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Journal of Fluorine Chemistry 89 (1998) 137–139

JOURNAL OF FLUORINE CHEMISTRY

Condensation of fluorinated carbonyl compounds with halobenzenes

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Received 28 March 1997; accepted 16 December 1997

Abstract

Fluoro- or chlorobenzenes undergo the Friedel–Crafts acylation with perfluoroacyl chlorides (I) without complications to give *p*-halophenylketones (**II**); however, the reaction of **I** with bromobenzene gives phenylketones (**IV**) and dibromobenzene in addition to *p*-bromophenylketones (**III**). An intermediate *p*-bromobenzyl cation (**V**) is assumed to be responsible for the formation of the abnormal products **IV** and dibromobenzene. Condensation of hexafluoroacetone with bromobenzene in anhydrous HF also affords the products of disproportionation probably via an intermediate benzyl cation (**IX**).

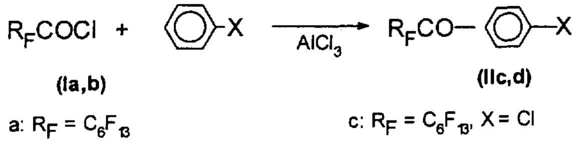
Keywords: Perfluoroacyl halides; Hexafluoroacetone; Friedel–Crafts reaction; Abnormal products; Mechanism

1. Introduction

Acyl halides enter the Friedel–Crafts reaction with halobenzenes to form corresponding arylketones in high yields, as a rule [1]. However, in some cases acylation of bromobenzene with either of aromatic [1,2] or saturated perfluoroalkyl etheracyl halides [3] results in a mixture of benzene, phenylketone, and isomeric dibromobenzenes. In these cases abnormal products of the Friedel–Crafts reaction were assumed to be formed as a result of disproportionation of bromobenzene under the action of $AlCl_3$ [4] followed by interaction of the benzene formed with acyl halide.

2. Results and discussion

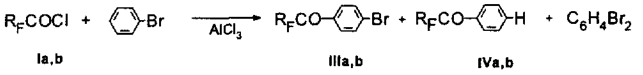
We have found that acyl halides (**Ia,b**) normally react with chloro- or fluorobenzene in the presence of $AlCl_3$ to give the corresponding *p*-halophenylketones (**IIc,d**) in high yields.



a: $R_F = C_6F_{13}$ c: $R_F = C_6F_{13}$, X = Cl

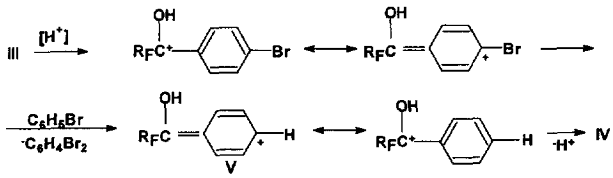
b: $R_F = (CF_3)_2CFCF{=}CF$ d: $R_F = (CF_3)_2CFCF{=}CF$, X = F

However, the reaction of acyl chloride (**Ia**) with bromobenzene and $AlCl_3$ gives dibromobenzene and phenylketone (**IVa**), in addition to bromoketone (**IIIa**), with the content of ketone **IIIa** in the mixture of products being not more than 12% (according to GLC data).



a: $R_F = C_6F_{13}$ b: $R_F = (CF_3)_2CFCF{=}CF$

Without excluding the conventional explanation of appearance of ketones **IV** in the reaction products, we propose an alternative mechanism for the formation of these products, involving generation of intermediate cation (**V**), which is capable of both brominating the starting bromobenzene and being converted simultaneously to the nonbrominated ketone.



This pattern is confirmed, to a certain extent, by a sharp increase in the content of bromoketone **IIIb** among the products of the reaction of acyl chloride **Ib** with bromobenzene; though some nonbrominated ketone **IVb** and $C_6H_4Br_2$ are also formed, in addition to **IIIb**.

