

FLUOROAROMATIC DERIVATIVES. CII. OXIDATION OF FLUORINATED  
BENZILIDENE ANILINES WITH PERACIDS

G.G. FURIN\*, A.O. MILLER, Yu.V. GATILOV, I.Yu. BAGRYANSKAYA  
and G.G. YAKOBSON

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

SUMMARY

Treatment of benzylidene aniline, having phenyl and polyfluorophenyl substituents at carbon and nitrogen of the azomethine group, with peracids gave products of azomethine bond cleavage. Oxidation of polyfluorinated compounds of the type  $C_6F_5CH=NC_6F_4X-4$  ( X = H, F,  $CH_3$ ,  $OCH_3$  ) with acetic peracid gave stable peroxides of  $\alpha$ -(polyfluoroanilido)-2,3,4,5,6-pentafluorobenzyl as the final products. The X-ray structure analysis data and some chemical properties of  $\alpha$ -(pentafluoroanilido)-2,3,4,5,6-pentafluorobenzyl peroxide are reported.

INTRODUCTION

Oxidation by peracids of Schiff bases with alkyl substituents leads to alkyloxaziridines [1]. Substitution of an alkyl substituent at the carbon atom of the azomethine group by an aryl one leads to the formation of both oxaziridines and nitrones on oxidation of the Schiff bases [1-3]. The Schiff bases with aryl substituents at the carbon and nitrogen atoms of an azomethine group cannot serve as starting materials to obtain oxaziridines. Recently, it has been shown that Schiff bases with three polyfluorinated aryl substituents are oxidized by trifluoroacetic peracid to the corresponding

nitrones [4]. At the same time, benzylidene anilines with one pentafluorophenyl ring are oxidized by peracids to acid amides, like their non-fluorinated analogues [1,4]. For example, treatment of pentafluorobenzylidene aniline II with trifluoroacetic peracid gives pentafluorobenzaldehyde and pentafluorobenzoic acid N-phenylamide [4].

As shown in [5], the reaction of acetic peracid with pentafluorobenzylidene pentafluoroaniline I leads to  $\alpha$ -(pentafluoroanilido)-2,3,4,5,6-pentafluorobenzyl hydroperoxide.

As part of our studies on the synthesis and the reactivity of nitrones, we investigated the reactions of peracids with fluorinated benzylidene anilines, each having one aryl substituent at the carbon and nitrogen atom of the azomethine group.

## RESULTS AND DISCUSSION

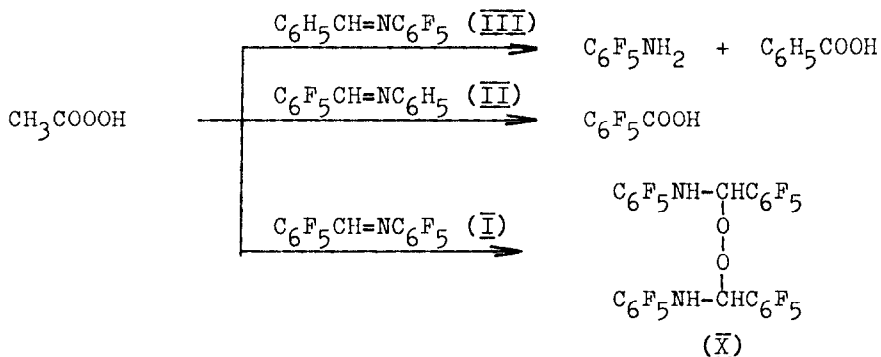
Treatment of pentafluorobenzylidene pentafluoroaniline, compound I, with excess trifluoroacetic peracid gave pentafluoronitrobenzene and pentafluorobenzoic acid. An equimolar quantity of trifluoroacetic peracid formed the trifluoroacetyl derivative of pentafluoroaniline and pentafluorobenzoic acid. Reference [4] reports formation of a mixture of pentafluorobenzaldehyde and pentafluorobenzoic acid N-phenylamide by oxidation of pentafluorobenzylidene aniline II with trifluoroacetic peracid. Oxidation of benzylidene pentafluoroaniline III with excess trifluoroacetic peracid also gave pentafluoronitrobenzene and benzoic acid.

