 1J ($^{31}\text{P}-^1\text{H}$) = 754 Hz (Table 1). The singlet signal can be assigned to the oxygen-protonated form (VIb) and the doublet to the phosphonium ion (VIa).



It should be noticed that the ratio of the ions (VIa) and (VIb) is opposite to that expected according to the suggestion that the interaction of the investigated phosphine with hard acid (proton) must be determined by the charges on heteroatoms at the possible reaction centres ([24]; see also [1]). That fact can be connected with the localization of the highest occupied MO (HOMO) in compound (VI) mainly on the phosphorus atom [1]. The necessity of taking of the localization of HOMO in the substrate into account in the protonation reaction has been noticed in the literature [24-26].

A more complicated situation has been observed in the solvation of compound (VI) in HSO_3F . The ^{31}P NMR spectrum of this solution at -70°C contains, besides the intense doublet of the phosphonium ion (VIa) at -44.3 p.p.m. two singlets of low intensity at -25.5 and -34.3 p.p.m. and also a doublet at -66.7 p.p.m. ($^1J(^{31}\text{P}-^1\text{H}) = 792$ Hz), each component of the latter being split into triplets with $^1J(^{31}\text{P}-^{19}\text{F}) = 1180$ Hz. Raising the temperature of this solution leads to the evolution of HF and SO_2 and the following changes in the ^{31}P NMR spectrum: decrease of the intensity of the signal at -44.3 p.p.m., increase of the signal at -66.7 p.p.m. and the appearance of a new signal at 2.1 p.p.m. a triplet with $^1J(^{31}\text{P}-^{19}\text{F}) = 1100$ Hz. The latter signal has been established by us to belong to the phosphonium ion (XIXa), indicating the substitution of methoxy-groups at phosphorus in compound (VI) by fluorine atoms (cf. [6]). The hydrolysis of this solution maintained during 1 hr at 20°C leads to the compound (XX).

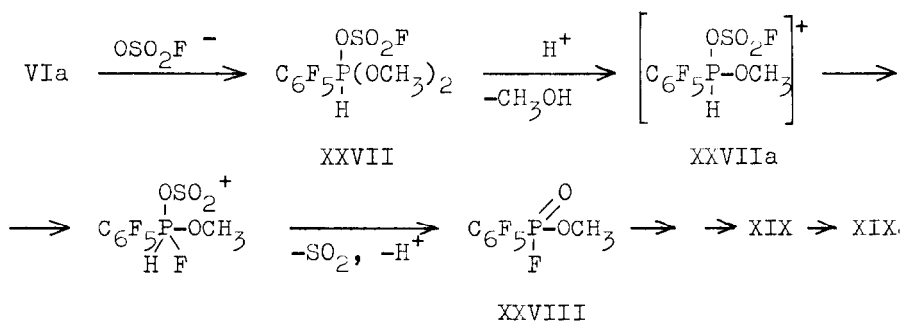
The observed substitution of methoxy-groups in compound (VI) by fluorine atoms in HSO_3F can occur possibly through the protonation of this compound on the oxygen atom followed by elimination of methanol from the ion (VIb) leading to a cation of dicoordinated phosphorus (VIc). This route is in accord with the presence of a protonated methanol signal in the ^1H NMR spectrum of this solution (Table 1):



The phosphonium ions of (VIc) type are known to be stable with alkylamine groups at phosphorus [27]. The alkoxy-groups can be supposed to play an analogous role.

Another possible route for this reaction involving the intermediate formation of the protonated form (XXIIIa) of the dimethyl ester of pentafluorobenzenephosphonic acid (XXIII) seems unfavourable because solvation of the latter in HSO_3F at 20°C does not lead to the phosphonium ion (XIXa).

A route for the observed transformation of compound (VI) into the phosphonium ion (XIXa) in HSO_3F involving the intermediate formation of the phosphorane (XXVII) by the interaction between the phosphonium ion (VIa) with fluoro sulphate anion also cannot be excluded. The alkoxyfluorophosphoranes formed by the action of HF on aryldifluorophosphines have been shown earlier [21,28] to be stable only up to 10°C . The decomposition of phosphorane (XXVII) at the raising of the temperature can take place with the intermediate formation of phosphonium ion (XXVIIa) generated by the elimination of the methanol from the protonated form of compound (XXVII). The structure of the ion (XXVIIa) allows the intramolecular migration of fluorine anion to the positively charged phosphorus atom with the following elimination of HF and SO_2 , leading to the methyl ester of pentafluorobenzene phosphonic acid monofluoroanhydride (XXVIII). This compound can undergo the further transformations in an analogous way to give finally the ion (XIXa) :

