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INTERACTION OF PENTAFLUOROPYRIDINE WITH 4-NITROPHENOL AND
PENTAFLUOROPHENOL IN THE PRESENCE OF POTASSIUM FLUORIDE
AND 18-CROWN-6-ETHER

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SUMMARY

The reactions of 4-nitro- and pentafluorophenols with C_5F_5N , 4- $ArOC_5F_4N$ and 2,4-(ArO) $_2C_5F_3N$ ($Ar = 4-NO_2C_6H_4, C_6F_5$) in the presence of KF and catalytic amounts of 18-crown-6-ether at various temperatures have been investigated. The leaving ability of the C_6F_5O -group is shown to be higher than that of the 4- $NO_2C_6H_4O$ -group in the reactions of 4- $ArOC_5F_4N$, 2,4-(ArO) $_2C_5F_3N$ and 2,4,6-(ArO) $_3C_5F_2N$ with F^- -anion, which is in agreement with the order of the basicity of anions ($C_6F_5O^- < 4-NO_2C_6H_4O^-$). The reaction pathways of pentafluoropyridine with ArO^- -anions are discussed.

INTRODUCTION

In recent years, alkali metal fluorides, particularly potassium and cesium fluorides, have been widely used as bases in organic synthesis [1]. For example, interaction of aromatic halides with hydroxy compounds in the presence of potassium fluoride gives the corresponding ethers in high yields [2]. However, in some cases these reactions have been found to occur rather slowly [3]. One of the methods to promote aromatic nucleophilic substitution reactions in the presence of alkali metal fluorides is to increase the basicity of fluoride ion by means of complexing the alkali metal cation with crown ethers, using, for example, the system:

KF - 18-crown-6-ether (18-C-6) [4-11]. However, it should be noted that only a few examples of the usage of 18-C-6 in nucleophilic substitution reactions are known [12-16]. On the other hand, the problem of nucleophilicity ratio of the reagents used in nucleophilic substitution reactions in general [17] and particularly in crown ether - catalyzed reactions is also important [18-19]. Reversible reactions involving fluoride ion [20] are of particular interest, due to the increased activity of the 'naked' fluorine anion [19].

In the present work, we report 18-C-6 - catalyzed reactions of pentafluoropyridine (I) with potassium 4-nitrophenolate and pentafluorophenolate, obtained by treatment of the appropriate phenols with potassium fluoride under the reaction conditions (cf. [21]).

Pentafluoropyridine was selected as a substrate, as in the reactions with a number of nucleophiles, including O-nucleophiles [e.g., CH_3O^- , OH^- , $(\text{CF}_3)_2\text{NO}^-$] [22], only the fluorine atom in the 4-position is substituted.

It was also interesting to compare the nucleophilicity ratio of $4\text{-NO}_2\text{C}_6\text{H}_4\text{O}^-$ and $\text{C}_6\text{F}_5\text{O}^-$ -anions in reactions with pentafluoropyridine, since it was difficult to predict any essential difference in their reactivities from pK_a values of the corresponding phenols (Table 1).

RESULTS AND DISCUSSION

The reactions of equimolar quantities of 4-nitrophenol (II) or pentafluorophenol (III) with pentafluoropyridine (I) in the presence of an excess of potassium fluoride at 0°C in acetonitrile occur by different routes (Tables 2,3). While the reaction with pentafluorophenol does not practically occur under these conditions [90-95% of pentafluorophenol have been recovered, and the yield of 4-pentafluorophenoxy-2,3,5,6-tetrafluoropyridine (IV) is small (Table 3, N 2)], the similar reaction with 4-nitrophenol leads to 4-(4'-nitrophenoxy)-2,3,5,6-tetrafluoropyridine (V) in about 50% yield (Table 2, N 1,3). The presence of catalytic amounts of 18-C-6 leads to a higher yield of compound (V) (80%; Table 2, N 2,4),

TABLE 1

The pK_a Values of 4-Nitrophenol, Pentafluorophenol and Hydrogen Fluoride in Various Solvents

Compound	pK_a		
	Solvent		
	H ₂ O	DMSO	CH ₃ CN
4-NO ₂ C ₆ H ₄ OH (II)	7.15 [23]	10.8 [24]	20.9 [25]
C ₆ F ₅ OH (III)	5.53 [26]	8.9*	19.5*
HF	3.16 [27]	17.6** -19.3 [28]	-

*The pK_a values were obtained by O.P. Sheremet by means of potentiometric titration.

**The pK_a value was estimated from the corrected value of deprotonation enthalpy [28].

whereas the yield of compound (IV) remains low (Table 3, N 1). The prolonged process or increased amounts of crown ether (from 0.1 up to 0.3 mol) do not lead to any noticeable change in the yield of compounds (IV) and (V).

The reactions between equimolar quantities of compounds (II) or (III) and pentafluoropyridine (I) in the presence of an excess of potassium fluoride in acetonitrile at 80°C also take place in different ways. Thus, interaction of 4-nitrophenol with pentafluoropyridine gives only compound (V) in a high yield. In this case, the addition of catalytic amounts of crown ether or modification of the solvating ability of the solvent (using sulpholan instead of acetonitrile) only slightly raise the yield of compound (V) (Table 2, N 5-8).