Treatment of compound III with formic peracid yielded pentafluorophenylformanilide and benzoic acid; reaction with pentafluorobenzylidene aniline II gave pentafluorobenzoic acid. The main products of the reaction of formic peracid with benzylidene 4-trifluoromethyl-2,3,5,6-tetrafluoroaniline, IV, and benzylidene 4-methoxy-2,3,5,6-tetrafluoroaniline, V, were 4-trifluoromethyl-2,3,5,6-tetrafluoroaniline, VI, and 4-methoxy-2,3,5,6-tetrafluoroaniline, VII, respectively.

Treatment of compound III with acetic peracid gave pentafluoroaniline VIII and benzoic acid. The products of azomethine cleavage (pentafluorobenzoic acid) were obtained also in the

reaction of this oxidizer with compound  $\overline{\text{III}}$ . In contrast to the results reported in [5], oxidation of compound  $\overline{\text{I}}$  with acetic peracid gave not  $\alpha$ -(pentafluoroanilido)-2,3,4,5,6-pentafluorobenzyl hydroperoxide, but  $\alpha$ -(pentafluoroanilido)-2,3,4,5,6-pentafluorobenzyl peroxide  $\overline{\text{X}}$ , which was obtained by the authors of [5] by thermolysis or irradiation of  $\alpha$ -(pentafluoroanilido)-2,3,4,5,6-pentafluorobenzyl hydroperoxide, which seems to be due to a different work-up of the reaction mixture.

The peroxide  $\overline{\text{X}}$  obtained by us shows  $^1\text{H}$  and  $^{19}\text{F}$  NMR chemical shifts similar to those reported in [5]. We have also obtained further data in support of the structure of compound  $\overline{\text{X}}$ . Thus, the  $^{15}\text{N}$  NMR spectrum of the  $^{15}\text{N}$ -labelled compound  $\overline{\text{X}}$  in acetonitrile solution contains a wide signal at 126.2 ppm (liquid ammonia as standard).



Crystallographic investigations have finally confirmed the structure of compound  $\overline{\text{X}}$ . The steric structure of compound  $\overline{\text{X}}$  is shown in Fig.1, the main torsion angles are given in Tables 1 and 2. In the crystal of the compound, the peroxide molecule is located on the torsion axis of the second order, which crosses the O8-O8' bond right in the middle. The fluorinated benzene rings are planar, the average length of the C-C bond is 1.368 Å, that of the C-F bond is 1.342 Å. This geometry is in agreement with the one reported in the literature [6]. The O8-O8' distance is the usual distance for peroxide compounds [7]. The C7-O8 bond length is 1.36 Å and the C7-N9 one is 1.31 Å (these values are slightly smaller than those in the adjacent fragment - 1.467 and 1.417

Å, respectively [8]). The N9-C7-O8 bond angle is increased up to  $127.7^\circ$  and the C7-N9-C10 one up to  $124.4^\circ$ . Distortion of the bond angles seems to be largely due to the intramolecular steric interaction. Reference [9] reports the following short contacts: C7-C7' 3.44 Å, C7-C11 3.40 Å, C7-C15 3.19 Å, C10-O8 2.93 Å and C2-N9 3.08 Å.

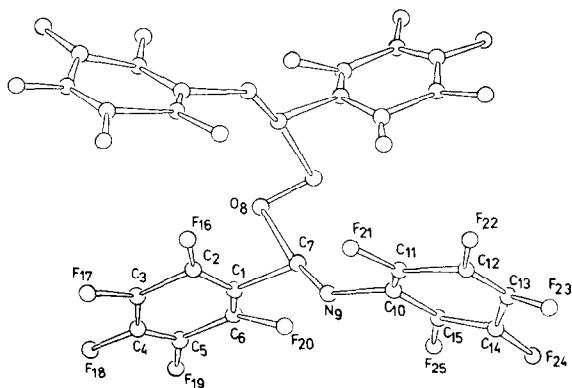


Fig.1. The structure of  $\alpha$ -(pentafluoroanilido)-2,3,4,5,6-pentafluorobenzyl peroxide,  $\bar{X}$ . The average error for bond lengths = 0.01 Å, for bond angles =  $0.8^\circ$ .

