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FLUOROAROMATIC DERIVATIVES. CI. TRANSFORMATIONS OF POLYFLUOROAZOXYBENZENES IN STRONG ACIDS. WALLACH REARRANGEMENT OF POLYFLUOROAZOXYBENZENES

G.G. FURIN*, O.I. ANDREEVSKAYA, A.I. REZVUKHIN and G.G. YAKOBSON

Institute of Organic Chemistry, 630090, Novosibirsk (U.S.S.R.)

SUMMARY

The present study discusses the behaviour of fluorinated azoxybenzenes in strong acids. 2,2',3,3',5,5',6,6'-Octafluoroazoxybenzene I reacted with chlorosulphonic acid giving the Wallach rearrangement product, the chlorosulphonate ester of 4-hydroxy-2,2',3,3',5,5',6,6'-octafluoroazobenzene. In HF, H_2SO_4 and HSO_3F compound I was stable, whereas in SbF_5-HSO_3F (1:1) at 20 °C, it gave quantitatively the reduction product, 2,2',3,3',5,5',6,6'-octafluoroazobenzene. Using ^1H, ^{13}C, ^{15}N and ^{19}F NMR, we studied cationoid species generated from fluorinated azoxybenzenes by treatment with strong acids. The role of these species in the Wallach rearrangement and formation of azobenzenes has been examined. In HSO_3Cl, cleavage of the C-N bond takes place, leading, e.g. in the case of decafluoroazoxybenzene, to pentafluorochlorobenzene and the pentafluorophenyldiazonium cation. A route for this reaction is suggested.

INTRODUCTION

Treatment of azoxybenzene and its derivatives with acids is known to result in the Wallach rearrangement, which leads to 2- or 4-hydroxyazobenzenes [1-3]. Starting from the 1960's, the mechanism of that rearrangement has been extensively

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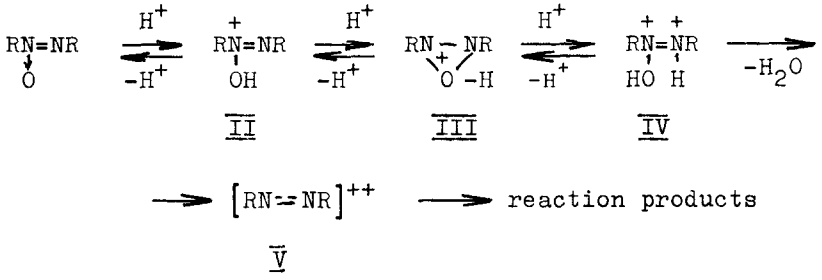
studied [4-8]. Labelling of atoms (^{14}C, ^{15}N, ^{18}O) has shown that the Wallach rearrangement is of intermolecular character and does not involve initial transformation of azoxybenzene to azobenzene [9,10]. Some authors assumed that the rearrangement proceeds with the formation of intermediate products [11,12]. According to modern views, first the monoprotonated form of azoxybenzene II or III is formed, which is then transformed to the diprotonated form IV , and dehydration of the latter gives the dication V . Kinetic studies of the Wallach rearrangement have shown the diprotonated form of azoxybenzene IV or the dication V to be responsible for the rearrangement [2,13].



For both cations (IV or V) nucleophilic attack on the *ortho*- and *para*-carbons of the benzene ring may lead to Wallach rearrangement products. However the data available do not allow us to determine which cation (whether IV or V) is responsible for the rearrangement products. By treatment of azoxybenzene with SbF_5-HF-SO_2, Olah and co-workers [14] generated a dication of the type V , stable at low temperatures. They suggested the dication V to be responsible for the Wallach rearrangement product. More recent studies use the concept of Olah to explain the mechanism of the Wallach rearrangement [3].

Analysis of the results of these investigations shows that variation of substituents and reaction conditions affects both the reaction rate and products. Thus some reactions gave azobenzenes along with the rearrangement product, the former sometimes dominating. As reported in [6], the Wallach rearrangement of azoxybenzenes with chlorine or fluorine in the 2- and 4-positions of the benzene ring gave the corresponding azobenzenes as the main reaction products. Oae and

co-workers [15] explain the formation of azobenzenes by transformation of the diprotonated form of an azoxybenzene of the type IV to an azobenzene radical cation.

The Wallach rearrangements of some substituted azoxybenzenes gave anomalous products. Thus treatment of 4,4'-dialkylazoxybenzenes with sulphuric acid leads to 3-hydroxy-4,4'-dialkylazobenzenes and 4-hydroxy-4,3'-dialkylazobenzenes [16]. The Wallach rearrangement, therefore, is a more complex process than was supposed earlier.

We studied the effect of aromatic fluorine atoms on the course and products of the Wallach rearrangement by investigating the transformations of fluorinated azoxybenzenes in strong acids. The following polyfluoroazoxybenzenes were used : 4-XC_6F_4N=NC_6F_4X-4' (X = H I; F VI; CH_3 VII; CF_3 VIII; Br IX), 4,4'-difluoroazoxybenzene X , 2,2',4,4'-tetrafluoroazoxybenzene XI and 2,2',3,3',4,4',5,5'-octafluoroazoxybenzene XII . Out of all these compounds, the behaviour in acids has been reported earlier only for compound X [15].

