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FLUORINE-CONTAINING CARBOCATIONS.
IV. THE USE OF SALT SOLUTIONS OF STABLE POLYFLUORINATED α, α-DIFLUOROBENZYL AND α-FLUORODIPHENYLMETHYL CATIONS IN ANTIMONY PENTAFLUORIDE IN THE SYNTHESIS OF POLYFLUORINATED BENZOIC ACIDS, BENZOPHENONES AND DIPHENYLDIFLUOROMETHANES

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Summary

Polyfluorinated benzoic acids have been prepared by the hydrolysis of solutions of salts of polyfluorinated α, α-difluorobenzyl cations in SbF_5. Polyfluorinated benzophenones and diphenyldifluoromethanes have been obtained both by hydrolysis and by pouring into HF solutions of the salts of polyfluorinated α-fluorodiphenylmethyl cations.

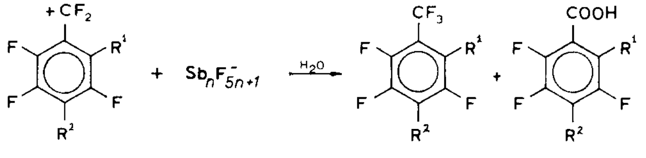
Introduction

It has been shown earlier [1, 2] that the action of SbF_5 on polyfluorinated trifluoromethylbenzenes results in the formation of polyfluorinated benzyl cations (I). The latter alkylate incompletely substituted polyfluorobenzenes in SbF_5, the diaryldifluoromethanes generated being converted into the polyfluorinated diarylfluoromethyl cations (II). The formation of ions of both types has been confirmed by ^{19}F and ^{1}H NMR spectral studies of solutions of their salts in SbF_5.

The present study deals with some transformations of the ions (I) and (II) which confirm their structures and open up methods for their synthetic application.

Results and discussion

When solutions of salts of the ions (I)(a)–(f) in SbF_5 [obtained by dissolving the trifluoromethylbenzenes (III)(a)–(f)] are poured onto ice, the respective benzoic acids are formed.

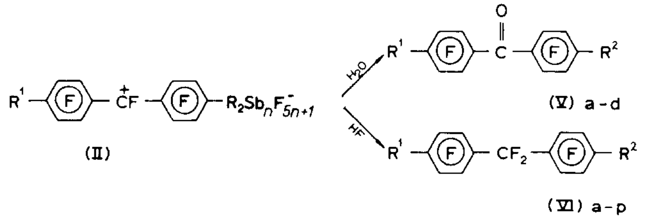


(I)(a) - (f) (IV)(a) - (f) (III)(a) - (f)

(a): $R^1 = F$; $R^2 = F$
(b): $R^1 = F$; $R^2 = H$
(c): $R^1 = H$; $R^2 = F$
(d): $R^1 = F$; $R^2 = Cl$
(e): $R^1 = F$; $R^2 = Br$
(f): $R^1 = F$; $R^2 = CH_3$

The yields obtained and some physicochemical constants for these acids are listed in Table 1. In each case some of the trifluoromethylbenzene was also recovered, although the ^{19}F NMR spectrum indicated that conversion of trifluoromethylbenzene in SbF_5 to the respective ion (I) is practically complete. Formation of the precursors (III)(a)–(f) during hydrolysis of solutions of the ions (I)(a)–(f) in SbF_5 is evidently due to the process of fluoride-ion capture by the ion (I) competing with hydrolysis.

When solutions of diphenylfluoromethyl ions (II) in SbF_5 [obtained by adding equimolar quantities of polyfluorobenzenes to solutions of ion (I), *cf.* Tables 2 and 3] are poured onto ice or into hydrogen fluoride, polyfluorinated benzophenones (V) and diphenyldifluoromethanes (VI) respectively are obtained in high yield.



(II) (V) a - d (VI) a - p

(a): $R^1 = F$; $R^2 = F$
(b): $R^1 = F$; $R^2 = H$
(c): $R^1 = F$; $R^2 = CH_3$
(d): $R^1 = H$; $R^2 = H$
(e): $R^1 = F$; $R^2 = Cl$
(f): $R^1 = F$; $R^2 = Br$
(g): $R^1 = F$; $R^2 = CF_3$
(h): $R^1 = Cl$; $R^2 = Cl$
(i): $R^1 = Cl$; $R^2 = H$
(j): $R^1 = Cl$; $R^2 = CH_3$
(k): $R^1 = Br$; $R^2 = Br$
(l): $R^1 = Br$; $R^2 = H$
(m): $R^1 = Br$; $R^2 = CH_3$
(n): $R^1 = H$; $R^2 = CH_3$
(o): $R^1 = CH_3$; $R^2 = CH_3$
(p): $R^1 = CH_3$; $R^2 = CF_3$

The yields obtained and the physical constants of the compounds are listed in Tables 2 and 3.