Obviously, in this reaction the intermediate cation

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PII S0022-1139(98)00126-2

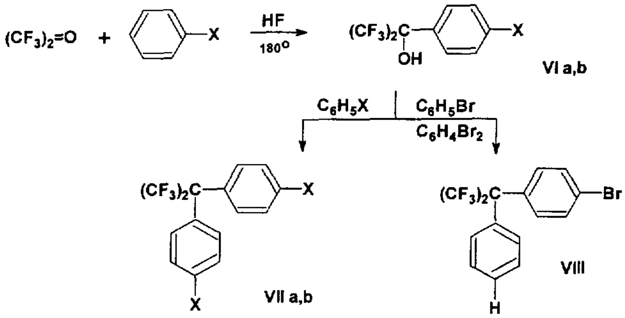
Table 1
Mass spectra of the synthesized compounds (for ions, containing bromine, *m/z* and intensity are given for ^{79}Br isotope)

Compound no.	
IIIa	502 $[M]^+$ (2.0); 483 $[M-F]^+$ (5.0); 455 $[M-F-CO]^+$ (2.0); 183 $[BrC_6H_4CO]^+$ (100.0); 155 $[BrC_6H_4]^+$ (30.0); 131 $[C_3F_5]^+$ (5.0); 104 $[C_6H_4CO]^+$ (5.0); 76 $[C_6H_4]^+$(28.0); 69 $[CF_3]^+$ (12.0); 50 $[CF_2]^+$ (15.0)
IVa	405 $[M-F]^+$ (5.0); 377 $[M-F-CO]^+$ (2.0); 131 $[C_3F_5]^+$ (2.0); 105 $[C_6H_5CO]^+$ (100.0); 77 $[C_6H_5]^+$ (60.0); 69 $[CF_3]^+$ (6.0)
IIIb	414 $[M]^+$ (40.0); 395 $[M-F]^+$ (5.0); 288 $[C_{11}H_4F_8]^+$ (3.0); 219 $[C_4F_9]^+$ (2.0); 183 $[BrC_6H_4CO]^+$ (100); 169 $[C_3F_7]$ (10.0); 155 $[BrC_6H_4]^+$ (25.0); 93 $[C_3F_3]^+$ (5.0); 76 $[C_6H_4]^+$ (25.0); 50 $[CF_2]^+$ (20.0)
IVb	336 $[M]^+$ (28.0); 317 $[M-F]^+$ (3.0); 200 $[C_4F_8]^+$ (2.0); 105 $[C_6H_5CO]^+$ (100.0); 93 $[C_3F_3]^+$ (3.0); 77 $[C_6H_5]^+$ (58.0); 69 $[CF_3]^+$ (7.0); 51 $[CF_2H]^+$ (20.0)
VIIb	460 $[M]^+$ (30.0); 391 $[M-CF_3]^+$ (27.0); 300 $[M-2Br]^+$ (14.0); 231 $[M-CF_3-2Br]^+$ (100)
VIII	384 $[M]^+$ (59.0); 313 $[M-CF_3]^+$ (34.6); 303 $[M-Br]^+$ (14.0); 234 $[M-2CF_3-Br]^+$ (73.0); 165 $[M-2CF_3-Br]^+$ (100)
X	304 $[M]^+$ (100.0); 235 $[M-CF_3]^+$ (44.3); 215 $[M-CF_3-HF]^+$ (40.0); 165 $[M-C_2F_6-H]^+$ (72.2)

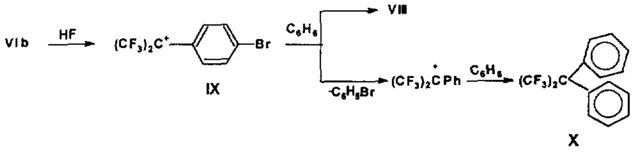
$(CF_3)_2CFCF{=}CFC^+(OH){-}C_6H_4{-}Br\text{-}p$

is involved in the allylic triad; this results in an increase in its stability, and therefore a decrease in its brominating action.