TABLE 2

Reactions of C_5F_5N (I) and its Derivatives (V,X,XI) with 4- $NO_2C_6H_4OH$ (II) in CH_3CN in the Presence of KF and 18-C-6 (Reaction time - 5 h; the ratio of initial reagents (moles) I:II (or V,X,XI):KF:18-C-6 is 1:1:2:0.1)

Reaction N	Compound N	18-C-6	t°C	The Yields of the Products in % with Respect to the Compound Obtained		
				V	X	XI
1 1)	I	-	0	46	-	-
2 1)	I	+	0	76	-	-
3	I	-	0	54	-	-
4 1)	I	+	0	80	-	-
5 1)	I	-	80	72	-	-
6 1), 2)	I	+	80	80	-	-
7 1), 2)	I	-	80	76	-	-
8 3), 2)	I	+	80	84	-	-
9 3)	I	-	80	74	20	-
10 3)	I	+	80	36	49	11
11 2), 3)	I	-	120	48	40	-
12 2), 3)	I	+	120	12	55	26
13 4)	I	-	80	39	58	traces
14 4)	I	+	80	8	40	50
15 2), 4)	I	-	80	24	37	35
16 2), 4)	I	+	80	6	28	63
17	V	-	80	58	40	-
18 5)	V	+	80	28	56	10
19 5)	V	-	80	78	6	-
20 5)	V	+	80	66	14	traces
21	X	-	80	-	44	51
22 2), 6)	X	+	80	-	20	74
23 2), 6)	X	-	80	-	94	traces
24 6)	X	+	80	traces	80	9
25 6)	XI	-	80	-	-	96
26 6)	XI	+	80	-	6	92

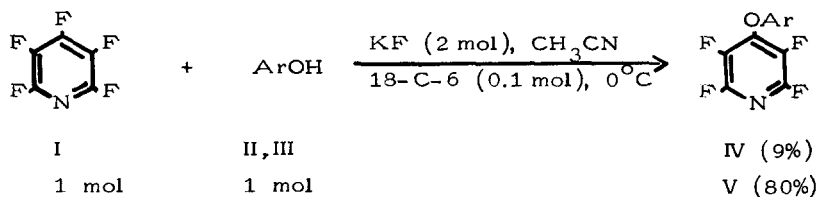
1) Reaction time - 1 hour. 2) Sulpholan as a solvent.

3) The ratio of reagents I:II = 1:2 (moles).

4) The ratio of reagents I:II = 1:3 (moles).

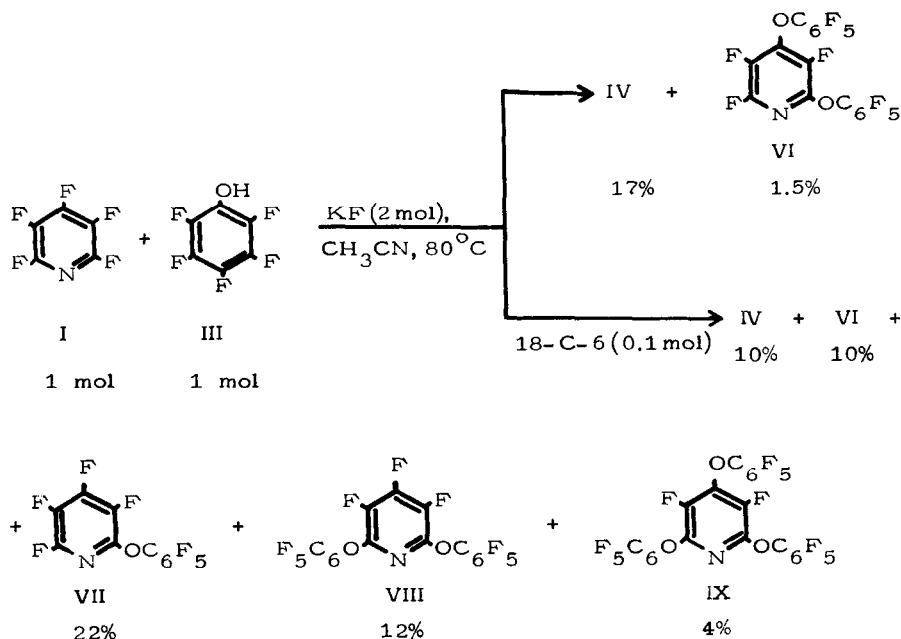
5) In the absence of 4- $NO_2C_6H_4OH$; C_5F_5N was detected in the reaction mixtures by GLC.

6) In the absence of 4- $NO_2C_6H_4OH$.



where Ar = 4-NO₂C₆H₄- (II, V);
 Ar = C₆F₅- (III, IV);

At the same time, the reaction of pentafluorophenol with pentafluoropyridine in acetonitrile at 80°C leads predominantly to the formation of monosubstitution product (IV), as well as to a small amount of 2,4-bis-pentafluorophenoxy-3,5,6-trifluoropyridine (VI). Under the same conditions, the crown ether - catalyzed reaction yields compounds (IV,VI,IX) (Table 3, N 3,4).



In this case, the increased amount of crown ether leads to greater yields of compounds (VIII) and (IX) (Table 3, N 5).