RESULTS AND DISCUSSION

We have shown that in H_2SO_4, HF or HSO_3F compound I did not undergo the Wallach rearrangement and hydrolysis of these solutions quantitatively gave the starting product. At the same time, in HSO_3Cl at 20°C the Wallach rearrangement occurred, leading to the chlorosulphonate ester of 4-hydroxy-2,2',3,3',5,5',6,6'-octafluoroazobenzene XIII [17]. Compound XIII was also produced by transformation of compound I in HSO_3F-HSO_3Cl (1:1). Compound I was transformed in SbF_5-HF (1:1) or SbF_5-HSO_3F (1:1), and the resulting mixtures underwent further hydrolysis to afford 2,2',3,3',5,5',6,6'-octafluoroazobenzene, XIV, in 80% yield, whereas at 40 to -60°C in the same acids the starting compounds were quantitatively recovered.

We considered it necessary to investigate by ^1H, ^{13}C, ^{15}N and ^{19}F NMR the nature of the resulting cationoid species generated from compound I in the above acids. The results are summarised in Tables 1 and 2 .

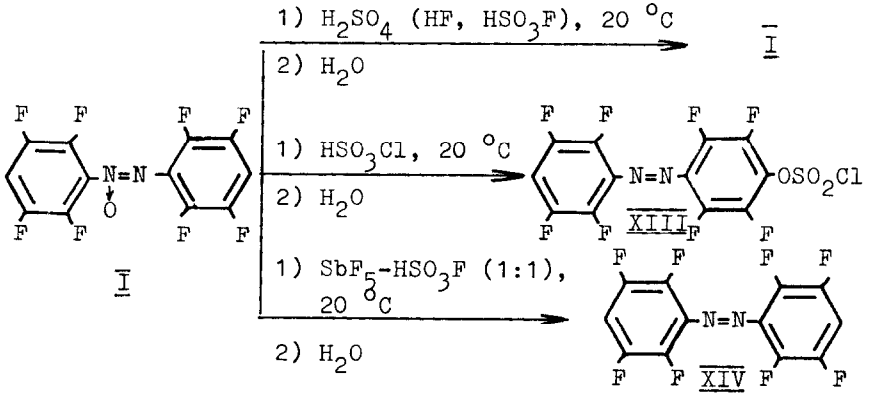
TABLE 1

^{19}F and ^{1}H NMR spectra of polyfluoroazoxybenzenes and their acid solutions

Compound	Position of fluorine atoms	^{19}F NMR, δ ppm, solvent				Position of hydrogen atoms	^{1}H NMR, δ ppm, solvent			
		HSO_3F 30°	SbF_5-HSO_3F (1:1) -70°	SbF_5-HSO_3F (1:1) 40°	$(CH_3)_2SO$ 30°		HSO_3F 30°	SbF_5-HSO_3F (1:1) -70°	SbF_5-HSO_3F (1:1) 40°	$(CH_3)_2SO$ 30°
I	3,5	28.9	29.8	32.8	20.8	$H_{arom.}$	7.93(2)	7.90(2)	8.33(2)	7.32, 7.54
	2,6	32.3	34.2	35.1	27.2	OH	14.1(1)	14.1(1)		
	2',6'	29.3	30.5	31.0	24.3	NH	8.1(1)	10.1(1)		
	3',5'	22.5	22.7	23.4	14.5	H_3O^+			10.2(3)	
VI	2,6	29.8	30.4	35.3	22.0	OH		14.4(1)		
	3,5	8.5	11.0	9.6	3.9	NH		10.0(1)		
	4	28.8	34.2	45.0	13.8	H_3O^+			10.2	

XII	2	43.8	33.8	26.1			
	3	8.1	14.3	10.6			
	4	37.5	26.8	13.8			
	5	22.2	17.2	22.2			
	2'	42.1	31.4	24.3			
	3'	5.1	13.3	6.9			
	4'	23.3	22.6	10.5			
	5'	19.8	14.3	19.5			
XIV	2,6	31.2	32.6	24.1	$H_{arom.}$		8.1(1) 7.57, 6.29
	3,5	27.0	32.0	12.4	NH		13.6(2)
	2',6'	31.2	31.2	24.1			
	3',5'	27.0	21.5	12.4			
XVII	2,6	29.0	35.1	13.5	NH		13.6
	3,5	8.5	9.0	0.9			
	4	39.2	42.2	13.9			
	2',6'	29.0	22.4	13.5			
	3',5'	8.5	7.7	0.9			
	4'	39.2	30.4	13.9			
XXII	2	18.3		15.4			
	3	11.3		8.0			
	4	16.6		13.5			
	5	28.0		25.1			

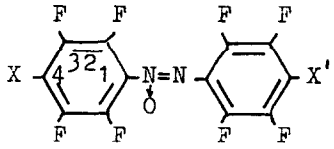
The ^{15}N NMR spectrum of an HSO_3F-SO_2 solution of compound I labelled with ^{15}N on both nitrogen atoms at 30 to -60°C shows a broad signal at 325 ppm (here and further on the standard is liquid ammonia). Comparison of the signal position with that for the precursor (two signals of equal intensities at 328 and 315.9 ppm) shows a small upfield shift of the signal ($\Delta\delta\,^{15}N$ = 4.1 ppm) relative to the averaged nitrogen signal of the precursor. The ^{1}H NMR signal of that solution at 30 to -60 °C does not show any signal of the proton different from that of acid. However in the ^{13}C NMR spectrum of that solution, the C_1 and C_1' atoms of the benzene rings are screened in different ways (see Table 2) which indicates an asymmetric structure of the cation. The ^{19}F NMR spectrum shows the signals of two tetrafluorophenyl rings (Table 1). This probably indicates protonation of azoxybenzene I in the acid and fast reversible transformations of type II and III intermediates and the starting compound. Hydrolysis of the solution gave the starting azoxybenzene I .