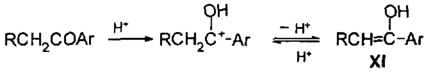
The ability of benzyl cations containing bromine in the benzene ring to be brominating agents is of the general character. This conclusion follows from the reaction of hexafluoroacetone with bromobenzene in anhydrous HF. Whereas the similar reaction with chlorobenzene unambiguously results in dichloride (**VIIa**), the reaction with bromobenzene gives a mixture of products containing dibromide **VIIb**, monobromide **VIII**, and dibromobenzene.



The role of brominated benzyl cation (**IX**) as a brominating agent was confirmed by an additional experiment: the reaction of carbinol (**VI**) with benzene in HF. In this experiment diphenylpropane (**X**) and bromobenzene were recorded along with the normal alkylation product.



We should note that the Friedel–Crafts acylation of bromobenzene with nonfluorinated acyl halides is not accompanied by formation of byproducts [5]. This may be attributed to the possibility of stabilization of the intermediate benzyl cation by its transformation to enol (**XI**).



$$RCH_2COAr \xrightarrow{H^+} RCH_2\overset{OH}{\overset{|}{C^+}}\text{-}Ar \underset{H^+}{\overset{-H^+}{\rightleftharpoons}} RCH{=}\overset{OH}{\overset{|}{C}}\text{-}Ar$$

XI

Thus, the data we obtained and the literature data [1–3] indicate that brominating action is typical of the benzyl cations that contain bromine in the ring and does not contain any groups, which favor their stabilization.

3. Experimental

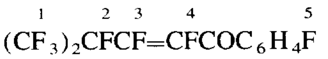
^{19}F NMR spectra were recorded on a Bruker WP-200 SY (188.3 MHz) spectrometer. Chemical shifts are reported in parts per million (ppm) from CF_3COOH used as the external standard. IR spectra were recorded on a UR-20 spectrophotometer. Mass spectra were obtained on a VG-7070E instrument (70 eV) at the temperature of the ion source 140°C; *m/z*, tentative assignment, and relative intensity (%) are given in Table 1.

3.1. Preparation of p-chlorophenylperfluoro-n-hexyl ketone (IIc)

A mixture of acyl chloride **Ia** (38.2 g, 0.1 mol), $AlCl_3$ (15 g, 0.115 mol), and chlorobenzene (80 ml) was stirred for 3 h at 65–80°C. The cooled reaction mixture was decomposed with dilute HCl. The organic layer was separated, dried over $MgSO_4$, filtered and distilled. Ketone **IIc** (40.2 g, 89%) was obtained as *p*-isomer, b.p. 107–108°C/7 mm Hg. Found: C, 33.98; H, 0.83; F, 53.59%. $C_{13}H_4ClF_{13}O$. Calculated: C, 34.06; H, 0.87; F, 53.93%. ^{19}F NMR: 5.1 m (3F); 36.1 m (2F); 44.5 (4F); 46.2 (2F); 49.8 (2F). ^{1}H NMR: 7.1 m (2H); 7.6 m (2H) (AA′BB′ pattern).

3.2. Preparation of p-fluorophenylperfluoro(3-methylbut-1-enyl) ketone (IId)

A mixture of acyl chloride **Ib** (10 g, 34 mmol), $AlCl_3$ (4.8 g, 0. 36 mmol), and fluorobenzene (30 ml) was stirred for 1 h at 50–60°C. The reaction mixture was poured into ice, and made acidic with dilute HCl. The products were extracted with ether, dried and distilled. Ketone **IId** (5.4 g, 46%) was obtained, in the form of a mixture of *cis* and *trans*-isomers (8:92) (GCL), b.p. 80–81°C/5 mm Hg. Found C, 40.48; H, 1.16; F, 53.32%. $C_{12}H_4F_{10}O$. Calculated (%) C, 40.68; H, 1.13; F, 53.67.