TABLE 3

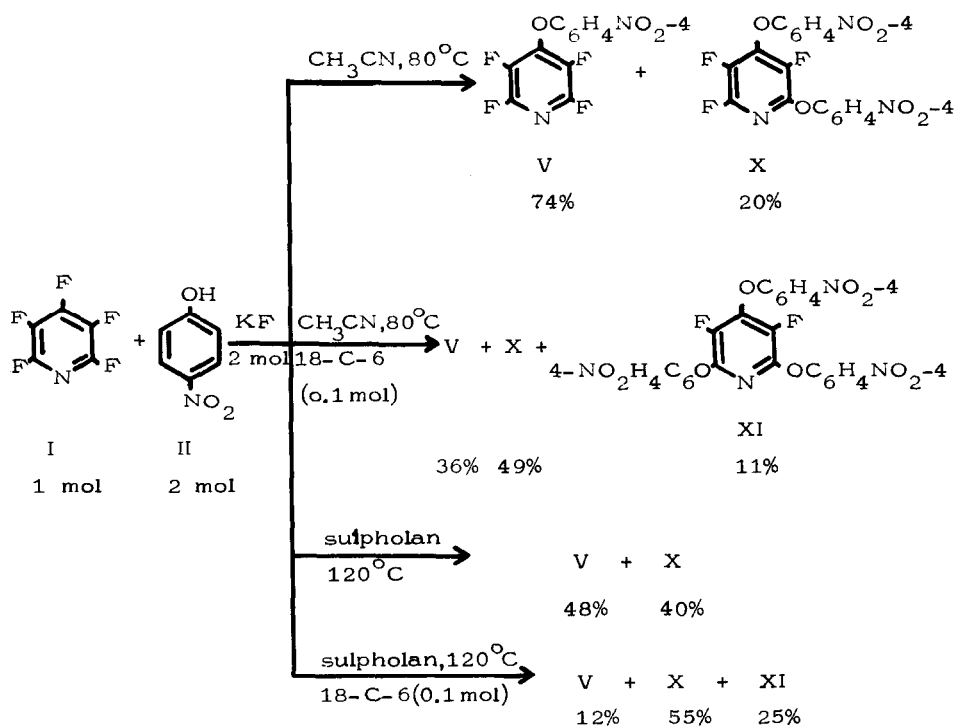
Reactions of C_5F_5N (I) and its Derivatives (IV, VI-IX) with C_6F_5OH (III) in CH_3CN in the Presence of KF and 18-C-6. Reaction time - 5 h; the ratio of initial reagents I:III (or IV, VI-IX):KF:18-C-6 is 1:1:2:0.1 (moles)

Reaction N	Compound N	18-C-6	t°C	The Yield of Reaction Products in %, Calculated from GLC Data for the Reaction Mixtures				
				IV	VI	VII	VIII	IX
1	I	+	0	9	traces	-	-	-
2 ₁₎	I	-	0	2.5	-	-	-	-
3 ₁₎	I	-	80	17	1.5	-	-	-
4 ₂₎	I	+	80	10	10	22	12	4
5 ₂₎	I	+	80	9	15	24	27	12
6 ₃₎	I	-	80	56	6	4	-	-
7 ₃₎	I	+	80	16	8	23	12	5
8 ₃₎	I	-	120	15	7	14	13	7
9 ₃₎	I	+	120	8	9	25	19	8
10 ₄₎	I	+	80	9	14	12	8	14
11 ₅₎	I	+	80	80	9	-	-	6
12 _{1), 6)}	I	+	80	100	-	-	-	-
13	IV	-	80	58	28	-	-	9
14 ₇₎	IV	+	80	36	36	-	-	25
15 ₇₎	IV	+	80	54	9	7	2	4
16	VI	-	80	-	60	-	-	27
17 _{2), 7)}	VI	+	80	-	55	-	-	38
18 _{2), 7)}	VI	+	80	-	25	13	21	32
19	VII	-	80	-	54	46	-	-
20 ₈₎	VII	+	80	-	34	25	18	23
21 ₈₎	VII	+	80	-	-	100	-	-
22 ₈₎	VIII	+	80	-	-	-	-	100
23 ₈₎	VIII	+	80	-	-	-	100	-
24 ₈₎	IX	+	80	-	-	-	20	79

1) Reaction time - 1 hour. 2) Crown ether amount - 0.2 mol.
 3) Sulpholan as a solvent. 4) The ratio of the reagents I:III=1:2 (moles). 5) The ratio of reagents I:III=1:3 (moles).
 6) The ratio of reagents I:III=1:0.1 (moles). 7) In the absence of C_6F_5OH ; C_5F_5N was detected in the reaction mixtures by GLC. 8) In the absence of C_6F_5OH .

Sulpholan, as a more solvating solvent, decreases the catalytic effect of crown ether, especially when the reaction between pentafluoropyridine and pentafluorophenol is carried out at 120°C (Table 3, N 6-9).

We have introduced several 4-nitrophenoxy groups into pentafluoropyridine by increasing the 4-nitrophenol - pentafluoropyridine ratio. Thus, interaction of pentafluoropyridine with two-fold excess of 4-nitrophenol at 80°C either in acetonitrile or in sulpholan gives, in addition to compound (V), 2,4-bis-(4'-nitrophenoxy)-3,5,6-trifluoropyridine (X) in a low yield (Table 2, N 9). When the same reaction was conducted

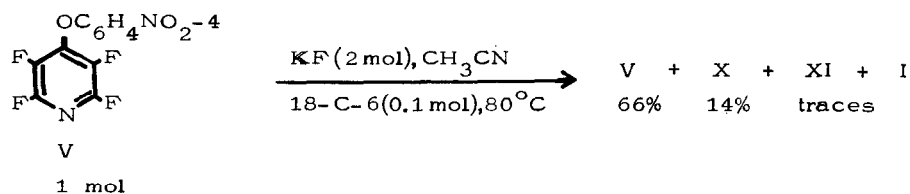
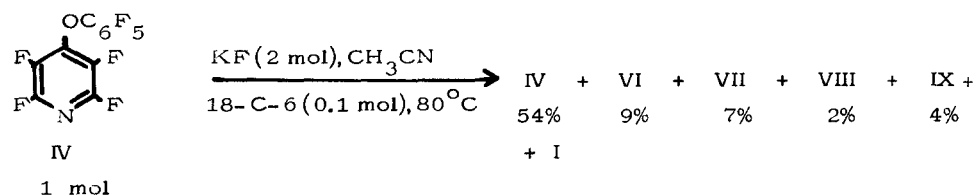


in sulpholan at 120°C the yield of compound (X) was increased two-fold, but the mixture of the reaction products still contained a considerable amount of compound (V) (Table 2, N11). The presence of crown ether leads to the formation of 2,4,6-tris-(4'-nitrophenoxy)-3,5-difluoropyridine (XI), as well as

compounds (V) and (X). At a higher temperature, the yield of compound (XI) was increased more than two-fold (Table 2, N 10, 12).