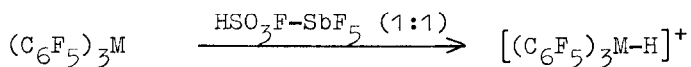


As has been mentioned above, the localization of HOMO in compound (VI) mainly on the phosphorus atom can facilitate the observed preferential protonation of the latter in spite of its substantial effective positive charge [1] in comparison with oxygen atoms. In this case the diminishing of phosphorus AC contribution in HOMO and the localization of the latter on

another heteroatom possessing negative charge led us to expect a change in the direction of the proton attack. That situation has been shown by us to occur, in particular, for compound (X) (see detailed discussion in [1]). Really, the solvation of compound (X) in HSO_3F , as follows from ^1H and ^{31}P NMR spectral data (Table 1) leads to the formation of species protonated on nitrogen. The observed signals have singlet structure and are shifted downfield with respect to precursor (X) indicating protonation on the nitrogen atom. Raising the temperature of this solution to 20°C is not accompanied by changes in NMR spectra. It is interesting to notice that the positive charge on phosphorus in compound (X) is less than in compounds (VI) and (IX) where the phosphorus atom is the preferential centre of proton attack. Nevertheless, protonation of the compound (X) occurs only on nitrogen.

The solvation of compound (XI) in $\text{HSO}_3\text{F}-\text{SbF}_5$ (1:1)- SO_2 at -70°C leads to protonation on nitrogen. The raising of the temperature of this solution is accompanied by substitution of the nitrile groups by fluorine atoms to give compound (VII), undergoing under these conditions the transformation into ion (VIIa). The ^1H , ^{19}F and ^{31}P NMR spectra of the latter obtained as a final product of transformations of compound (XI) in HSO_3F at 20°C are identical to those generated by the protonation of the known compound (VII) under the same conditions.

The same character of chemical behaviour in acids has been found by us in the cases of the polyfluoroaromatic arsines and stibines. Thus, tris(pentafluorophenyl)arsine (XIII) and -stibine (XIV) in $\text{HSO}_3\text{F}-\text{SbF}_5$ (1:1) solution form the cationic species, protonated on arsenic and antimony atoms respectively, as follows from ^{19}F NMR spectral data (Table 2) :

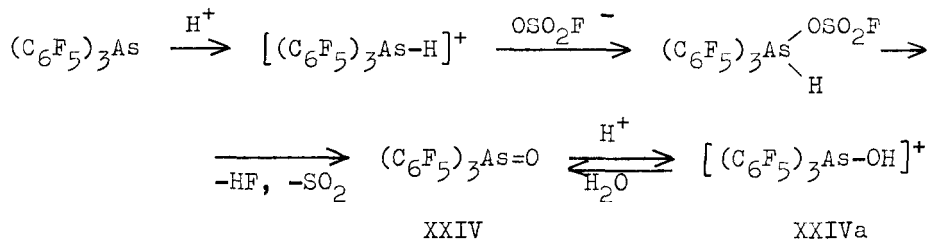


M = As (XIII), Sb (XIV)

The hydrolysis of these solutions leads respectively to the initial compound (XIII) and tetrakis(pentafluorophenyl)-

antimony oxide $[(C_6F_5)_2Sb]_2O$ (XXIX). The formation of compound (XXIX) by the hydrolysis of compound (XIV) has been shown earlier [29].

As arsenic is less electronegative than phosphorus the fast transformation of the cation (XIIIa) in HSO_3F to give the corresponding protonated oxide could be expected. In fact the reaction occurs easily at $20^\circ C$ and the ^{19}F NMR spectrum of the solution of the compound (XIII) in HSO_3F differs from those of the analogous solution in HSO_3F-SbF_5 (1:1) (Table 2). In both cases the signals of the fluorine atoms have been observed to shift downfield with respect to the precursor, especially the signal from the para-fluoro atom (Table 2). Hydrolysis of the solution of compound (XIII) in HSO_3F leads to tris(pentafluorophenyl)arsine oxide (XXIV). This reaction can occur by a scheme analogous to those for the corresponding phosphines :



