

# Selective Hydrolysis of Pentafluorobenzotrichloride

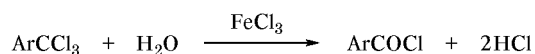
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Received November 15, 2002

**Abstract**—Selective hydrolysis of pentafluorobenzotrichloride has been studied in the presence of a catalytic amount of iron(III) chloride. The main products are pentafluorobenzoyl chloride, pentafluorobenzoyl fluoride, and 4-chlorotetrafluorobenzoyl chloride. The two latter products are formed by hydrolysis of dichlorofluoromethylpentafluorobenzene and 4-chlorotetrafluorobenzotrichloride which result from halogen exchange between the methyl group and aromatic ring in the initial pentafluorobenzotrichloride. A probable mechanism for halogen exchange is proposed.

A large-scale procedure for the synthesis of benzoyl chlorides is based on selective hydrolysis of the corresponding trichloromethyl derivatives (benzotrighlorides) with water in the presence of iron(III) chloride [1, 2].

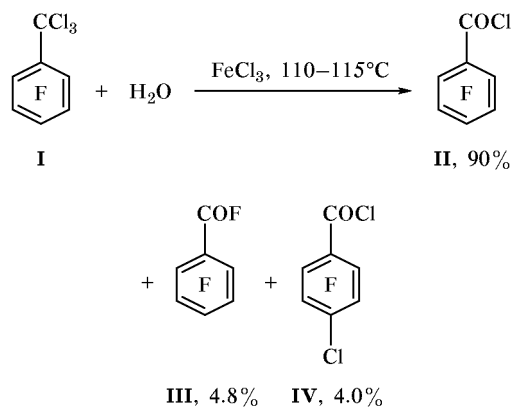


Depending on the substituents present in the aromatic ring, the reaction can follow both  $\text{S}_{\text{N}}1$  and  $\text{S}_{\text{N}}2$  mechanism [1]. As a rule, the yield of benzoyl chlorides ranges from 90 to 98%. We have studied an analogous process with a view to obtain pentafluorobenzoyl chloride. When the hydrolysis of pentafluorobenzotrighloride (**I**) was performed with equimolar amounts of the reactants at 110–120°C in the

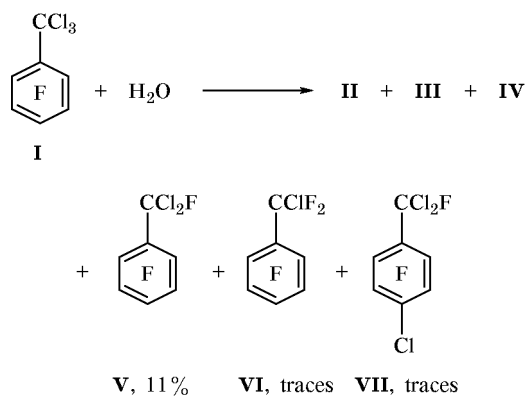
presence of a catalytic amount of iron(III) chloride (1–2 mol %), pentafluorobenzoyl chloride (**II**) was obtained in 70–90% yield. Unexpectedly, among the reaction products we detected pentafluorobenzoyl fluoride (**III**) and 4-chlorotetrafluorobenzoyl chloride (**IV**) (Scheme 1). The results are summarized in Table 1. In some experiments (run nos. 1–3), the overall yield of benzoyl halides **III** and **IV** reached ~30%. The goal of the present study was to elucidate the ways and mechanism of formation of compounds **III** and **IV**.

Heating of pentafluorobenzoyl chloride (**II**) in the presence of iron(III) chloride for 3 h at ~120°C (with no water added) did not result in formation of appreciable amounts of other products, specifically of compounds **III** and **IV** (Table 1, run no. 6). When the hydrolysis of pentafluorobenzotrighloride (**I**) was per-

Scheme 1.



Scheme 2.



**Table 1.** Hydrolysis of pentafluorobenzotrichloride in the presence of iron(III) chloride

Run no.	Amounts of reactants, g (mol)			Reaction conditions			Product composition, <sup>a</sup> %			
	I	FeCl <sub>3</sub> ·6H <sub>2</sub> O	H <sub>2</sub> O	temperature, °C	addition time, h	reaction time, h	II	III	IV	V
1	285.5 (1)	4.28 (0.017)	18.0 (1)	110–115	3.0	1	90	4.8	4.0	Traces
2	285.5 (1)	4.28 (0.017)	18.0 (1)	120–125	3.0	1	73	15.0	8.5	Traces
3	190.0 (0.665)	2.85 (0.011)	12.0 (0.665)	110–115	3.5	1	69	17.7	9.8	Traces
4	285.5 (1)	4.28 (0.017)	16.2 (0.9)	110–115	3.0	1	73	9.5	5	11
5	285.5 (1)	4.28 (0.017)	12.9 (0.72)	115–120	3.0	2	32	23.0	20.5	24.4
6	153.0 (0.665) <sup>b</sup>	1.43 (0.01) <sup>c</sup>	–	120	–	3	98	Traces	–	–
7	285.5 (1)	4.28 (0.017)	–	120	–	3	–	–	–	15 <sup>d</sup>
8	Reaction mixture from run no. 7 was used		18.0 (1)	120	3	1	60	23	17	Traces

<sup>a</sup> According to the GLC data.