The reaction with three-fold excess of 4-nitrophenol (II) with respect to pentafluoropyridine (I) in acetonitrile leads mainly to compounds (V) and (X), while the same reaction in sulpholan gives, in addition to these compounds, a substantial amount of compound (XI) (Table 2, N 13,15). In the catalytic conditions, compound (XI) was obtained as the major product, as well as a considerable amount of compound (X) (Table 2, N 14,16); the difference in the solvating ability of a solvent is smaller in a catalytic process than in the non-catalytic one (Table 2, N 14,16; cf. N 13, 15). A catalyzed reaction of pentafluoropyridine (I) with two-fold excess of pentafluorophenol (III) leads to compounds (IV, VI-IX) in similar yields, while interaction with three-fold excess of pentafluorophenol gives predominantly compound (IV) and small amounts of compounds (VI) and (IX) (Table 3, N 10,11). Thus, the formation of compounds (VII) and (VIII) may be considered as the result of the contribution of competing reactions involving $C_6F_5O^-$ and F^- -anions as nucleophiles (cf. [29]).

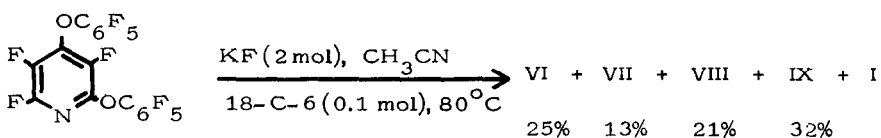
This competing ability is well observed in the comparison of the reaction of compounds (IV, VI-IX) and (V,X,XI) with potassium fluoride in the absence of phenols (II,III). Thus,



interaction of compound (IV) with potassium fluoride in the presence of catalytic amounts of crown ether leads, in addition to the substrate, to compounds (VI-IX) (Table 3, N15), while compound (V) gives under these conditions only compound (X) in a low yield, even in catalyzed process (Table 2, N19,20). In some reactions without phenols, pentafluoropyridine was detected in the reaction mixture by GLC.

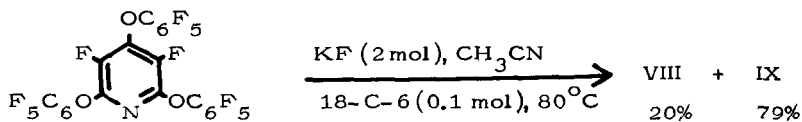
The results on evaluation of the leaving ability of 4-NO₂C₆H₄O- and C₆F₅O-groups show the latter to be more easily substituted by fluorine than the former. This is in agreement with the lower basicity of C₆F₅O⁻-anion in comparison with 4-NO₂C₆H₄O⁻-anion [cf. pK_a values of compounds (II) and (III) in Table I] .

The competing reactions of C₆F₅O⁻- and F⁻-anions are also observed in a catalyzed reaction of compound (VI), where, in the absence of pentafluorophenol, the reaction products contain compounds (VII-IX), in addition to the substrate (VI) (Table 3, N18). The formation of compound (VII) and the absence of compound (IV) in that reaction indicate that the F⁻-anion attacks predominantly position 4 in compound (VI).



VI

1 mol

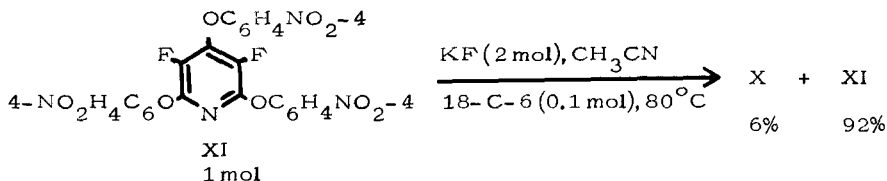
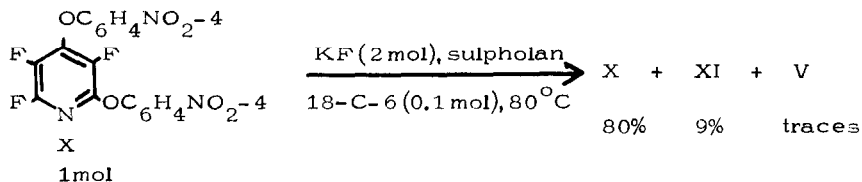


IX

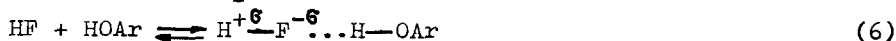
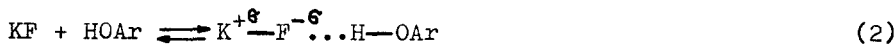
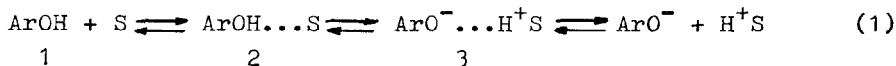
1 mol

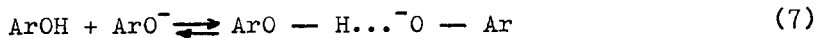
This is also confirmed by the results of the catalyzed reactions of compounds (VII) or (VIII) with potassium fluoride in the absence of pentafluorophenol, where these compounds remain unchanged (Table 3, N 21,23). At the same time, in the catalyzed reaction of compound (IX) and potassium fluoride, partial substitution of C_6F_5O -group by fluorine takes place to give compound (VIII) (Table 3, N 24).