The solvation of tertiary amines in HSO_3F-SbF_5 (1:1) and HSO_3F leads, according to 1H and ^{19}F NMR spectral data, to the corresponding ammonium ions. The maintaining of these solutions at 20° does not lead to further transformations occurring on the quaternary nitrogen atoms, being forbidden by the octet rule. Thus, N-(pentafluorophenyl)piperidine (XXV) in HSO_3F-SbF_5 (1:1) and HSO_3F at -60 to $40^\circ C$ gives only the cation (XXVa) corresponding to protonation on nitrogen. The structure of cation (XXVa) has been proved by 1H and ^{19}F NMR spectral data (Table 2). The hydrolysis of this solution returns the initial compound.

The octet rule makes the scheme of the formation of phosphine and arsine oxides, discussed above, forbidden for the conversion of amines in amine oxides. Nevertheless other routes to the products of oxidation of trivalent nitrogen derivatives in acid media cannot be excluded. The search of such routes required the investigation of the behaviour of tertiary amine

TABLE 2

^1H , ^{19}F and ^{31}P NMR data for polyfluoroaromatic derivatives of arsenic, antimony and nitrogen

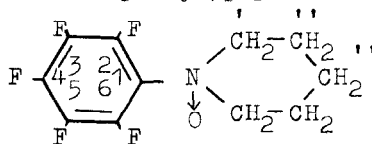
Compd	Medium (temperature, °C)	^1H		^{19}F				^{15}N	
		$(\text{CH}_3)_4\text{Si}$	Chemical shifts (p.p.m.) from						
			C_6F_6			F^3	F^4	NH_3	
XIII	$(\text{CH}_3)_2\text{CO}$ (40)		F^2 2.6						
	HSO_3F (40)		-35.0			F^3 3.5	-13.0		
	$\text{HSO}_2\text{P-SbF}_5$ (1:1) (40)		-36.4				-31.4		
	HSO_3F (20) *		-37.6				-35.0		
XIV	CH_3CN (40)		-41.9				-11.7		
	HSO_3F (40)		-37.1				-23.6		
	$\text{HSO}_2\text{P-SbF}_5$ (1:1) (40)		-39.1				-28.6		
XV	CH_2Cl_2 (20)		-20.0				-2.7	893.3	
	H_2SO_4 (-5)		-21.6				-4.1		
	HSO_3F (-60)	16.33	-34.2, -35.6			-13.0, -14.0	-64.0	410.8	
	HSO_3F (-20)	16.33	-33.9			-12.4	-64.0	410.8	
	$\text{HSO}_2\text{P-SbF}_5$ (1:1)- SO_2ClF (-60)	16.33	-34.2, -35.6			-13.5, -14.7	-70.2	410.8, 397.6	
	HSO_3F (20)		-18.9			-5.1	-18.6	363.3	

XVI	CH_2Cl_2 (20) $\text{HSO}_3\text{F-SO}_2\text{ClF}$ (-60) $\text{HSO}_3\text{F-SbF}_5$ (1:1)- SO_2ClF (-60) HSO_3F (20)	16.20 16.30	-1.7 -21.5 -38.0, -36.6 -15.6	-25.0 -31.2 -33.2, -33.0 -27.6	-18.8 -35.7
XXIV	$(\text{CH}_3)_2\text{CO}$ (40) $\text{HSO}_3\text{F-SbF}_5$ (1:1) (40)		-31.4 -37.9	-4.6 -12.1	-2.6 -15.8
XXV	CH_2Cl_2 (40) HSO_3F (40)	8.00 8.00	-12.1 -19.5	-2.1 -6.2	
XXVI	CH_2Cl_2 (20) HSO_3F (-60) CF_3COOH (20) H_2SO_4 (20) $\text{HSO}_3\text{F-SbF}_5$ (1:1)- SO_2ClF (-60) $\text{HSO}_3\text{F-SbF}_5$ (1:1) (-20) HSO_3F (20)	6.90 6.90, 10.2	-23.9 -29.5 -27.1 -27.2 -20.8, -16.1 -18.3 -26.5	-2.6 -10.6 -7.1 -7.0 -5.8, -5.5 -5.8 -7.3	-8.9 -21.8 -18.1 -15.2 -15.8 -15.8 -18.6
XXIX	CH_3CN (40)		-38.5	-2.3	-11.3

oxides in acid media. The latter have been known to undergo protonation in acid media to give very reactive species [30]. N-(Pentafluorophenyl)piperidine oxide (XXVI) has been shown by us to undergo protonation on the oxygen atom in HSO_3F and $\text{HSO}_3\text{F-SbF}_5$ (1:1) at -60 to 20°C leading to the cationic species. The structure of the latter has been proved by ^{19}F NMR (Table 2) and ^{13}C NMR (Table 3) spectral data. The signals of the aromatic fluorine atoms are shifted downfield with respect to precursor (Table 2). The signals of the carbon atoms in the ^{13}C NMR spectra are also shifted (Table 3).