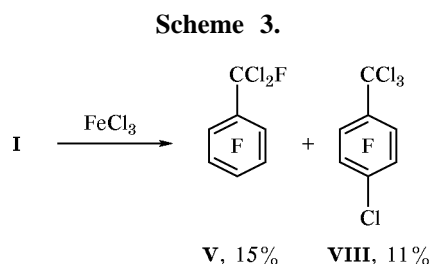
<sup>b</sup> Compound **II** contained ~99% of the main substance.

<sup>c</sup> Anhydrous FeCl<sub>3</sub> was used.

<sup>d</sup> The mixture also contained 11% of **VI**, 2% of **VII**, 1.5% of **VIII**, and 70% of **I**.

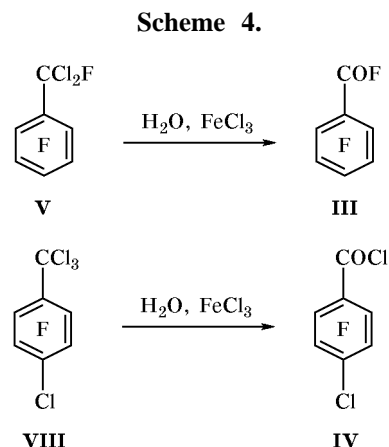
formed with insufficient water (the **I**-to-H<sub>2</sub>O molar ratio was 1:0.9), the reaction mixture contained a series of new products, among which we identified dichlorofluoromethylpentafluorobenzene (**V**) and small amounts of chlorodifluoromethylpentafluorobenzene (**VI**) and 1-chloro-4-dichlorofluoromethyltetrafluorobenzene (**VII**) (Scheme 2; Table 1, run no. 4).

The fraction of compound **V** in the product mixture increased to ~25% at a **I**-to-H<sub>2</sub>O ratio of 1:0.72 under more severe conditions (Table 1, run no. 5). When pentafluorobenzotrichloride was kept under conditions similar to the hydrolysis conditions (120°C, 3 h) but in the absence of water, the yield of products of halogen exchange between the methyl group and aromatic ring also increased: 4-chlorotetrafluorobenzotrichloride (**VIII**) and compound **V** were obtained in an overall yield of greater than 25% (Scheme 3, Table 1, run no. 7).



The subsequent hydrolysis at 120°C of the mixture obtained in run no. 7 gave ~60% of **II**, ~23% of **III**, and ~17% of **IV** (Table 1, run no. 8). These data

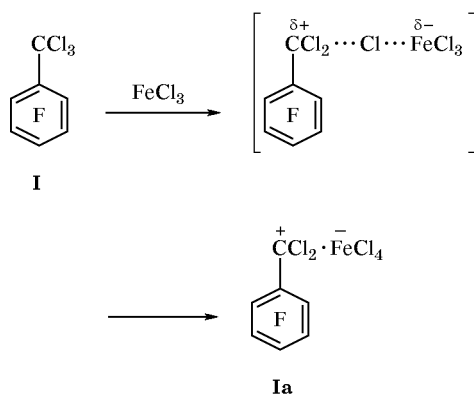
unambiguously indicate that benzoyl halides **III** and **IV** are formed as a result of hydrolysis of intermediate products **V** and **VIII** (Scheme 4).



Compounds **V** and **VIII** are formed in turn via halogen exchange between the methyl group and aromatic ring. Presumably, this process begins with formation of a complex between iron(III) chloride and benzotrichloride (**I**), which is converted into the corresponding ion pair **Ia** (Scheme 5). The formation of analogous cationoid intermediates in the reaction of PhCCl<sub>3</sub> with Lewis acids was reported previously [3]. It should be noted that, according to the high-resolution NMR data, complex **Ia** is characterized by a considerably stronger charge separation, as compared to the corresponding benzoyl chloride–Lewis

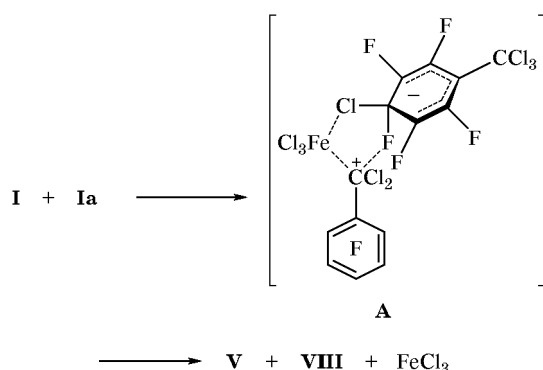
acid complex [3]. This explains the formation of benzoyl halides as hydrolysis products and their failure to undergo further transformations.

Scheme 5.