The ^{15}N NMR spectrum of an SbF_5-HSO_3F (1:1)-SO_2 solution of compound I at -60 °C first showed a wide signal at 325 ppm. But 15 min. after, the spectrum showed two signals of equal intensities at 220 and 209 ppm. The intensities of the signals increased, reached maxima in an hour and then remained constant. An upfield shift of the ^{15}N signal indicates generation of a cationoid species and has been

reported earlier [18]. The ^1H NMR spectrum at -70 to -40 °C exhibits, along with the signals of aromatic hydrogen atoms, a singlet at 14.4 (NOH) and a wide signal at 10.1 ppm (NH), whose position changed with time (the same tendency was reported in [14] for the proton of the NH-fragment of the azoxybenzene diprotonated form).

TABLE 2
^{13}C NMR spectral data for compounds of the type and their acid solutions



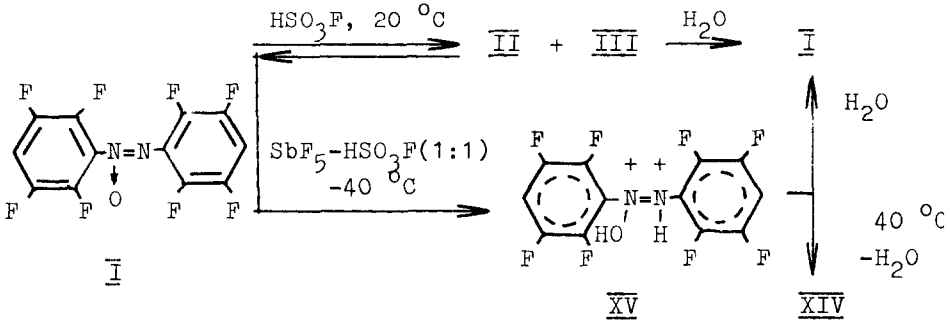
Compound	Solvent (temperature, °C)	Chemical shift from $(CH_3)_4Si$ in ppm				
		$C_1(C_1')$	$C_2(C_2')$	$C_3(C_3')$	$C_4(C_4')$	C with X (C' with X')
I	CH_2Cl_2 (30)	129.4	147.1	140.4	111.0	
		(123.5)	(147.1)	(140.4)	(103.6)	
	HSO_3F (30)	125.4	147.4	141.2	118.0	
		(111.7)	(147.2)	(141.2)	(109.9)	
VI	CH_2Cl_2 (40)	118.1	140.9	137.0	143.1	
		(124.5)	(140.9)	(137.0)	(145.3)	
	HSO_3F (40)	106.3	142.4	138.9	148.3	
		(121.4)	(142.4)	(138.9)	(145.3)	
	SbF_5-HSO_3F (1:1) (-40)	108.1	152.3	138.9	150.3	
		(120.9)	(142.3)	(138.9)	(146.5)	
	SbF_5-HSO_3F (1:1) (40)	105.2	142.3	138.7	154.8	
		(120.7)	(142.4)	(138.7)	(149.0)	
VII	CH_2Cl_2 (40)	116.9	146.0	140.1	120.9	6.1
		(126.5)	(146.0)	(140.1)	(119.8)	(6.1)
	HSO_3F (-40)	107.7	146.3	141.2	122.8	7.2
		(131.6)	(146.3)	(141.2)	(125.7)	(7.2)
VIII	CH_2Cl_2 (40)	125.3	145.0	140.9	113.4	120.9
		(130.1)	(145.0)	(140.9)	(106.4)	(120.9)
	HSO_3F (40)	122.0	145.3	141.3	114.2	120.5
		(129.4)	(145.3)	(141.3)	(112.7)	(120.5)

The ^{19}F NMR spectrum of this solution (-40 °C) shows a downfield shift of the aromatic fluorine signals relative to their position in the spectrum of the precursor, which indicates the presence of a positive charge on the functional group. Screening of the fluorine atoms in positions 2,2',6,6' of the benzene ring somewhat varies from compound to compound (Table 1). These data indicate practically complete diprotonation of azoxybenzene I in the system of I - (HSO_3F-SbF_5-SO_2) at -70 to -40 °C, to form the intermediate XV (cf. [14]). Hydrolysis of the cation gave the starting azoxybenzene I in practically quantitative yield. At the same time, as shown by NMR, azoxybenzene I underwent some irreversible transformations in solutions of SbF_5-HSO_3F (1:1) or SbF_5-HF (1:1) at temperatures above 20 °C. Thus the ^1H NMR spectrum exhibits no signals of the diprotonated form XIV at 14.4 and 10.1 ppm, but shows a singlet at 10.2 ppm, which is a signal of the protons of the H_3O^+-cation. This indicates dehydration of the diprotonated form of the azoxybenzene I . The ratio of the intensity of this signal to that of the aromatic hydrogen, which is shifted to low field and resonates at 8.33 ppm, is 3:2. Lowering of the temperature of the solution down to -60 °C did not restore the previous pattern of the ^1H NMR spectrum. In the ^{19}F and ^{13}C NMR spectra, when the temperature is changed from -40 to 40 °C, the positions of the aromatic carbon and fluorine signals are changed insignificantly (Tables 1, 2).

The NMR spectra suggest that dehydration of the intermediate XV in SbF_5-HSO_3F (1:1) at 20 to 40 °C leads to the formation of a cationoid species, which is the precursor of the azobenzene XIV formed by hydrolysis of the solution. This species does not represent the diprotonated form of the azobenzene XIV, since the ^1H and ^{19}F NMR spectra of SbF_5-HSO_3F (1:1) solution of compound XIV at 40 °C differ from those of azoxybenzene I solution in the same acid. This implies that the octafluoroazobenzene XIV is not formed when the azoxybenzene I is treated with SbF_5-HSO_3F (1:1) at 20 to 40 °C, but is produced by hydrolysis of the resulting solution (see [9,10]). There is not sufficient data for a more close discussion of the mechanism of the conversion of compound I to compound XIV and the structu-

re of the intermediates formed from I at 20 to 40 °C; literature reports give various views in this respect, including those on the generation of dications of the type V (cf. [12,14]).