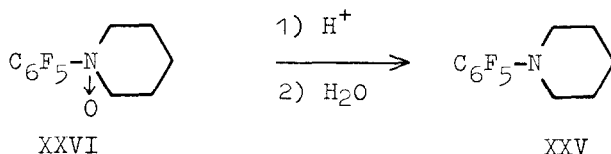
TABLE 3

^{13}C NMR spectral data for N-(pentafluorophenyl)piperidine oxide in various media at 30°C



Medium	Chemical shifts of p.p.m. from $(\text{CH}_3)_4\text{Si}$					
	C^1	$\text{C}^{2,6}$	$\text{C}^{3,5}$	C^4	C'	C''
CH_2Cl_2	130.0	141.5	137.9	140.1	68.9	20.5
HSO_3F	130.2	141.2	138.6	143.4	68.9	20.5
$\text{HSO}_3\text{F-SbF}_5$ (1:1)	115.8	140.8	138.6	143.0	59.5	23.4

The upfield shift of signals of C_1 and C' carbon atoms (Table 3) indicate the increase of electron density on these atoms participating in the stabilizing of positive charge on nitrogen atoms. The C_4 atom signal is shifted downfield in accordance with the cationic character of the species. The hydrolysis of the solution of compound (XXVI) in $\text{HSO}_3\text{F-SbF}_5$ (1:1) leads to compound (XXV).



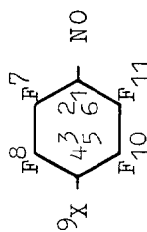
Thus, the presented experimental data lead us to conclude that for the series of trivalent nitrogen derivatives in comparison with the corresponding phosphorus and arsenic derivatives the reverse reaction - the transformation of tertiary amine oxides into amines - becomes the main process in acid media. Hence even if the oxidation of tertiary amines into oxides in acid media could take place, the instability of latter compounds under the reaction conditions would lead nevertheless to the initial amines as the final products of the reaction. However, the oxidation of the organic nitrogen-containing compounds in acid media could be realized in another way, namely the formation of dicoordinated nitrogen cations (by analogy with the cation (VIc) supposed by us above to form from compound (VI) in HSO_3F). In that case the interaction of the nitrenium cation with the anion of medium must lead to a tricoordinated nitrogen compound with N - O bonds. The latter could transform in strong acid into a stable compound of pentavalent nitrogen.

Nitrenium cations are very reactive and their stable salts have been obtained only in few cases [31]. The generation of nitrenium cations has been supposed in the case of the action of acids on nitrosobenzenes [30, 32]. These cations have been known to form, in reaction with benzene, the C-phenylation products. The N-phenylation products have not been obtained. We supposed that the presence of the fluorine atoms in the benzene ring can lead to the redistribution of the charges on the nitrogen and carbon atoms. The positive charge on the nitrogen atom in mono- and diprotonated forms of polyfluorinated nitrosobenzenes could be expected to be relatively high and comparable with the charge on the C_4 atom of the aromatic ring. Our calculations by the CNDO/2 method have shown that in monoprotinated forms ((XVa) and (XVIa) respectively) of pentafluoronitrosobenzene (XV) and 2,3,5,6-tetrafluoronitrosobenzene (XVI) the positive charges on the nitrogen atoms are substantially higher than those on the C_4 atoms of aromatic rings (Table 4). The structure of the lowest unoccupied MO in cations (XVa) and (XVIa) also indicates the preferability of nucleophilic attack by the medium anion on the nitrogen atoms.