By contrast, interaction of compound (X) with potassium fluoride leads to compound (XI), with the yields of the latter increased in the catalytic process (Table 2, N 23,24). The same compounds are also formed as a result of the reaction of compound (XI) with potassium fluoride in the presence of catalytic amounts of crown ether (Table 2, N 25,26).



Interaction of pentafluoropyridine (I) with phenols (II) and (III) in the presence of potassium fluoride can be represented by the following equation:





where Ar = 4-NO₂C₆H₄⁻, C₆F₅⁻ ; S - solvent.

The activation of weakly acidic ArO — H bonds in dipolar aprotic solvents is known to occur by formation of either hydrogen-bonded complexes or ionic pairs (2,3)(eq.1), and the latter may be associated to form large agglomerations [30]. On the other hand, in the presence of an excess of KF (eq.2), the formation of strong hydrogen bonds between phenols (II) and (III) and KF (80 - 150 kJ/mol) increase the reactivity of these phenols [31,32] (in the absence of KF, the reaction between 4-nitro- or pentafluorophenol and pentafluoropyridine does not take place). This reaction gives HF which reacts further with excess KF to produce KHF₂(eq.5)(cf. [33]), and it may also form strong hydrogen bonds with phenols (II) and (III)(eq.6).

The excess of KF leads also to the formation of potassium phenolates as ionic pairs (eq.3; cf. [21]). Due to a great difference in the acidity of phenols (II) and (III) and HF (see pK_a in Table 1), the equilibrium is considerably shifted to the right. The reactivity of ArO⁻K⁺ ionic pairs is substantially increased as they are divided into free ions (the shift of equilibrium 4 to the right) due to complexation of the potassium cation with crown ether [4-11]. Association of phenols with phenolate anion to give complexes with hydrogen bond should not be neglected (eq.7 [34] eq.8 [34,35]). The increased solubility of KF [36] and the increased nucleophilicity of F⁻-anion in the presence of 18-C-6 should also be taken into account [19].

Therefore, the formation of compounds (VII-IX) in the reaction of pentafluoropyridine (I) and pentafluorophenol (III) at 80°C in the catalytic process (unlike the non-catalytic one, leading only to compounds (IV) and (VI) may be explained by the greater nucleophilicity of C₆F₅O⁻ and F⁻-anions (Table 3, N 3-5). But the presence of crown ether practically has no catalytic effect on the reaction of pentafluoropyridine

with 4-nitrophenol (II) at 80°C (Table 2, N 5-8) because of the greater reactivity of 4-NO₂C₆H₄O⁻-anion with respect to C₆F₅O⁻-anion, which corresponds to the difference in the basicity of these anions [cf. the pK_a values for compounds (II) and (III) in Table 1]. Only lowering of the temperature down to 0°C allowed us to observe the catalytic effect of crown ether in this reaction (Table 2, N 1-4; cf. Table 3, N 1,2).

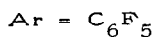
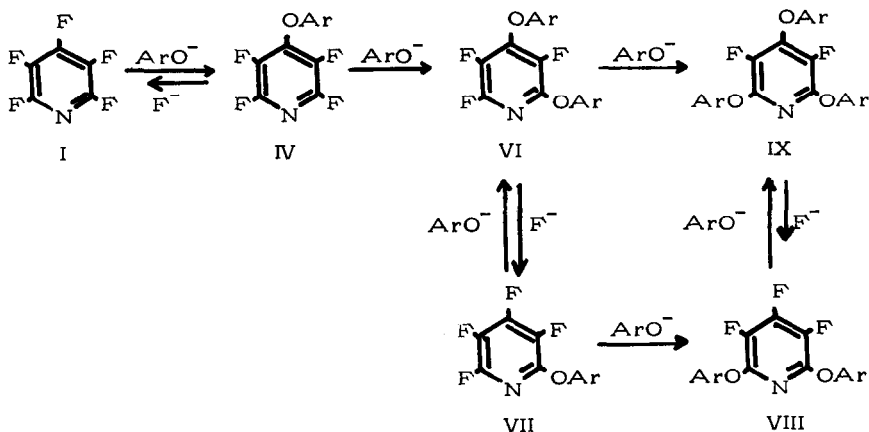
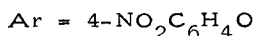
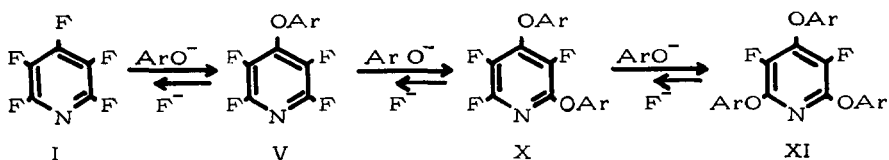
Thus, the catalytic effect of 18-C-6 was observed only at certain reaction rates of anions with substrates. This is also confirmed by the fact that in the reactions involving substitution of fluorine in compounds (IV,VI) and (V,X), occurring at the less reactive positions 2 and 6 under the action of the corresponding phenoxy anions, the catalytic effect of crown ether was observed at the higher temperature (80°C) (Table 2, N 17,18,21,22; Table 3, N 13,14,16,17). The same effect was also found in the reaction of pentafluoropyridine with the excess of 4-nitrophenol and KF in acetonitrile, as well as in sulpholan (Table 2, N 9-16). At the same time, a significant decrease in nucleophilicity of C₆F₅O⁻-anion in the reaction with pentafluoropyridine in the presence of excess pentafluorophenol may be due to the formation of hydrogen-bonded associates (eq. 7). The increased amount of pentafluorophenol in the reaction mixture leads to the decreased effect of crown ether catalysis (Table 3, N 10, 11).

A decrease in the relative yields of compounds (VII) and (VIII) in the reaction products in the case of two-fold excess of pentafluorophenol (Table 3, N 10; cf. N 4,5) may be caused in part by suppression of the competing substitution of C₆F₅O-group by fluorine, due to increased constant concentration of C₆F₅O⁻-anion in the reaction medium (cf. [18]).