It seemed worthwhile to compare the data on the transformations of octafluoroazoxybenzene I in superacids with those for azoxybenzene. As reported in [14], hydrolysis of SbF_5-HF-SO_2 solutions of azoxybenzene gives 4-hydroxyazobenzene XVI (yield and details of the experiment are not specified), whereas the fluorinated azoxybenzene I gives only the octafluoroazobenzene XIV .



Due to this we studied in detail transformations of azoxybenzene in acids. Hydrolysis of azoxybenzene in HSO_3F-SO_2 and SbF_5-HF-SO_2 solutions kept at -80 °C for 30 min quantitatively gave the starting compound. At the same time, keeping HSO_3Cl or HSO_3F solutions of azoxybenzene at -10 °C resulted in the Wallach rearrangement, which gave the chlorosulphonate ester of 4-hydroxyazobenzene XVII and 4-hydroxyazobenzene XVI, 85 and 80% yields respectively. Azobenzene in these conditions was formed in trace quantities (cf. [7,19]). Its yield somewhat increased (up to 10%) when azoxybenzene was treated with HSO_3Cl at 20 °C. In the reaction of azoxybenzene with SbF_5-HF-SO_2, the ratio of the reagents plays an important role. Thus treatment of azoxybenzene at -50 °C for 10 min with SbF_5-HF (1:1)-SO_2 (SbF_5 : azoxybenzene = 20 : 1, as in the work of Olah [14]) resulted in a mixture of azobenzene (62% yield) and 4-hydroxyazobenzene (12% yield). Increased quantities of SbF_5 led to a considerable amount of tarry products, whereas decreased quantities required increased reaction time for complete transformation of the substrate.

The product ratio in this case was the same. When SO_2ClF was used instead of SO_2, the yield of 4-hydroxyazobenzene was decreased to 5%. In all cases tarry products were formed as well.

Thus, our results for the reaction of azoxybenzene with SbF_5-HF-SO_2 at -50 °C are not fully consistent with the data reported in [14]. Therefore we considered it necessary to re-examine here the ^1H NMR spectra of acid solutions of azoxybenzene reported in [14], and to analyse the ^{15}N NMR spectra of these solutions. The ^1H NMR spectra of azoxybenzene in various acids obtained by us are identical to those given in this work [14]. This suggests that hydrolysis of SbF_5-HF-SO_2 solution of azoxybenzene has been carried out in conditions described in [14].

Figure 1 shows the ^{15}N NMR data for solutions of azoxybenzene, labelled with ^{15}N on both nitrogen atoms, in the same acids. As with the case of compound I , increased acidity of the medium resulted in mono- and di-protonation, which is indicated by the presence of one (329 ppm) and two (213 and 173 ppm) nitrogen signals, respectively, in the ^{15}N NMR spectrum. In the case when the ^1H NMR spectrum loses the N-OH and N-H hydrogen signals and shows the signal at 10.2 ppm (H_3O^+), the ^{15}N NMR spectrum loses the signals of the diprotonated form at 213 and 173 ppm and exhibits two broadened signals at 410 and 362 ppm. Hydrolysis in this case gave azobenzene instead of 4-hydroxyazobenzene. Thus compound I and azoxybenzene were transformed in SbF_5-HF-SO_2 to generate a species hydrolysed to give the corresponding azobenzenes, but not the Wallach rearrangement products, which is indicated by disappearance of the signal of the diprotonated form of these compounds from the ^1H and ^{15}N NMR spectra and the appearance of the H_3O^+ proton signal.

These results suggest that two processes take place, which lead to the Wallach rearrangement product and the reduction product. We consider the cationoid intermediates generated by dehydration of the azoxybenzene diprotonated form to be responsible for the reduction product, and the azoxybenzene diprotonated form itself for the Wallach rearrangement product. This