Compound  $\bar{X}$  undergoes reactions typical of peroxides. Thus it reacts in ethanolic solution with KI to give iodine and compound  $\bar{I}$ . Thermal decomposition of peroxide  $\bar{X}$  may follow two pathways: cleavage of the C-O bond or of the O-O bond. Indeed, heating ( $100^\circ\text{C}$ ) of peroxide  $\bar{X}$  in carbon tetrachloride leads to compound  $\bar{I}$ , whereas boiling it in acetonitrile gives decafluorobenzanilide  $\bar{XIV}$ . UV irradiation of the hexane solution of compound  $\bar{X}$  leads to compound  $\bar{I}$ , pentafluorobenzaldehydes, pentafluoroaniline and decafluorobenzanilide.

Peroxide  $\bar{X}$  was stable to treatment with acetic peracid in the range up to  $50^\circ\text{C}$ . However, its treatment with trifluoroacetic peracid at  $20^\circ\text{C}$  gave the product of the N-C bond cleavage - perfluoroacetanilide  $\bar{XV}$ . This may indicate the

TABLE 1  
Coordinates of atoms ( $\times 10^4$ ) Å

Atom	x	y	z	Atom	x	y	z
C1	4118(4)	0786(12)	2683(4)	C14	3610(4)	5646(11)	0059(5)
C2	4359(4)	2185(11)	3331(4)	C15	3809(4)	5034(12)	0784(4)
C3	4301(4)	1740(12)	3342(4)	F16	4679(2)	4048(6)	3489(3)
C4	3988(3)	-0127(11)	3718(4)	F17	4549(2)	3118(7)	4475(3)
C5	3739(4)	-1545(11)	3078(4)	F18	3941(2)	-0595(7)	4220(3)
C6	3799(4)	-1066(12)	2581(4)	F19	3437(3)	-3383(7)	2956(3)
C7	4195(4)	1246(14)	2139(4)	F20	3541(2)	-2495(7)	1957(3)
O8	4944(2)	0961(8)	2753(3)	F21	2890(2)	0031(7)	0010(3)
N9	3763(4)	2791(12)	1547(4)	F22	2504(2)	1184(8)	-1415(3)
C10	3594(3)	3166(11)	0820(4)	F23	2967(3)	4986(9)	-1396(3)
C11	3153(4)	1905(11)	0058(5)	F24	3860(3)	7526(7)	0095(3)
C12	2938(4)	2460(13)	-0693(4)	F25	4252(2)	6368(7)	1508(3)
C13	3173(4)	4337(13)	-0680(4)				

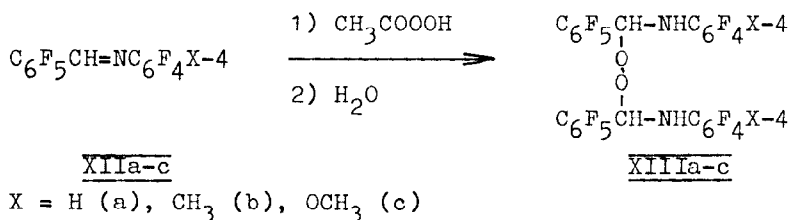
TABLE 2  
Torsion angles ( $^{\circ}$ )

Angle	Value	Angle	Value
C2C1C7N9	+68.5	O8O8C7N9	+55.1
C6C1C7N9	-111.4	C7'O8'O8C7	-164.0
C1C7N9C10	+163.4	C7N9C10C11	+69.1
O8C7N9C10	-64.3	C7N9C10C15	-118.0

ability of peroxide  $\bar{X}$  to undergo hydrolysis under the action of strong acids. Treatment of compound  $\bar{X}$  with 90% sulphuric acid (or trifluoroacetic acid) afforded pentafluoroaniline, pentafluorobenzaldehyde and compound  $\bar{I}$ .

We studied the effect of the aryl fragment at the nitrogen atom of the azomethine group on the course of the reaction of benzylidene anilines with peracids, by investigating the

reaction of the latter with polyfluorinated benzylidene anilines containing the groups  $\text{CF}_3$ , H,  $\text{CH}_3$ ,  $\text{OCH}_3$  in the *para*-position. Substitution of fluorine in benzylidene aniline I by the  $\text{CF}_3$ -group resulted in 4-trifluoromethyl-2,3,5,6-tetrafluoroaniline and pentafluorobenzoic acid as the products of oxidation of pentafluorobenzylidene - (4-trifluoromethyl-2,3,5,6-tetrafluoroaniline) XI with acetic peracid. At the same time, substitution of fluorine in compound I with H,  $\text{CH}_3$ ,  $\text{OCH}_3$  (compounds XIIa-c) gave rise to the corresponding peroxides in the reactions of the respective compounds with acetic peracid. The structure of peroxides XIIIa-c has been confirmed by the elemental analysis and the spectra (Table 3).