$(\overset{1}{CF_3})_2C\overset{2}{F}C\overset{3}{F}{=}C\overset{4}{F}COC_6H_4\overset{5}{F}$

^{19}F NMR (*cis*-isomer): − 1.0 (F^1); 25.4 (F^5); 37.2 (F^4); 46.5 (F^3); 110.5 (F^2). (*trans*-isomer): −1.0 (F^1); 25.4 (F^5); 68.0 (F^4); 78.0 (F^3); 110.5 (F^2); $J(F^3–F^4) = 138$ Hz; $J(F^2–F^4) = 145$ Hz. IR (ν, cm^{-1}): 1615 (C=C); 1690, 1720 (C=O).

3.3. Interaction of acyl chlorides **Ia,b** with bromobenzene

A mixture of **Ia** (26 g, 70 mmol), 11.4 g (80 mmol) of $AlCl_3$ and 70 ml of bromobenzene was stirred for 2 h at 40–45°C and for 1 h at 45–50°C and decomposed with cooled dilute HCl; the organic layer was washed with a dilute K_2CO_3 solution, dried over $MgSO_4$, and distilled. A fraction (25.8 g) boiling at 70–112°C/6–8 mm was obtained as a mixture of products **IIIa**, $C_6H_4Br_2$, and **IVa**, which contained 12% **IIIa** (GLC and GC–MS).

A fraction with b.p. 72–108°C/7 mm (15.2 g) was obtained similarly from a mixture of **Ib** (15 g, 50 mmol), 7 g (53 mmol) $AlCl_3$, and 50 ml of bromobenzene stirred for 4 h at 70–85°C. The fraction contained *cis–trans*-**IIIb**, $C_6H_4Br_2$, and *cis–trans*-**IVb**, the content of **IIIb** was 37%.

3.4. Preparation of 2,2-bis(p-chlorophenyl)-hexafluoropropane (VIIa)

Chlorobenzene (17 g), anhydrous HF (40 ml) and hexafluoroacetone (5.5 ml, −78°C) were placed in a 100 ml steel autoclave, which was then heated with shaking at 180°C for 20 h. The reaction mixture was poured into ice, the organic layer was extracted with CH_2Cl_2. The solvent was removed by distillation, and according to ^{19}F NMR data, the resulting mixture (24.5 g) contained (by GLC) 54.5% **VIIa**, 4.8% **VIa** and 32% *p*-$ClC_6H_4CF(CF_3)_2$ (**XII**). ^{19}F NMR: **VIIa** (−19.3 s), **VIa** (−1.8 s), **XII** (−1.4 d, +105 hept.; $J=7.5$ Hz). Distillation gave 7 g (36%) of dichloride **VIIa**, b.p. 125–130°C/2 mm, m.p. 53–54°C (from water–MeOH) (see Ref. [6]).

3.5. Interaction of hexafluoroacetone with bromobenzene

The process was carried out similarly to the previous procedure. Two fractions were obtained from 40 g of bromobenzene, 40 ml of HF, and 6 ml of HFA: (1) a fraction (5 g) with b.p. 55–57°C/1 mm; according to GLC, ^{19}F NMR, and MS it contained $C_6H_4Br_2$, *p*-$BrC_6H_4CF(CF_3)_2$ (**XIII**) (−11.0 d, +106 hept.; $J=7.6$ Hz), **VIb** (−1.3 s), $(C_6H_5)_2C(CF_3)_2$ (**X**) (−13 s), *p*-$BrC_6H_4C(CF_3)_2C_6H_5$ (**VIII**) (−12.7 s), (*p*-$BrC_6H_4)_2C(CF_3)_2$ (**VIIb**) (−12.45 s); (2) a fraction (4.5 g) (b.p. 148–151°C/1 mm, m.p. 78–80°C), which contained 80% **VIIb** and 20% **VIII**.

Compound **VIb** (7.7 g), benzene (10 g), and HF (30 ml) were heated in a 100 ml autoclave at 180°C for 30 h and treated using the same procedure. After distillation of benzene and bromobenzene, 5.4 g of a mixture were obtained, which contained (according to GLC and MS) 14.5% **VIb**, 3.5% **XIII**, 11% **X**, and 60% **VIII**. The structures of compounds VIb, VIIb, and VIII were confirmed by mass spectroscopy data (Table 1).

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