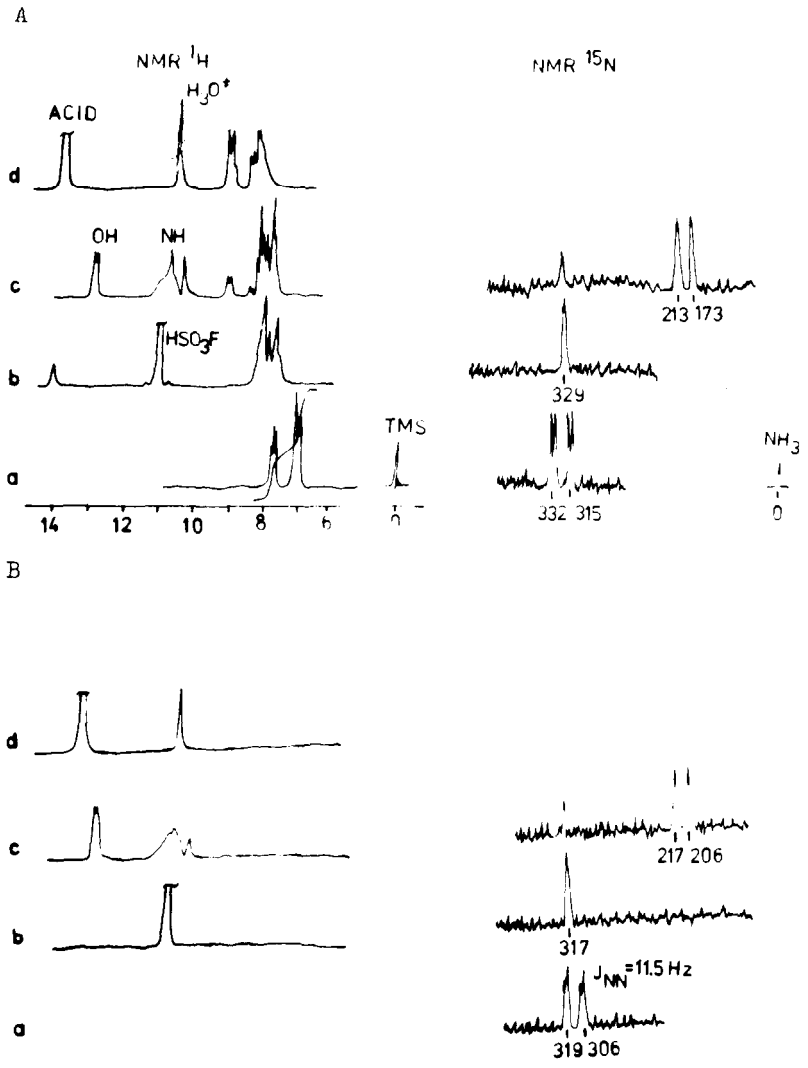


Fig.1. ^{1}H and ^{15}N NMR spectra of solutions of A - azoxybenzene: (a) in SO_2 at -80 °C; (b) HSO_3F-SO_2 at -80 °C; (c) SbF_5-HSO_3F (1:1)-SO_2 at -80 °C; (d) SbF_5-HSO_3F (1:1)-SO_2 at -50 °C (15 min after dissolution); B - decafluoroazoxybenzene: (a) in SO_2 at -80 °C; (b) HSO_3F-SO_2 at -80 °C; (c) SbF_5-HSO_3F (1:1)-SO_2 at -40 °C; (d) SbF_5-HSO_3F (1:1) (24 h after dissolution).

suggestion could be tested using azoxybenzenes, for which the Wallach rearrangement is impossible, by tracing the reactivity of the diprotonated form of the azoxybenzene and the dication of type V . In these studies we used decafluoroazoxybenzene VI , 4,4'-dimethyloctafluoroazoxybenzene VII, 4,4'-di(trifluoromethyl)-octafluoroazoxybenzene VIII and 4,4'-dibromooctafluoroazoxybenzene IX .

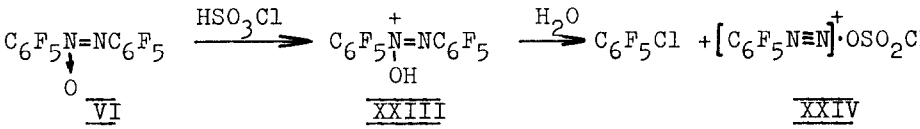
As seen from Tables 1-3 and Fig. 1, the ^{1}H, ^{13}C, ^{15}N and ^{19}F NMR spectra of acid solutions of these compounds reveal the same consistencies as those of solutions of compound I in the same acids. Treatment of these compounds with HSO_3F and SbF_5-HSO_3F (1:1) at -40 °C leads to diprotonated forms, hydrolysis of which gives the starting compounds. As shown by the ^{1}H and ^{19}F NMR spectra, treatment of compounds VI, VII and IX with SbF_5-HSO_3F (1:1) at 20 °C resulted in the generation of cationoid intermediates generated by dehydration of the diprotonated forms, followed by hydrolysis to give decafluoroazobenzene, 4,4'-dimethyloctafluoroazobenzene XVIII and 4,4'-dibromooctafluoroazobenzene XIX respectively, as *trans* isomers (dipole moments measured in benzene are equal to zero). At the same time, treatment of 4,4'-di(trifluoromethyl)-octafluoroazoxybenzene XI with SbF_5-HSO_3F (1:1) at 40 °C resulted in the formation of only the diprotonated form of that compound; no H_3O^+ proton signal was observed in the ^{1}H NMR spectra, and hydrolysis of the diprotonated form gave back the starting product. Introduction of electron-accepting trifluoromethyl groups in positions 4,4' of octafluoroazoxybenzene presumably complicates transformation of its diprotonated form to the cationic intermediate leading to abstraction of H_2O.

Thus the nature of the resulting products will depend on the ability of azoxybenzenes to generate cationoid species of type IV, or cationoid intermediates generated by dehydration of these diprotonated forms. In the case of diprotonation, hydrolysis will give either the starting products or the Wallach rearrangement products, whereas hydrolysis of cationoid intermediates generated by dehydration of diprotonated forms should, in our view, yield the reduction products, azobenzenes. Indeed, the reaction of SbF_5-HF (1:1)-SO_2 with 4,4'-difluoroazoxybenzene X (-50 °C, 10 min), 2,2',4,4'-tetrafluoro-

azoxybenzene XI (-10 °C, 15 min) and 2,2',3,3',4,4',5,5'-octafluoroazoxybenzene XII (20 °C, 10 h) and subsequent hydrolysis (under conditions where the ^1H NMR spectrum shows the H_3O^+ signal) gave the corresponding azobenzenes XX, XXI and XXII (yields 70, 75 and 60% respectively), whereas the same reactions at -80 °C and -50 °C respectively led after hydrolysis to the starting azoxybenzenes.

Rationalisation of the routes of reactions of azoxybenzenes with acids should be based on the analysis of the products formed and the studies of cationoid species generated under the above conditions. Data on the reactions of azoxybenzene and its fluoroderivatives with acids suggest that it is the diprotonated form of azoxybenzene that is responsible for the Wallach rearrangement, whereas the precursors of the reduction products, azobenzenes, are cationoid intermediates generated by dehydration of diprotonated forms.