The solvation of compound (XV) in $\text{HSO}_3\text{F}-\text{SbF}_5$ (1:1) or HSO_3F at -60°C (using SO_2ClF as a solvent) has been shown by us

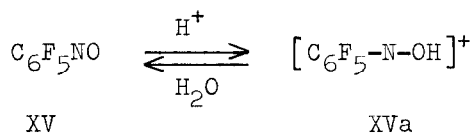
TABLE 4

CNDO/2 calculations on polyfluoronitrosobenzenes and derived cationic species

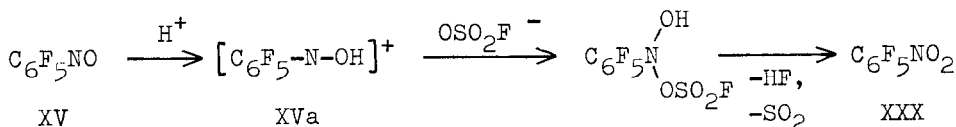


Compound	Charges on atoms, \bar{e}						Structure of orbitals, %						
	C ₄	F ₇ (F ₁₁)	F ₈ (F ₁₀)	F ₉ (H)	N	O	HOMO		LUMO		N	O	
							C ₄	N	C ₄	N			
C ₆ F ₅ NO	0.1839	-0.1527 (-0.1559)	-0.1562 (-0.1602)	-0.1508	0.0732	-0.1410	25	-	13	16	25	23	23
[C ₆ F ₅ N-OH] ⁺	0.2502	-0.1176 (-0.1147)	-0.1128 (-0.1392)	-0.1020	0.2817	0.0016	21	2	5	9	50	17	17
4-H-C ₆ F ₄ NO	-0.0698	-0.1592 (-0.1722)	-0.1724 (-0.1666)	(-0.0585)	0.0694	-0.1381	23	5	24	16	23	26	26
[4-H-C ₆ F ₄ N-OH] ⁺	-0.0130	-0.1235 (-0.1312)	-0.1289 (-0.1452)	(0.1051)	0.2821	0.0034	32	2	7	9	50	17	17
[4-H-C ₆ F ₄ N-OH] ⁺⁺ H	0.0851	-0.1128 (-0.0721)	-0.0899 (-0.0872)	(0.1500)	0.2634	0.0172							

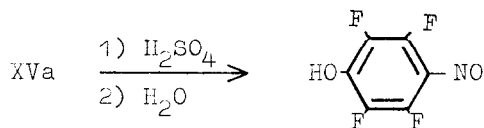
according to ^1H , ^{15}N and ^{19}F NMR spectral data to give the cation (XVa) (Table 2).



The ^1H NMR spectrum of the solution of compound (XV) in $\text{HSO}_3\text{F-SO}_2\text{ClF}$ at -60°C contains a singlet at 16.33 p.p.m.; the signal in ^{15}N NMR spectrum of this solution is shifted upfield with respect to precursor (Table 2) indicating the species with the cationic centre on nitrogen. The ^{19}F NMR spectrum consists of 5 signals of equal intensity shifted downfield from the precursor, the greater shift being for para-fluorine atom (Table 2). That is in accordance with CNDO/2 calculations on charges on fluorine atoms (Table 4). Non-equivalence of the ring fluorine atoms can be explained probably in terms of the planar structure of cation (XVa) determining the different screening of both ortho- and both meta-fluorine atoms. The raising of the temperature of the solution up to 20°C leads to the equivalence of these atoms because of the free rotation around the C-N - bond lacking at low temperatures. Free rotation takes place both for solutions of compound (XV) in $\text{HSO}_3\text{F-SbF}_5$ (1:1) and HSO_3F , but in latter case it is accompanied by the appearance of new signals which remain with lowering of the temperature to -60°C again. In the ^{15}N NMR spectrum of the solution of compound (XV) in HSO_3F after raising the temperature to 20°C the signal at 410.8 p.p.m. disappears and a new signal at 362.3 p.p.m. (in respect to NH_3) is observed. After the maintaining of this solution at 20°C during 1 hr the initial signals completely disappear and hydrolysis of the solution leads to pentafluoro-nitrobenzene (XXX). Protonation of the latter under the same conditions leads to a solution with the same spectral characteristics. The formation of compound (XXX) can be explained as follows :