In the replacement of phenoxy groups in compounds (X,XI) and (VI,IX) by fluorine, formal change of orientation of F⁻-attack has been observed. In compounds (X) and (XI), containing 4-nitrophenoxy groups, the attack by F⁻-anion occurs preferably at the 2-position, while in compounds (VI,IX), containing pentafluorophenoxy groups, position 4 is preferably

attacked (cf. [37], [38]). The small degree of transformation of compounds (X) and (XI) under the action of F^- -ion as compared to compounds (VI) and (IX), which is possibly connected with the worse leaving ability of 4-nitrophenoxy group relative to pentafluorophenoxy one, does not allow to explain a different direction of the F^- -ion attack in 2,4- and 2,4,6-substituted phenoxy pyridines (X,XI) and (VI,IX).

The data presented lead us to suggest the following reaction routes of pentafluoropyridine with 4-nitrophenol and pentafluorophenol in the presence of KF:



Compound (VII) may also be formed as a result of C₆F₅O⁻-anion attack at the 2 and 6 positions in the pentafluoropyridine molecule, especially in the presence of crown ether, leading to the greater nucleophilicity of C₆F₅O⁻-anion. But the reaction of pentafluorophenol with excess pentafluoropyridine gives only compound (IV), which precludes the formation of compound (VII) as a result of the direct attack

by pentafluorophenoxy anion at the 2 and 6 positions in pentafluoropyridine (Table 3, N 12). The attack by that anion at the 6 position in compound (VII) is possible only in the catalytic process (Table 3, N 19,20).

Thus, despite small differences in the basicity of $4\text{-NO}_2\text{C}_6\text{H}_4\text{O}^-$ and $\text{C}_6\text{F}_5\text{O}^-$ -anions, their nucleophilicity and the tendency to elimination are substantially different, though they change in the same direction as their basicity.

The structure of compounds (V), (X), (XI) was proved by spectral methods (Tables 4,5) and by elemental analysis data (Table 5).

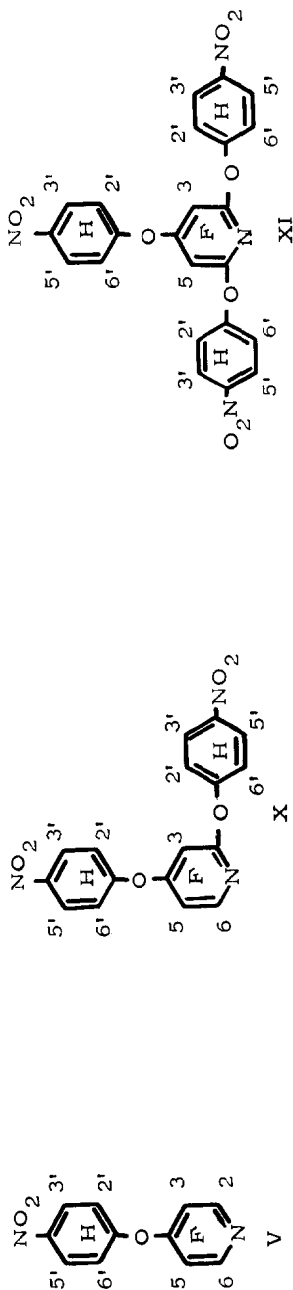
Compounds (IV,VI-IX) were described in [14].

EXPERIMENTAL

^{19}F and ^1H NMR spectra were recorded on the Varian A56-60A spectrometer at 56.4 and 60 MHz respectively, for 25% solutions in acetone and nitrobenzene. Hexafluorobenzene was used as an internal standard (downfield shifts were taken as positive). IR-spectra were recorded for 1% solutions in CCl_4 and KBr disks (0.25% concentration) on the UR-20 spectrometer. GLC analysis was carried out on the LKhM-7a chromatograph with programming of temperature from 50 to 270°C, at the rate of 10°C/min, with catharometer as a detector, the column 400 x 4 mm, the carrier gas - He, 60 ml/min. Stationary phase - 15% SKTFT -50 or 15% SE-80 (of the weight of the carrier - chromosorb W-DMCS). The quantitative analysis of the mixture was carried out by the internal normalization method. Identification of the components was made by adding known samples to a mixture.

Directly before the reaction, the anhydrous KF was maintained at 350°C for 2 hours. Purification and preparation of anhydrous acetonitrile and sulpholan were carried out as described in [39]. 18-C-6 was used as a complex with acetonitrile. Pentafluoropyridine was dried over MgSO_4 and distilled, b.p. 84°C [40]. 4-Nitrophenol was used without any additional purification, m.p. 112-113°C.

TABLE 4

 ^{19}F and ^1H NMR Data for the Compounds:

Compound IV	^{19}F Chemical Shifts (ppm)				^1H Chemical Shifts (ppm)			The Absolute Values of J_{FF} and J_{HH} Constants Hz
	F ₂	F ₃	F ₅	F ₆	H _{2;6'}	H _{3;5'}	Hz	
V ¹⁾	+73.0	+ 8.9	+ 8.9	+73.0	3.74	4.15	$J_{\text{HH}}^{2,3'} = J_{\text{HH}}^{5,6'} = 5$	
X ¹⁾	-	+12.8	+ 6.5	+73.6	3.76	4.18	$J_{\text{FF}}^{3,5} = 27$; $J_{\text{FF}}^{2,3'} = 21.5$; $J_{\text{FF}}^{3,5} = 0$	
XI ²⁾	-	+10.0	+10.0	-	3.76	4.18	$J_{\text{HH}}^{2,3'} = J_{\text{HH}}^{5,6'} = 5$	