It seemed intersting to study the behaviour of decafluoroazoxybenzene in HSO_3F, in which the Wallach rearrangement of compound I had been realised. At first monoprotonation was observed, as in the case of HSO_3F. The ^{15}N NMR spectrum of that compound shows a singlet at 317 ppm. Eventually (150-200) h), cation XXIII underwent irreversible transformations, as revealed by the NMR spectra. Thus in the ^{15}N NMR spectrum the signal at 317 ppm disappeared and the spectrum contained two signals of equal intensities at 213.3 and 333.5 ppm. The ^{19}F NMR spectrum of the HSO_3Cl solution of compound VI maintained at 10 °C for 200 h, exhibits 6 signals of intensity ratios 1:2:2:2:1:2, at 49.3, 41.3, 21.5, 14.3, 6.2 and 1.2 ppm respectively, and no signals from the fluorine atoms of cation XXIII. The signals at 21.5, 6.2 and 1.2 ppm are those of the fluorine atom of C_6F_5Cl, which is confirmed by the increase of their intensities when the authentic C_6F_5Cl is added to the solution. After the solution had been poured into water, pentafluorochlorobenzene was isolated.



The rate of conversion of cation XXIII depends on the temperature. Thus, as shown by the ^{19}F and ^{15}N NMR spectra, at 40 °C the cation is completely transformed in 3.5 h, whereas at 10 °C 200 h is necessary.

We assumed that in HSO_3Cl solution decafluoroazoxybenzene is converted to form pentafluorochlorobenzene and the pentafluorophenyldiazonium ion XXIV. Indeed, addition of pentafluorochlorobenzene to the solution resulted in the increased intensity of signals at 21.5, 6.2 and 1.2 ppm in the ^{19}F NMR spectrum. The ^{19}F NMR spectrum of the solution of the diazonium salt obtained by diazotisation of pentafluoroaniline with nitrosyl sulphate, according to [20], contains at 0 °C three signals of intensity ratios 1:2:2 at 48.5, 41.3 and 14.3 ppm respectively, which are rather close to the above values. The ^{15}N NMR spectrum of the solution of diazonium salt obtained from ^{15}N - labelled pentafluoroaniline, shows a singlet at 333.5 ppm, hence the nitrogen signal at 213.3 ppm is the signal of the β-nitrogen of the pentafluorophenyldiazonium cation XXIV. Neutralisation of the solution of cation XXIV with potassium carbonate and treatment with dimethylaniline, as described in [20], gave 4-hydroxy-2,3,5,6-tetrafluoro-4'-dimethylaminoazobenzene XXV.

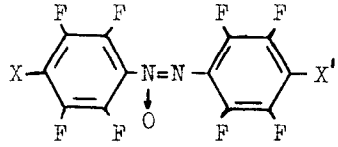
An attempt to react pentafluorophenyldiazonium cation XXIV with 2,3,5,6-tetrafluoroaniline in HSO_3Cl was unsuccessful. Even at 140 °C no reaction between these compounds was revealed by the ^{19}F NMR spectrum, which results from the low nucleophilicity of the 2,3,5,6-tetrafluoroaniline ammonium salt. Increase in the electrophilicity of the diazonium cation XXIV by introducing electron-accepting substituents into the aromatic ring is insufficient to perform the reactions with low nucleophilic substrates. This should inhibit acid-catalysed rearrangements of polyfluorinated diazoaminobenzenes. Indeed, 2,2',3,3',5,5',6,6'-octafluorodiazoaminobenzene XXVI was not rearranged to 4-aminoazobenzene in acid media. Dissolution of compound XXVI in HSO_3F or SbF_5-HSO_3F (1:1) resulted in -N-N= bond cleavage in that compound, to form the salts of 2,3,5,6-tetrafluoroaniline and 2,3,5,6-tetrafluorophenyldiazonium cation. The ^{19}F NMR spectrum of HSO_3F

solution of compound XXVI contains 4 signals of equal intensities at 40.3, 37.3, 29.5 and 15.6 ppm (the ^{19}F NMR spectrum of compound XXVI in acetone shows 2 signals of equal intensities at 23.9 and 12.1 ppm). The signals at 29.5 and 15.6 ppm were assigned to the fluorine atoms of the 2,3,5,6-tetrafluoroaniline salt, those at 37.3 and 40.3 ppm to the fluorine atoms of 2,3,5,6-tetrafluorophenyldiazonium cation (identical ^{19}F NMR spectrum was obtained for the solution of the diazonium salt formed by diazotisation of 2,3,5,6-tetrafluoroaniline with nitrosyl sulphate as described in [20]). Pouring the solution into water and its subsequent neutralisation with soda gave 2,3,5,6-tetrafluoroaniline.