These results indicate the electronic effects of the aryl radical, bonded to the nitrogen of the azomethine group, on the course of oxidation of fluorinated benzylidene anilines by peracids. The low nucleophilicity of nitrogen under the influence of the aromatic fluorine atoms (the sharp lowering of nucleophilicity on going from aniline to pentafluoroaniline and its N-substituted derivatives has been reported earlier [10]) precludes its attack on oxygen of the initially formed hydroperoxyde [5]. Therefore neither oxaziridine nor nitron are formed and the hydroperoxide either dimerises or reacts with the second molecule of benzylidene aniline giving a peroxide of the type X. We suppose that introduction of the fluorine atoms to the aryl radicals of benzylidene anilines does not affect the initial reaction of benzylidene anilines with peracids, but influences further transformations of the primary product of oxidation.

Thus oxidation of benzylidene anilines with peracids possibly gives peroxides as intermediate products. Accumulation of fluorine atoms in the aryl substituents at the nitrogen of

the azomethine group of benzylidene anilines leads to increased stability of peroxides of type  $\bar{X}$ , whereas deficiency of fluorine atoms results in N-C bond cleavage even under the cation of such weak acids as trifluoroacetic acid.

## EXPERIMENTAL

The  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra were measured on a Varian A56/60A instrument at 60 and 56.4 MHz, respectively (HMS and  $\text{C}_6\text{F}_6$  as internal standards), the IR spectra (in KBr) on a UR-20 spectrometer, the UV spectra (ethanolic solutions) on a Specord UV-VIS spectrophotometer.

The X-ray structure analysis has been carried out on a Synthex-P2<sub>I</sub> diffractometer, using Mo-irradiation with a graphite monochromator. The crystallographic results for compound  $\bar{X}$  are as follows:  $a = 28.68(1)$ ,  $b = 6.2823(7)$ ,  $c = 23.64(1)$ ,  $c = 23.64(1)$  Å,  $\beta = 141.91(2)^\circ$ ,  $z = 4$ , steric group C2/C,  $d_{\text{calc.}} = 1.91 \text{ g/cm}^3$ . The intensities of 1836 independent reflections in the range of  $2\theta < 50^\circ$  have been measured by  $2\theta/\theta$  scanning. In the calculations, 868 reflections with  $I > 2\sigma$  have been used. The structure has been decoded by the direct method using the MULTAN-XTL program and finally determined by the least-squares method in anisotropic approximation to  $R = 0.063$  and  $R = 0.047$ , where  $W^{-1} = \sigma_{\text{F}}^2 + 0.013(\text{F})^2$ . Attempts to locate the hydrogen atoms on difference maps failed. The atom coordinates are listed in Table 1. Compound  $\bar{X}$  crystals have been obtained by its crystallization from hexane.

Fluorinated benzylidene anilines  $\bar{\text{I}} - \bar{\text{V}}$  were obtained as described in [11]. Yields and other characteristics of the new products (recrystallized from aqueous ethanol and sublimed at  $120-140^\circ/3 \text{ mm Hg}$ ) are listed in Table 3. The known compounds obtained in this work were identified by the IR and  $^{19}\text{F}$  NMR spectra, mixing with authentic samples did not depress the melting points.

Reactions of peracids with benzylidene anilines containing polyfluorinated benzene rings

a) Compound I (5 g) was added to a solution of trifluoroacetic peracid obtained by adding 10 ml of 90% hydrogen peroxide to 25 ml of trifluoroacetic anhydride in 150 ml of  $\text{CH}_2\text{Cl}_2$ , and the mixture was boiled with stirring for 10 h. Then the reaction mixture was washed with water, the organic layer separated and dried over  $\text{MgSO}_4$ . Distillation gave 2.5 g (85%) of pentafluoronitrobenzene, b.p. 159 °C, identified by the IR and  $^{19}\text{F}$  NMR spectra. Continuous extraction of the aqueous solution with diethyl ether gave 2.4 g (82%) of pentafluorobenzoic acid, m.p. 102°, identified by the IR and  $^{19}\text{F}$  NMR spectra.