Nucleophilic attack by  $\text{FeCl}_4^-$  on the second molecule of initial pentafluorobenzotrichloride gives a  $\sigma$  complex. Decomposition of the latter is accompanied by elimination of fluoride ion and its replacement by chlorine; fluoride ion adds to the cationic part of ion pair **Ia** at the methyl group. The process is likely to involve five-center transition state **A** (Scheme 6). We believe that Scheme 6 explains halogen exchange between the methyl group and aromatic ring.

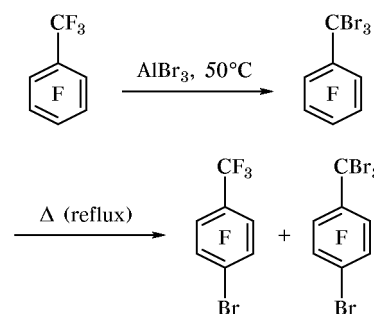
Scheme 6.



This assumption does not contradict published data. It is known that both aromatic and benzylic fluorine atoms in poly- or perfluorinated aromatic compounds are smoothly replaced by chlorine or bromine by the action of the corresponding aluminum halide ( $\text{AlCl}_3$  and  $\text{AlBr}_3$ ) [4–9]. As a rule, benzylic fluorine atom is replaced under milder conditions than those necessary for replacement of aromatic fluorine. Here, aluminum chloride or bromide acts as fluorine

acceptor. However, Dvornikova *et al.* [7] and Cherstkov *et al.* [8] showed that the reaction of octafluorotoluene with insufficient  $\text{AlBr}_3$  at  $50^\circ\text{C}$  initially gives pentafluorobenzotribromide which is converted into *p*-bromoheptafluorotoluene and a small amount of *p*-bromotetrafluorobenzotribromide on further heating of the reaction mixture at the boiling point. Taking into account the high strength of the aluminum–fluorine bond in aluminum fluoride formed in the first reaction stage, it is possible that in this case halogen exchange between the methyl group and aromatic ring also occurs (Scheme 7).

Scheme 7.



Thus, our results show that the hydrolysis of pentafluorobenzotrichloride to pentafluorobenzoyl chloride in the presence of iron(III) chloride is accompanied by exchange of the aromatic fluorine atom and chlorine atom in the methyl group between pentafluorobenzotrichloride molecules with intermediate formation of dichlorofluoromethylpentafluorobenzene and 4-chlorotetrafluorobenzotrichloride. Hydrolysis of these intermediate products yields pentafluorobenzoyl fluoride and 4-chlorotetrafluorobenzoyl chloride.

## EXPERIMENTAL

The  $^{19}\text{F}$  NMR spectra were recorded on a Bruker WP 80 instrument (75.398 MHz) in acetone- $d_6$  using hexafluorobenzene as internal reference. The mass spectra (70 eV) were run on a Finnigan Mat ITD 800 spectrometer (batch inlet temperature  $200^\circ\text{C}$ ). GLC analysis was performed on a Chrom-5 chromatograph equipped with a thermal conductivity detector; 5-m  $\times$  3.5-mm column packed with 20% of FS-169 on Chromaton-W; oven temperature  $150^\circ\text{C}$  (isothermal mode); carrier gas helium (flow rate 50 ml/min).

Iron(III) chloride hexahydrate  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  of pure grade was used without additional purification. Pentafluorobenzotrichloride was synthesized by the procedure described in [10]. Its purity was  $\sim 99\%$ , according to the GLC data.

**Table 2.**  $^{19}\text{F}$  NMR spectral parameters of polyfluorobenzenes

Compound no.	Chemical shifts $\delta_{\text{F}}$ , ppm (relative to $\text{CCl}_3\text{F}$ )					
	1-F	2-F	3-F	4-F	5-F	6-F
<b>I</b>	–	133.8	161.1	150.0	161.1	133.8
<b>II</b>	–	138.4	159.9	146.0	159.9	138.4
<b>III</b>	–46.3 (COF)	134.4	160.4	143.3	160.4	134.4
<b>IV</b>	–	139.3	134.6	–	134.6	139.3
<b>V</b>	45.2 ( $\text{CCl}_2\text{F}$ )	133.5	161.0	149.0	161.0	133.5
<b>VI</b>	55.1 ( $\text{CClF}_2$ )	137.8	159.8	147.1	159.8	137.8
<b>VII</b>	45.9 ( $\text{CCl}_2\text{F}$ )	134.8	137.8	–	137.8	134.8
<b>VIII</b>	–	134	140.3	–	140.3	134

**Hydrolysis of pentafluorobenzotrichloride.**

Pentafluorobenzotrichloride, 285.5 g, was heated to 110–120°C, and 18 g of water containing 4.28 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was added with stirring over a period of 3.5 h. The mixture was then stirred for 1 h at that temperature and analyzed. The other experiments were carried out following the same procedure. The amounts of the reactants, reaction conditions, and yields of the products are collected in Table 1. The  $^{19}\text{F}$  NMR spectra of the products are given in Table 2. The mass spectra of all the products contained the molecular ion peaks.

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