1) Acetone as a solvent, C=25%, t°=40°C

2) Nitrobenzene as a solvent, C=25%, t°=100°C

TABLE 5

Melting Points, IR and Elemental Analysis Data of Compounds (V, X, XI)

Comp. M.p. (°C)	IR-Spectra, cm^{-1}		Found (%)				Calculated (%)								
	C-F	C-O-C	Ar-f-ring	NO ₂	C	H	F	N	Mol. wt.	Formula	C	H	F	N	Mol. wt.
V	782 792	990 1080 (vs)	1480- (vs)	1510 (vs)	1350 45.9 (vs)	1.69 46.0	26.4 1.53	26.4 26.7	289 289	$\text{C}_{11}\text{H}_4\text{FN}_2\text{O}_3$	45.6	1.40	26.4	9.74	288
X ¹⁾	121- 1233)	990 1070 (vs)	1470- (vs)	1500 (vs)	1350 50.2 (vs)	1.97 50.4	13.4 2.02	13.7 13.7	399 400	$\text{C}_{17}\text{H}_8\text{FN}_3\text{O}_6$	50.1	1.97	13.9	10.3	407
XI ¹⁾	209- 2114)	990 1070 (vs)	1460- (vs)	1490 (vs)	1350 52.6 (vs)	2.36 52.7	7.55 2.24	7.68 7.68	525 530	$\text{C}_{23}\text{H}_{12}\text{FN}_4\text{O}_9$	52.5	2.28	7.23	10.6	526

1) KBr disk, C=O.25%.

2) Recrystallization from petroleum ether (b.p. 70-100°C).

3) Recrystallization from ethanol.

4) Recrystallization from nitrobenzene.

5) By isothermic distillation method.

All IR spectra of compounds (V,X,XI) contain the band at 1220 (vs) cm^{-1} .

Interaction of Pentafluoropyridine (I) with 4-Nitrophenol (II) in the Presence of KF (the typical experiment, see Table 2)

1.5 g (0.025 mol) of anhydrous KF, 0.21 g (0.0007 mol) of 18-C-6, 1.64 g (0.0118 mol) of 4-nitrophenol and 12 ml of the solvent were mixed in a vessel under a stream of dry argon or nitrogen. Then 2 g (0.0118 mol) of pentafluoropyridine in 5ml of the solvent were added, and the reaction mixture was heated to a certain temperature while stirring it for some time (Table 2), then cooled and poured into 100 ml of 5% HCl, extracted with diethyl ether (3 x 25 ml). The ether extract was washed with water and dried over $MgSO_4$. The solvent was evaporated and the residue was recrystallized from petroleum ether (70-100°C) to obtain 4-(4'-nitrophenoxy)-2,3,5,6-tetrafluoropyridine (V) (nc).

In the case of excess 4-nitrophenol, after pouring the reaction mixture into 5% solution of HCl, the aqueous solution was filtered off from 2,4,6-tris-(4-nitrophenoxy)-3,5-difluoropyridine (XI) (nc). The filtrate was extracted with diethyl ether (3 x 25 ml), the ether extract was washed with water, dried over $MgSO_4$, and the solvent was evaporated. The residue was chromatographed on the silica gel column (120 x 2.5 cm), the eluent being the mixture of C_6H_6 : CCl_4 (3:1), to obtain compound (V) and 2,4-bis-(4'-nitrophenoxy)-3,5,6-trifluoropyridine (X) (nc).

Experimental conditions and results are presented in Table 2. The ^{19}F and 1H NMR spectral data of the individual compounds are presented in Table 4. IR and elemental analysis data are summarized in Table 5.

Interaction of Pentafluoropyridine (I) with Pentafluorophenol (III) in the Presence of KF (a typical experiment, see Table 3)

8.1 g (0.14 mol) of KF, 2.1 g (0.007mol) of 18-C-6 and 15 ml of a solvent were placed into a flask under the stream of dry nitrogen or argon, and were maintained at 20-25°C for

15 min. After that, 12.8 g (0.07 mol) of pentafluorophenol in 5 ml of the solvent were added, and the mixture was maintained for another period of 15 min. Then 12 g (0.07 mol) of pentafluoropyridine in 5 ml of the solvent were added to the reaction mixture; the mixture was heated for some time at the required temperature while stirring it, then the solution was cooled and poured into 150 ml of 5% HCl. The organic layer was extracted with diethyl ether, the extract was washed and dried over MgSO_4 . The solvent was evaporated, and the residue (16-17 g) was analysed by GLC. The products were obtained by vacuum distillation, recrystallization or by the preparative GLC.

Experimental conditions and results are presented in Table 3. ^{19}F NMR and IR spectral data of compounds (IV, VI-IX) are reported, together with their constants and elemental analysis data, in [14].