b) Similarly, 6 g of compound III was reacted with trifluoroacetic peracid obtained from 25 ml of trifluoroacetic anhydride and 10 ml of 90%  $\text{H}_2\text{O}_2$ , to give 3.8 g (80%) of pentafluoronitrobenzene and 2 g (74%) of benzoic acid.

c) Compound I (2.3 g) was added to a solution of trifluoroacetic peracid obtained by adding 0.3 ml of 90%  $\text{H}_2\text{O}_2$  to 2 ml of trifluoroacetic anhydride in 25 ml of  $\text{CH}_2\text{Cl}_2$ , and the mixture was stirred for 10 h. Then the mixture was washed with water, dried over  $\text{MgSO}_4$ , the solvent distilled off and the residue sublimed to yield 1.0 g (57%) of  $\text{C}_6\text{F}_5\text{NHCOCF}_3$ , m.p. 92-93° (sublimed at 90°/3 mm Hg), identified by the IR [12] and  $^{19}\text{F}$  NMR spectra. Continuous extraction of the aqueous layer gave 0.8 g (59%) of pentafluorobenzoic acid.

d) Compound II (2 g) was added to a solution of formic peracid obtained by adding 1.0 ml of 90%  $\text{H}_2\text{O}_2$  to 20 ml of formic acid, and the mixture was stirred for 5 h. Then 100 ml of  $\text{CH}_2\text{Cl}_2$  was added to the reaction mixture, which was then washed with water. The organic layer was separated and dried over  $\text{MgSO}_4$ . After distillation, the residue was sublimed in vacuum to give 1.4 g (89%) of pentafluorobenzoic acid.

e) Similarly, 2 g of compound III was reacted with formic peracid, obtained by adding 1.0 ml of 30%  $\text{H}_2\text{O}_2$  to 5 ml of formic acid, to give 0.8 g (52%) of  $\text{C}_6\text{F}_5\text{NHCHO}$ , m.p. 100 °C



(sublimed at  $90^{\circ}/3$  mm Hg), identified by the  $^{19}\text{F}$  NMR spectrum [13]. Mixing the sample with an authentic one did not result in m.p. depression. Continuous extraction of the aqueous layer gave 0.7 g (78%) of benzoic acid, m.p.  $122.5^{\circ}\text{C}$ .

f) Compound IV (2 g) was added to a solution of acetic peracid, obtained by adding 0.34 ml of 89%  $\text{H}_2\text{O}_2$  to 1 ml of  $\text{CH}_3\text{COOH}$  in 20 ml of  $\text{CH}_2\text{Cl}_2$ , the mixture was stirred at  $20^{\circ}\text{C}$  for 5 h and poured into water; the organic layer was separated and dried over  $\text{MgSO}_4$ . After distilling off the solvent, the residue was distilled and the fraction boiling at  $60^{\circ}/3$  mm Hg collected. Yield of compound VI was 1.0 g (70%) (b.p.  $186^{\circ}\text{C}$  [14]), identified by the IR and  $^{19}\text{F}$  NMR spectra. Continuous extraction of the aqueous layer gave 0.6 g (76%) of benzoic acid.

g) Similarly, 2 g of compound V was reacted with acetic peracid, obtained by adding 0.34 ml of 90%  $\text{H}_2\text{O}_2$  to 1 ml of  $\text{CH}_3\text{COOH}$  in 20 ml of  $\text{CH}_2\text{Cl}_2$ , to afford 1.2 g (81%) of compound VII, m.p.  $77-78^{\circ}$  (m.p.  $77.5-78^{\circ}$  [15]) and 0.6 g (70%) of benzoic acid.

h) Compounds I and XIIa-c (0.01 mol) were added to a solution of acetic peracid obtained by adding 0.02 mol of 90%  $\text{H}_2\text{O}_2$  to 0.02 mol of acetic acid in 40 ml of  $\text{CH}_2\text{Cl}_2$  (or  $\text{CCl}_4$ ), the mixture was stirred for 10 h, the solution washed with water, the organic layer separated and dried over  $\text{MgSO}_4$ . The solvent was distilled off and the residue crystallised from petroleum ether ( $40-60^{\circ}\text{C}$ ). Yields and other characteristics of the products are summarised in Table 3.