The authors of [21] recently discovered an unusual transformation of azoxybenzenes under conditions of the Wallach rearrangement (in *para*-toluene sulphonic acid, in the presence of acetic anhydride) giving the rearrangement product together with the product of phenyldiazonium cation transformation. They suggested that such an unusual route of the reaction of azoxybenzene with the acid is caused by the attack of a cationoid species other than the proton, on azoxybenzene oxygen. We believe one of the routes of the transformations of compound VI in HSO_3Cl to be electrophilic chlorination in the cation generated by the interaction of Cl^+ or SO_2Cl^+ with azoxy oxygen. In this case, the aromatic carbon atom with the highest negative charge will be involved in the reaction. The charge may be qualitatively estimated from the ^{13}C NMR data. As seen from Table 3, protonation of compound VI leads to the upfield shift of C_1 and C_1' signals relative to the signals of these atoms in the precursor. The carbon signal shift increases in the order of cations containing CF_3, F and CH_3 substituents in the benzene ring, which indicates increase of the negative charge on the C_1 and C_1' atoms in the order of these cations. The rates of chlorination and formation of phenyldiazonium cation are also expected to increase in this series. The electronic effects that induce stabilisation of phenyldiazonium cations act in the same direction. Indeed, decrease of the negative charge on the C_1 atom, which is observed, *e.g.* when a stronger (than fluorine) electronegative substituent, CF_3, is introduced

TABLE 3

^1H and ^{19}F NMR data for polyfluoroazoxybenzene of the type in various solvents



Compound	Solvent (temperature, °C)	^1H NMR, δ ppm (intensities signals)	^{19}F NMR, δ ppm					
			$F^{2,6}$	$F^{3,5}$	CF_3	$F^{2',6'}$	$F^{3',5'}$	CF_3'
VII	CH_2Cl_2 (40)	3.75	22.7	19.8		12.8	19.8	
	HSO_3F (-40)	4.39(6), 13.6(1)	28.2	27.3		20.5	25.0	
	SbF_5-HSO_3F (1:1)(40)	4.79(2), 10.2(1)	28.0	28.0		18.3	26.6	
VIII	CH_2Cl_2 (40)		23.6	26.8	107.5	17.8	23.4	107.1
	HSO_3F (-40)		31.1	31.2	106.8	24.0	28.1	106.3
	SbF_5-HSO_3F (1:1)(40)	14.5(1), 10.0 (1)	33.0	34.0	106.7	25.7	30.3	106.2
IX	CH_2Cl_2 (40)		33.7	23.1		30.2	16.1	
	HSO_3F (-40)		38.4	29.8		35.3	22.2	
	SbF_5-HSO_3F (1:1)(-70)	14.4(1), 10.1(1)	38.7	28.4		35.3	21.5	

into the aromatic ring (see Table 3, protonated forms of compounds VII and VIII in HSO_3F, (leads to the high stability of compound VIII in HSO_3Cl solution, and after 200 h at 20 °C the reaction did not give the C-N bond cleavage products. At the same time, compound VII, the charge on C_1 of the monoprotonated form of which is comparable with that for the monoprotonated form of compound VI, was transformed in HSO_3Cl solution to 4-chloro-2,3,5,6-tetrafluorotoluene and 4-methyl-2,3,5,6-tetrafluorophenyldiazonium cation. The structure of these compounds was assigned as above.

To sum up, in HSO_3Cl, whereas we have performed the Wallach rearrangement of compound I, completely substituted polyfluorinated azoxybenzenes did not give the reduction products, azobenzenes. As to the Wallach rearrangement, it possibly proceeds via diprotonated forms of the type IV. The low rate of rearrangement of compound I in HSO_3Cl, presumably results from the low extent of its diprotonation in this acid.

EXPERIMENTAL

The ^1H and ^{19}F NMR spectra were recorded on a Varian A56/60A spectrometer at 60 and 56.4 MHz respectively (with standards TMS and C_6F_6). The ^{15}N and ^{13}C NMR spectra were measured on a Bruker HX-90 pulse spectrometer at 9.12 and 22.6 MHz respectively (with standards liquid ammonia and TMS) in the Fourier transform mode. The ^{15}N NMR spectra were recorded for ^{15}N-enriched compounds (94-96% enrichment), spectrometer settings: pulse width 20 μs (90° pulse - 30 μs), delay time between pulses - 8 s. For stabilisation of resonance conditions D_2O was used; it was placed in a 5 mm tube inserted in a 10 mm tube with the solution of the compound. The UV spectra were recorded on a Specord UV-VIS spectrophotometer for ethanolic solutions.

^{15}N-labelled compounds I and VI were obtained according to [22] from polyfluoroanilines labelled with this isotope. Compound XXV was prepared as described in [19], compound X as in [23], compounds I, VII, IX as in [24].

Interactions of polyfluoroazoxybenzenes with acids

a) A solution of 1 g of compound I in 20 ml of HSO_3F was kept at 20 °C for 72 h, then poured onto ice; the precipitate was filtered off and dried to produce 0.9 g (90%) of the starting compound.

b) A solution of 1 g of compound I in 10 ml of HSO_3Cl was kept at 20 °C for 72 h, then poured onto ice; the precipitate was filtered off and dried to give 1.15 g (89%) of compound XIII, m.p.110-112°. The UV spectrum (ethanol), λ_{max},nm (lg ε): 208 (3.94), 310 (4.27) and 417 (3.27). The ^{19}F NMR spectrum contains 4 signals of equal intensities at 23.6, 12.8, 11.5 and 0.5 ppm. The IR spectrum, cm^{-1} : 530, 565 and 600 (SO_2), 1000, 1020 (C-F), 1500, 1530 (fluorinated aromatic ring),3090. Found %: C 33.3, 33.4; Cl 8.14, 8.03; F 34.5, 34.7; N 6.71, 6.73; S 7.81, 7.61; M 439, 441 (isothermal distillation). $C_{12}HClF_8N_2O_3S$: Calculated %: C 32.8; Cl 8.06; F 34.5; N 6.36; S 7.27.

c) Compound I (1 g) was added with vigorous stirring to 20 ml of SbF_5-HF (1:1) mixture at 20 °C. The reaction mixture was kept for 20 h, poured onto ice, the precipitate filtered off and dried. Sublimation at 110 °C/3 mm Hg gave 0.95 g (95%) of compound XIV, m.p.125-128 °C, identified as the authentic sample by the IR and ^{19}F NMR spectra. Mixing with the authentic sample did not depress the melting point [17].