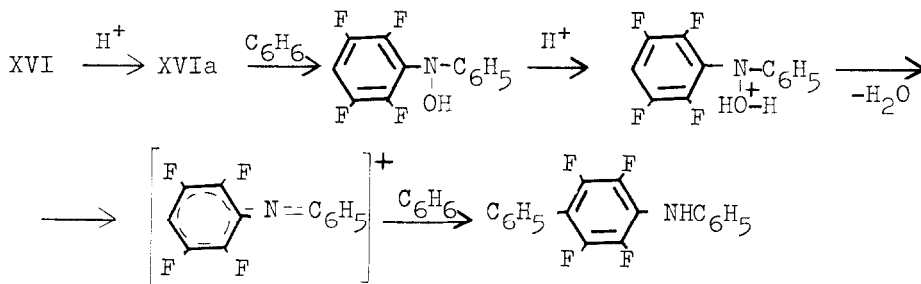
Weaker acids (CF_3COOH or H_2SO_4 conc.) protonate compound (XV) to a substantially less degree as shown by the small downfield shift of the signals of the fluorine atoms in the ^{19}F NMR spectra with respect to precursor (Table 2). Hydrolysis of these solutions returns the initial compound. The maintaining of the solution of compound (XV) in concentrated sulfuric acid at 20° during 3 hrs gave 4-hydroxy-2,3,5,6-tetrafluoronitrosobenzene (XXXI).



XXXI

The solvation of compound (XVI) in strong acids leads to the formation of cation (XVIa) according to ^1H and ^{19}F NMR spectral data (Table 2). The spectral changes in that case are similar to those for the formation of the cation (XVa) from the compound (XV). The maintaining of the solution of the compound (XVI) in HSO_3F at 20°C during 2 hrs leads after hydrolysis to 2,3,5,6-tetrafluoronitrobenzene (XXXII) with high yield.

The cation (XVIa) is highly electrophilic and reacts with benzene both by the nitrogen and aromatic para-carbon atoms. Thus, in $\text{CF}_3\text{COOH-HSO}_3\text{Cl}$ (3:1) medium at -10°C 4-(N-phenylamino)-2,3,5,6-tetrafluorodiphenyl (XXXIII) has been obtained probably by the following route:



XXXIII

The maintaining of compound (XVI) in concentrated sulphuric acid at 20°C during 3 hrs leads after hydrolysis to fluoroanil (XXXIV) and 2,3,5,6-tetrafluorophenol (XXXV) together with the expected compound (XXXII).

Hence, the polyfluorinated nitrosobenzenes can be oxidized in acid media. The formal analogy of the products of those reactions and also their mechanisms for trivalent nitrogen and the corresponding phosphorus and arsenic compounds lead us to conclude that the reaction of oxidation of aromatic derivatives of trivalent group VA elements into derivatives of pentavalent ones described in the present work is a general one.

EXPERIMENTAL

^1H and ^{19}F NMR spectra have been recorded on a Varian A56/60A spectrometer at the frequencies 60 and 56.4 MHz respectively (the standards - TMS and C_6F_6). ^{31}P NMR spectra have been recorded on a Bruker WP-80 spectrometer (standard - 85% H_3PO_4) and on a Bruker HX-90 spectrometer (at low temperatures; standard - $\text{P}(\text{C}_2\text{H}_5)_3$, $\delta(^{31}\text{P}) = 19.3$ p.p.m. from 85 % H_3PO_4). ^{15}N NMR spectra have been recorded for enriched samples (94-96 % enrichment) on the Bruker HX-90 spectrometer at the frequency 9.12 MHz. ^{15}N chemical shifts are referred to liquid NH_3 using as a standard trans-azobenzene ($\delta(^{15}\text{N}) = 510$ p.p.m. from liquid NH_3). The working regime of spectrometer : pulse width 20 μsec (90° -pulse - 30 μsec), the time between pulses - 8 sec., the number of scans 150-300. UV spectra have been recorded for ethanol solutions on a Specord UV-VIS spectrophotometer ; IR spectra - on UR-20 spectrometer. The quantum-chemical calculations have been provided on the computer BESM-6 (computer centre of Siberian Division of Academy of Sciences of USSR) using the set of programs for calculations by semi-empirical methods "Viking", described in [33].

Compound (I) has been obtained as in [34], compounds (II) and (III) as in [35], (XIII) and (XIV) as in [36]. The reactions of compound (VIII) with diethylamine, lead thiocyanate and silver cyanide lead to compounds (X), (IX) and (XI) respectively. The interaction of compound (VIII) with methanol in ether lead to compound (XVII), while in presence of triethylamine compound (VI) was obtained. The yield and the characteristics of previously unknown products have been given in Table 5 .