i) Compound XI (3 g) was added to a solution of acetic peracid, obtained by adding 0.5 ml of 90%  $\text{H}_2\text{O}_2$  to 1.5 ml of  $\text{CH}_3\text{COOH}$  in 30 ml of  $\text{CH}_2\text{Cl}_2$ , the mixture was stirred at  $20^{\circ}\text{C}$  for 5 h and poured into water; the organic layer was separated and dried over  $\text{MgSO}_4$ . After distilling off the solvent, the residue was distilled and the fraction boiling at  $60^{\circ}/3$  mm Hg collected. Yield of 4-trifluoromethyl-2,3,5,6-tetrafluoroaniline was 1.2 g (70%) (b.p.  $186^{\circ}\text{C}$  [14]), identified by the IR and  $^{19}\text{F}$  NMR spectra. Continuous extraction of the aqueous layer gave 0.9 g (58%) of pentafluorobenzoic acid, m.p.  $102^{\circ}$ .

TABLE 3

The Schiff bases containing polyfluoroaryl substituents and  $\alpha$ -(polyfluoroanilido)-polyfluoro-benzyl peroxides

Compound	Yield %	M.p. °C	Found, %		Formula	Calculated, %		UV-spectrum		<sup>19</sup> F NMR spectra, $\delta$			
			C (H)	F (N)		C (H)	F (N)	$\lambda_{\max}$ , nm (lg $\epsilon$ )	F <sub>2,6</sub> (F <sub>2',6'</sub> )	F <sub>3,5</sub> (F <sub>3',5'</sub> )	F <sub>4</sub> (F <sub>4'</sub> )	F <sub>3,5</sub> (F <sub>3',5'</sub> )	F <sub>4</sub> (F <sub>4'</sub> )
<u>IV</u>	90	161-162	52.6 (1.97)	41.1 (4.32)	C <sub>14</sub> H <sub>6</sub> F <sub>7</sub> N	52.3 (1.87)	41.4 (4.36)	220(4.27)	265(3.94)	(21.3)	(1.7)		
<u>V</u>	92	78-79	59.7 (2.85)	26.2 (4.89)	C <sub>14</sub> H <sub>9</sub> F <sub>4</sub> N <sub>2</sub> O	59.3 (3.18)	26.9 (4.95)	215(4.41)	264(4.42)	(7.9)	(3.7)		
<u>VI</u>	95	126-127	41.7 (0.55)	50.3 (3.72)	C <sub>26</sub> H <sub>4</sub> F <sub>20</sub> N <sub>2</sub> O <sub>2</sub>	41.3 (0.53)	50.3 (3.70)	220(4.23)	264(3.45)	21.8 (9.1)	1.6 (-0.9)	10.7 (-2.9)	
<u>XIIa</u>	87	94-95	46.3 (0.72)	49.4 (4.03)	C <sub>13</sub> H <sub>2</sub> F <sub>9</sub> N	45.5 (0.58)	49.8 (4.08)	254(4.29)	332(3.60)	22.9 (23.8)	1.0 (9.8)	14.5	
<u>XIIIa</u>	92	141-142	42.8 (0.75)	39.9 (3.99)	C <sub>26</sub> H <sub>6</sub> F <sub>18</sub> N <sub>2</sub> O <sub>2</sub>	43.3 (0.83)	43.3 (3.89)	232(4.29)	267(3.62)	21.6 (7.9)	1.6 (23.3)	10.6	
<u>XIIIb</u>	90	146-147	44.7 (1.14)	37.0 (3.70)	C <sub>28</sub> H <sub>10</sub> F <sub>18</sub> N <sub>2</sub> O <sub>2</sub>	44.9 (1.34)	44.9 (3.74)	223(4.32)	268(3.62)	21.6 (18.3)	1.4 (7.0)	10.3	
<u>XIIIc</u>	95	133-134	43.2 (1.08)	35.6 (3.56)	C <sub>28</sub> H <sub>10</sub> F <sub>18</sub> N <sub>2</sub> O <sub>4</sub>	43.1 (1.28)	43.1 (3.59)	223(4.32)	268(3.62)	21.8 (7.8)	1.6 (4.6)	10.5	

j) Similarly, 3 g of compound II was reacted with acetic peracid, obtained by adding 0.5 ml of 90%  $\text{H}_2\text{O}_2$  to 1 ml of  $\text{CH}_3\text{COOH}$  in 20 ml  $\text{CH}_2\text{Cl}_2$ . Continuous extraction of the aqueous layer gave 1.8 g (77%) of pentafluorobenzoic acid.