REFERENCES

- 1 J.H.Clark, Chem.Rev., 8 (1980) 429.
- 2 N.N.Vorozhtsov, G.G.Yakobson, Zh.Org.Chim., 27 (1957) 1672;
N.N.Vorozhtsov, G.G.Yakobson, Zh.Org.Chim., 28 (1958) 40.
- 3 W.Dmowski, W.T.Flowers, R.N.Haszeldine, J.Fluorine Chem., 9 (1977) 94.
- 4 H.R.Hanna, J.M.Miller, Canad.J.Chem., 57 (1979) 1011.
- 5 D.J.Sam, H.E.Simmons, J.Amer. Chem.Soc., 96 (1974) 2252.
- 6 C.L.Liotta, H.P.Harris, J.Amer.Chem.Soc., 96 (1974) 2250.
- 7 I.Belsky, J.Chem.Soc., Chem.Comm., (1977) 237.
- 8 M.Makosza, M.Ludwikov, Angew.Chem., 86 (1974) 744.
- 9 A.R.Butler, J.Chem.Soc., Perkin Trans. I, (1975) 1557.
- 10 F.Terrier, G.Ah -Kow, M.J.Pouet, M.P.Simmonin, Tetrahedron Let., (1976) 227.
- 11 V.V.Litvak, S.M.Shein, Zh Org.Khim., 12 (1976) 1723.
- 12 R.D.Chambers, P.D.Philpot, P.L.Russel, J.Chem.Soc., Perkin Trans.I, (1977) 1605.
- 13 N.E.Akhmetova, V.M.Vlasov, G.G.Yakobson, Izv.Akad.Nauk SSSR, Ser.Khim., (1978) 949.
- 14 V.M.Vlasov, V.V.Aksenov, N.E.Akhmetova, G.Z.Mustakimova, G.G.Yakobson, Izv.Sib.Otd.Akad.Nauk SSSR, Ser.Khim.Nauk (1978) 130.

- 15 W.Rabhofer, G.Oepen, F.Vögtle, *Isr.J.Chem.*, 18 (1979) 249.
- 16 V.M.Vlasov, V.V.Aksenov, G.G.Yakobson, *Zh.Org.Chim.*, 15 (1979) 2156.
- 17 J.Miller, 'Aromatic Nucleophilic Substitution', Elsevier, Amsterdam (1968); 'Correlation Analysis in Chemistry' Ed. N.B.Chapman, J.Shorter, Plenum Press, N.Y.-London (1978) p.313; G.Bartoli, P.E.Todesco, *Accoun.Chem.Res.*, 19 (1977) 125.
- 18 M.J.V.de Oliveira Baptista, D.A.W.Son, *J.Chem.Soc., Perkin Trans.I*, (1978) 295.
- 19 C.L.Liotta, E.E.Grisdale, H.P.Hopkins, *Tetrahedron Let.*, (1975) 4205.
- 20 R.J.De Pasquale. C.Tamborsky, *J.Org.Chem.*, 33 (1969) 1658.
- 21 I.N.Rozhkov, I.D.Kuleshova, I.L.Knunyants, *Izv.Akad.Nauk SSSR, Ser.Khim.*, (1973) 128.
- 22 G.G.Yakobson, T.D.Petrova, L.S.Kobrina, *Fluorine Chem.Rev.*, 7 (1974) 115.
- 23 A.Albert, E.P.Sergeant, 'Ionization Constants of Acids and Bases', Wiley, New York, (1962).
- 24 V.S.Pilyugin, Yu.I.Umanski, S.V.Vasin, L.I.Khrustaleva, A.A.Girfanova, *Zh.Obshch.Khim.*, 50 (1980) 1625.
- 25 I.M.Kolthoff, M.K.Chantooni, *J.Am.Chem.Soc.*, 91 (1969) 4621.
- 26 J.Birchall, R.Haszeldine, *J.Chem.Soc.*, (1959) 3653.
- 27 B.G.Cox, A.Gibson, *J.Chem.Soc., Perkin Trans.II*, (1977) 1812.
- 28 E.M.Arnett, L.E.Small, *J.Am.Chem.Soc.*, 99 (1977) 808.
- 29 R.E.Banks, R.N.Haszeldine, K.H.Leggi, F.E.Rickett, *J.Chem.Soc., Perkin Trans.I.*, (1974) 2367.
- 30 *The Chemistry of Non-aqueous Solvents*, v.3, Acad.Press, N.Y.-London, 1970, p.1; A.Ghosh, S.R.Ralit, *Ind.J.Chem.*, 12 (1974) 383.
- 31 J.H.Clark, J.Emsley, *J.Chem.Soc., Dalton Trans.*, (1974) 1125.
- 32 J.H.Clark, J.Emsley, *J.Chem.Soc., Dalton Trans.*, (1973) 2154; (1975) 2129; J.H.Clark, J.M.Miller, *Chem.Communs.*, (1976) 229; *J.Am.Chem.Soc.*, 99 (1977) 498; J.H.Clark, J.Emsley, O.P.Hoyte, *J.Chem.Soc., Perkin Trans.I*, (1977) 1091; J.H.Clark, J.M.Miller, Kwok-Hung So, *J.Chem.Soc.*,

- Perkin Trans.I, (1978) 941; J.Emsley, O.P.Hoyte, E.Overill, J.Chem.Soc., Chem.Communs., (1977) 225.
- 33 D.N.Reinhoudt, F. de Jong, H.P.M.Tomassen, Tetrahedron Let., (1979) 2067.
- 34 I.M.Kolthoff, M.K.Chantooni, J.Am.Chem.Soc., 92 (1970) 2025; 93 (1971) 3843; M.K.Chantooni, I.M.Kolthoff, J.Phys.Chem., 80 (1976) 1306.
- 35 C.Reichard, 'Solvent Effects in Organic Chemistry', Verlag Chemie, Weinheim-N.Y., 1979, p.159.
- 36 T.Ando, J.Yamawaki, J.Synthetic Org.Chem., Japan, 39 (1981) 14.
- 37 R.D.Chambers, J.Hutchinson, W.K.R.Musgrave, J.Chem.Soc., Suppl.I, (1964) 5634.
- 38 J.Bratt, B.Iddon, A.G.Mack, H.Suschitzky, J.A.Taylor, B.J.Wakefield, J.Chem.Soc., Perkin Trans.I, (1980) 648.
- 39 A.J.Gordon, R.A.Ford, 'The Chemist's Companion', Wiley, N.Y.-London-Sydney-Toronto, 1972.
- 40 'Synthesis of Fluoroorganic Compounds', Ed. I.L.Knunyants, G.G.Yakobson, Moscow, 'Khimia' (1973) p.134.