HSO_3F (b.p. 162-163°C) and doubly distilled SbF_5 (b.p. 143-145°C) have been used as a components of acid media.

TABLE 5

Physical properties and spectral data of polyfluoroaromatic phosphines

Compound	Yield %	B.p., °C (Torr)	Found, %			Requires, %			UV-spectrum λ_{\max} , mμ (lgε)
			C	F	P	C	F	P	
$C_8H_6F_5PO_2$ (VI) (nc)	93	76-77 (6)	35.98 36.21	36.82 36.78	11.26 11.56	36.92 36.54	11.92	206 (3.92) 230 (3.16)	
$C_8F_5N_2PS_2$ (IX) (nc)	86	126-127 (5)	29.62 29.53	30.96 30.74	8.97 9.32	30.57 30.25	9.87	208 (4.17) 230 (3.18)	
$C_{14}H_{20}F_5N_2P$ (X) (nc)	87	116-117 (3)	49.10 49.00	27.56 27.56	8.89 9.00	49.12 27.78	9.06	220 (3.91) 290 (3.56)	
$C_7H_4F_5PO_2$ (XVII) (nc)	91	78-79 (5)	33.97 33.90	38.75 39.10	11.99 12.06	34.15 38.62	12.60	210 (3.90) 230 (3.09)	

The interaction of aromatic phosphines, arsines, stibines, tertiary amine oxides and nitrosocompounds with acids.

The corresponding polyfluoroaromatic compound was added under stirring to 1 ml HSO_3F (or the other acid) in 2 ml SO_2 at -70 to -60°C . The mixture was kept at that temperature during 30 min. After the recording of ^1H , ^{19}F , ^{15}N and ^{31}P NMR spectra the temperature was raised to 0 to 20°C , maintained during 1-2 hours and the solution was poured onto ice, and extracted by ether. After distillation of the ether the residue was identified by elemental analysis and spectral data. There was no depression of m.p. on admixture with an authentic sample.

Pentafluoronitrosobenzene labelled by ^{15}N isotope was obtained from labelled by ^{15}N pentafluoroaniline.

2 g compound (XV) were added under stirring to the solution of 2 g of HSO_3F in 10 ml SO_2ClF at -60°C . The temperature of the mixture was raised to 0°C and the mixture was maintained during 30 min at that temperature, poured on ice and extracted by ether. The extract was dried by MgSO_4 and distilled to give 2 g (98.%) of the compound (XXX), b.p. $61-62^\circ\text{C}$ / 17 Torr identical to the known substance obtained by [38].

5 ml of $\text{HSO}_3\text{F}-\text{SbF}_5$ (1:1) were added to 10 ml of SO_2ClF at -60°C and then 2 g of the compound (XXVI) were added to that mixture under stirring. The temperature of solution was raised to 0°C and after NMR spectra recording and the procedures described above in case of compound (XV) 1.2 g (64 %) of the compound (XXV), b.p. $83-86^\circ\text{C}$ / 5 Torr was obtained. The product was identical by IR and ^{19}F NMR spectra to that obtained in [39]

A mixture of 3 g of compound (XIII) and 10 ml HSO_3F at 20° was kept during 12 hrs and poured on ice. The solid precipitate was filtered off and dried in air to give 2,68 g (87 %) of the compound (XXIV), m.p. $198-199^\circ\text{C}$ (lit. $198-199^\circ\text{C}$ [40]).

A mixture of 1.5 g of compound (XIII) and 10 ml $\text{HSO}_3\text{F}-\text{SbF}_5$ (1:1) was maintained at 20°C during 3 hrs and poured on ice. The precipitate was filtered off and dried in air to give 1.4 g (93 %) of the initial compound, m.p. and mixed m.p. 106°C , identical by IR and ^{19}F NMR spectra to the known substance.

A solution of 2 g of compound (XIV) in 20 ml of $\text{HSO}_3\text{F}-\text{SbF}_5$ (1:1) was maintained at 20° during 2 hrs and poured on ice. The precipitate was filtered off and dried to give 1.2 g (80 %) of compound (XXIX), m.p. 142°C , identical by IR and ^{19}F NMR spectra to the known substance obtained by the hydrolysis of compound (XIV).