k) Similarly, 3 g of compound III was reacted with acetic peracid, obtained by adding 0.5 ml of 90%  $\text{H}_2\text{O}_2$  to 1 ml of  $\text{CH}_3\text{COOH}$  in 20 ml  $\text{CH}_2\text{Cl}_2$  (at 20 °C for 10 h) to afford 1.5 g (74%) of pentafluoroaniline VIII, b.p.157°, identified by the IR and  $^{19}\text{F}$  NMR spectra. Continuous extraction of the aqueous layer gave 0.9 g (67%) of benzoic acid.

#### Chemical properties of compound X

a) A solution of 0.5 g of compound X in 20 ml of ethanol and 0.25 g of KI were maintained at 50 °C for 3 h, then 40 ml of water was added and the mixture extracted twice with diethyl ether. The extract was dried over  $\text{MgSO}_4$ . After distilling off the solvent on a rotary vacuum-evaporator, the residue was crystallised from aqueous ethanol to give 0.4 g (85%) of compound I, m.p.88-89°, identified by the IR and  $^{19}\text{F}$  NMR spectra.

b) A solution of 1 g of compound X in 22 ml of acetonitrile was refluxed for 20 h. Acetonitrile was distilled off on a rotary vacuum-evaporator and the residue extracted with hot hexane. The undissolved part was crystallised from ethanol to give 0.4 g (40%) of compound XIV, m.p.182-184°, identified by the IR [16] and  $^{19}\text{F}$  NMR spectra. The hexane extract was evaporated on a rotary vacuum-evaporator and crystallised from aqueous ethanol to give 0.5 g (52%) of compound I, m.p. 88-89°, identified by the IR and  $^{19}\text{F}$  NMR spectra.

c) Compound X (0.5 g) was added to a solution of trifluoroacetic peracid, obtained by adding 0.2 ml of 90%  $\text{H}_2\text{O}_2$  to 1 ml of trifluoroacetic anhydride in 25 ml of  $\text{CH}_2\text{Cl}_2$ , and the mixture was stirred for 5 h. Then the mixture was washed with water and dried over  $\text{MgSO}_4$ . The solvent was distilled off.

Sublimation gave 0.29 g (79%) of perfluoroacetanilide XV. Continuous extraction of the aqueous layer yielded 0.2 g (71%) of pentafluorobenzoic acid, m.p. 102°.

d) A solution of 0.5 g of compound X in 10 ml of  $\text{CHCl}_3$  was heated for 5 h in a sealed tube at 100 °C. Then the solution was evaporated and the  $^{19}\text{F}$  NMR spectrum recorded. As shown by the spectrum, the mixture contained 30% of compound I and 70% of compound X.

e) Compound X (0.5 g) was added to a solution of 0.5 ml of trifluoroacetic acid in 30 ml of  $\text{CCl}_4$  and the mixture was stirred for 8 h. Then the mixture was washed with water and dried over  $\text{MgSO}_4$ . The solvent was distilled off on a rotary vacuum-evaporator and the  $^{19}\text{F}$  NMR spectrum recorded. As shown by the spectrum, the mixture contained 41% of compound X, 34% of compound I, 12% of pentafluoroaniline and 13% of pentafluorobenzaldehyde.

f) A solution of 1 g of compound X in 10 ml of ethanol and 0.3 ml of concentrated sulphuric acid was stirred at 20 °C for 10 h, then poured into water and extracted with diethyl ether. The extract was dried over  $\text{MgSO}_4$  and evaporated on a rotary vacuum-evaporator to yield 0.8 g of a mixture containing equal quantities of pentafluorobenzaldehyde and pentafluoroaniline, as shown by the  $^{19}\text{F}$  NMR.

g) A solution of 0.3 g of compound X in 100 ml of hexane was irradiated in a quartz reactor with a mercury lamp ( $\lambda = 254 \text{ nm}$ ) at 20 °C for 6 h. The solution was concentrated and its  $^{19}\text{F}$  NMR spectrum recorded. As shown by the spectrum, the mixture contained 27% pentafluorobenzaldehyde, 23% pentafluoroaniline, 32% compound I, 7% compound XIV, and 11% compound X.

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