d) Compound VI was added at 20 °C and with vigorous stirring to 20 ml of SbF_5-HSO_3F (1:1). The mixture was kept for 20 h at 20 °C, then poured onto ice; the precipitate was filtered off and dried to give 0.86 g (95%) of compound XVII, m.p.142-143 °C, identified by the IR and ^{19}F NMR spectra.

e) Azoxybenzene (1 g) in 10 ml of SO_2ClF was added to a solution of SbF_5 (20 g), HF (10 ml) and SO_2ClF (15 ml) at -80 °C. The temperature was raised up to -50 °C and the mixture kept for 10 min, then poured onto ice and extracted

with ether. The ether extract was dried over $MgSO_4$. After the ether had been distilled off on a rotary vacuum-evaporator, the residue was passed through a silica gel column (2 cm). In the petroleum ether-diethyl ether (3:1) system, after evaporation of the solvents, 0.7 g (76%) of azobenzene was obtained, m.p.65°, together with 0.05 g (5%) of 4-hydroxyazobenzene, m.p.152°, identified with the authentic samples by the IR spectrum. Apart from the products, 0.25 g of black tar was isolated.

f) Similarly, 2 g of azoxybenzene was treated with 30 g of SbF_5, 10 ml of HF and 35 ml of SO_2 at -50 °C for 10 min. to produce 1.14 g (62%) of azobenzene and 0.24 g (12%) of 4-hydroxyazobenzene. Apart from the products, 0.25 g of black tar was isolated.

g) 4,4'-Difluoroazoxybenzene (0.2 g) was added with stirring to a solution of 6 g of SbF_5, 7 ml of HF and 20 ml of SO_2 at -80 °C. The temperature was raised up to -50 °C and mixture kept for 10 min., poured onto ice and extracted with ether. The ether extract was dried over $MgSO_4$. After the ether had been distilled off on a rotary vacuum-evaporator, the residue was passed through a silica gel column (eluent - petroleum ether (40-60°)-diethyl ether (3:1)), to yield 0.13 g (70%) of compound XX, m.p.101°, identified by the IR spectrum.

h) Compound VI (10 g) was added to 50 ml of HSO_3Cl at 10 °C and kept at that temperature for 200 h. The mixture was then poured onto ice, and the lower organic layer was separated and dried over $MgSO_4$. Distillation of the mixture gave 5.1 g (95%) of C_6F_5Cl, b.p.117°, identified by the IR and ^{19}F NMR spectra. The aqueous layer was neutralised with solid potassium bicarbonate to pH 7 and 10 g of dimethylaniline added. Subsequent workup was carried out as described in [20]. The procedure gave 2.1 g (25%) of compound XXV, m.p. 156-157° (from methanol)(m.p.157° [20]). The ^{19}F NMR spectrum: two signals of equal intensities at 21.2, 1.0 ppm.

i) Compound VII (4.5 g) was added to 20 ml of SbF_5-HSO_3F (1:1) at 0 °C and the mixture stirred for 1 h. The solution was kept for 20 h at 20 °C, then poured on ice, the precipitate was filtered off and dried. After sublimation in vacuum at 150°/3 mm Hg, 3 g (64%) of compound XVIII was obtained, m.p. 140-141°. The UV spectrum: λ_{max},nm (lg ε): 232 (3.88), 316 (4.32) and 455 (2.96). Found %: C 47.16; F 42.94; N 7.96. $C_{14}H_6F_8N_2$: Calculated %: C 47.46; F 42.94; N 7.91.

j) Similarly, 0.3 g of compound XI was treated with 20 g of SbF_5, 6 ml of HF and 30 ml of SO_2 at -10 °C for 15 min to yield 0.21 g (75%) of compound XXI, m.p.146-147° (m.p. 146-147° [25]).

k) Similarly, 1.8 g of compound IX was treated with 20 g of SbF_5, 20 ml of HSO_3F and 25 ml of SO_2FCl at 20 °C for 20 h to yield 1.39 g (80%) of compound IX, m.p.198-199°. The UV spectrum: λ_{max},nm (lg ε): 203 (4.21), 321 (4.39) and 453 (3.10). Found %: C 28.44; F 29.98; N 5.37. $C_{12}Br_2F_8N_2$: Calculated %: C 28.57; F 30.16; N 5.55.

l) Similarly, 1.5 g of compound XII was treated with 20 g SbF_5, 20 ml of HF and 25 ml of SO_2 at 20 °C for 20 h to yield 1.17 g (82%) of compound XXII, m.p.137-138°. The UV spectrum: λ_{max},nm (lg ε): 227 (4.00), 330 (4.29) and 448 (3.13). The ^{19}F NMR spectrum: 4 signals of equal intensities at 25.1 (F^3), 15.4 (F^6), 13.5 (F^4) and 8.0 (F^5) ppm. Found %: C 44.02; F 55.67; N 8.44. $C_{12}H_2F_8N_2$. Calculated %: C 44.17; F 55.83; N 8.59.

Interaction of compound XXVI with acids

A mixture of compound XXVI (3 g) with 25 ml of HSO_3F (or SbF_5-HSO_3F (1:1)) was kept for 3 h at 20 °C, poured onto ice, neutralised with potassium bicarbonate to pH 7 and extracted with ether. The ether extract was dried over $MgSO_4$. The solvent was distilled off on a rotary vacuum-evaporator and the residue distilled to give 1.3 g (90%) of 2,3,5,6-tetrafluoroaniline, identified by the IR and ^{19}F NMR spectra.

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