A mixture of 1.5 g of compound (XV) and 30 ml of H_2SO_4 (d = 1.84) was stirred during 3 hrs at 20°C , poured into water and extracted by ether. The ether extract was dried by MgSO_4 . After distillation of the solvent on a vacuum-evaporator 1.45 g (98 %) of the compound (XXXI)(nc) was obtained. The product was sublimed at $100-110^\circ\text{C} / 14$ Torr, m.p. $130-132^\circ\text{C}$. ^{19}F NMR spectrum - two signals of equal intensity at -25.1 ($\text{F}^{3.5}$) and -8.5 ($\text{F}^{2.6}$) p.p.m. UV spectrum - $\lambda_{\text{max, nm}} (\lg \epsilon)$: 304 (4.08). Found, % : C - 37.01; F - 39.02; N - 7.20. $\text{C}_6\text{HF}_4\text{NO}_2$ requires C - 36.92; F-38.97; N - 7.18.

A mixture of 1.5 g of the compound (XVI), 3 ml benzene and 18 ml of CF_3COOH was cooled to -10°C . 2 ml of HSO_3Cl were added and the mixture was stirred during 30 min at that temperature, poured onto ice and extracted by ether. The ether extract was dried by MgSO_4 , the ether was distilled and the residue was sublimed at $200^\circ\text{C} / 4$ Torr to give 2.2 g (80 %) of the compound (XXXIII)(nc), m.p. $180-185^\circ\text{C}$, ^{19}F NMR spectrum of compound (XXXIII); 2 signals of equal intensity at -13.3 and -24.3 p.p.m. Found, % : C - 67.92; F - 24.52; N - 5.02. $\text{C}_{18}\text{H}_{11}\text{F}_4\text{N}$ requires C - 68.14; F - 23.97; N - 4.42.

2 g HSO_3F were slowly added to 4.7 g of compound (VII) in 20 ml of 1,1,2-trichloro-1,2,2-trifluoroethane at 0°C under vigorous stirring. After the evolution of gaseous products the residue was distilled to yield 4.7 g (96 %) of compound (XIX), b.p. $61-62^\circ\text{C} / 10$ Torr (lit. $73^\circ\text{C} / 14$ Torr [41]).

2 g of compound (VI) were added to 5 ml of HSO_3F at 0°C , then the temperature was raised to 20°C with constant stirring. After the evolution of gaseous products (identified by IR spectra as a mixture of SO_2 and HF) the mixture was maintained during 1.5 hrs at 20°C , poured on ice, and extracted by ether. After the drying of extract by MgSO_4 the ether was distilled to give 1.5 g (79 %) of compound (XX), m.p. $141-142^\circ\text{C}$ (lit. $141-142^\circ\text{C}$

[23]). ^{31}P NMR spectrum of compound (XX) - singlet at -0.8 p.p.m. ^{19}F NMR spectrum - 3 signals with 2:1:2 intensity ratio at -31.2 , -14.7 and -1.9 p.p.m.

A mixture of 2 g compound (XVI) and 10 ml of HSO_3F was maintained at 25°C under stirring during 1.5 hrs, poured on ice and extracted by ether. The ether extract was dried by MgSO_4 and distilled to give 2.1 g (93 %) of compound (XXXII), b.p. $93-94^\circ\text{C} / 52$ Torr (lit. b.p. $76^\circ\text{C} / 25$ Torr) [43]), identical by IR and ^{19}F NMR spectra to a known sample.

A mixture of 2 g of compound (XVI) and 20 ml of H_2SO_4 ($d = 1.84$) was stirred during 2 hrs at 20°C . The mixture became intensively coloured. After pouring on ice and extraction by ether the extract contained (by GLC data) 32 % of compound (XXXII), 29 % of compound (XXXV) and 39 % of compound (XXXIV). The extract was washed by 10 % aqueous NaOH and from the alkaline solution 0.6 g (33 %) of compound (XXXV) were obtained, b.p. $146-146.5^\circ\text{C}$ (lit. b.p. 146.5°C [43]). The washed extract was dried by MgSO_4 and distilled to give 0.6 g (27 %) of compound (XXXII), b.p. $61-62^\circ\text{C} / 15$ Torr, identified by comparison of IR and ^{19}F NMR spectra with those of known compound obtained by [42]. The residue was sublimed at $130^\circ\text{C} / 4$ Torr to give 0.4 g (20 %) of compound (XXXIV), m.p. $177-179^\circ\text{C}$, identified by spectral characteristics described in [44].

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