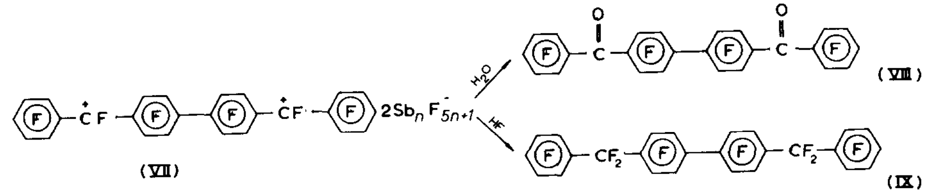
Similar treatment of the dication (VII) leads to the formation of the perfluoro-4,4′-dibenzoyldiphenyl (VIII) and perfluoro-4-4′-dibenzyldiphenyl (IX).

TABLE 1

Characteristics of polyfluorinated aromatic acids obtained by hydrolysis of solutions of the salts of polyfluorinated benzyl cations in antimony pentafluoride.

Benzyl cation	Hydrolysis product	Yield (%)	M.p./° C	Reference
(I)(a)	(IV)(a)	66	100 - 102 (103 - 104)*	3
(I)(b)	(IV)(b)	56	148 - 149 (152 - 153)	4, 14
(I)(c)	(IV)(c)	30	84 - 86 (86 - 86.5)	10
(I)(d)	(IV)(d)	84	125 - 127 (128 - 130)	12
(I)(e)	(IV)(e)	68	140 - 142 (142 - 142.5)	14
(I)(f)	(IV)(f)	73	169.5 - 170.5 (174)	4, 12

*Figures in brackets are quoted from the literature.



(VII) (VIII) (IX)

The above transformations of the ions (I) and (II) open up the way for the synthetic application of polyfluorinated trifluoromethylbenzenes through conversion of the trifluoromethyl group. The hydrolyses of polyfluorinated trifluoromethylbenzenes by heating with sulphuric acid described earlier required drastic conditions and a long reaction time [3, 4]. As has been shown for the synthesis of compound (VI)(a) from the ketone (V)(a) [5], polyfluorinated diaryldifluoromethanes can be prepared by the action of SF_4 on the respective benzophenones. The ketone (V)(a) was obtained [6] by the reaction of a pentafluorophenylmagnesium halide with methylchlorocarbonate, or with ethyl formate followed by oxidation, and by interaction of pentafluorophenyl-lithium with dimethylcarbonate [7].

The methods for the synthesis of the ketones (V) and diaryldifluoromethanes (VI) proposed here are simpler experimentally, while the trifluoromethylbenzenes used as starting materials are becoming increasingly more readily available due to advances in the study of the thermal trifluoromethylation of polyfluoroaromatic compounds [8].

TABLE 2

Characteristics of polyfluorinated benzophenones obtained by hydrolysis of solutions of salts of polyfluorinated diphenylmethyl cations in antimony pentafluoride

Alkylating agent	Aromatic compound	Product obtained	Yield (%)	M.p./°C	Found (%) C	Found (%) H	Found (%) F	Mol. wt. (mass spectrum)	Calculated (%) C	Calculated (%) H	Calculated (%) F	Mol. wt.
(III)(a)	Pentafluorobenzene (XII)(a)	(V)(a)	93	91.5 - 92.5 (91 - 92)[6]*								
(III)(a)	2,3,5,6-Tetrafluoro-benzene (XII)(b)[15]	(V)(b)(nc)	75	73.5 - 74.5	45.2 45.2		49.5 49.8	344	45.4		49.7	344
(III)(a)	2,3,5,6-Tetrafluoro-toluene (XII)(c)[12]	(V)(c)(nc)	90	69.5 - 70.5	47.5 47.6	0.99 0.61	47.6 47.6	358	46.9	0.84	47.8	358
(III)(b)[12]	(XII)(b)	(V)(d)(nc)	82	71.0 - 73.0	47.5 47.8	0.49 0.57	46.8 47.0	326	47.8	0.61	46.6	326
(III)(a)	4,4′-di-*H*-Octafluoro-diphenyl (X)[16]	(XI)(nc)	100	107 - 108	46.0 46.4		59.5 49.4	492	46.3		50.2	492
(XIII)	(XII)(a)	(VIII)(nc)	84	186.5 - 188	45.2 45.3		[illegible] 49.9	[illegible] 695**	45.5		49.8	686

*Figures in brackets are quoted from the literature.

**The molecular weight of compound (VIII) was determined using isothermal distillation.

The attempted double alkylation of 4,4′-di-*H*-octafluorodiphenyl (X) with a five-fold excess of the perfluorobenzyl cation (I)(a) was unsuccessful, 4*H*,4′-pentafluorobenzoyloctafluorodiphenyl (XI) being obtained after hydrolysis (Table 2). It follows from this that alkylation of the 4-(2′,3′,5′,6′-tetrafluorophenyl)nonafluorodiphenylfluoromethyl cation is complicated and its equilibrium product, 4-(2′,3′,5′,6′-tetrafluorophenyl)nonafluorodiphenyldifluoromethane, evidently either is not alkylated or is present in negligible amounts. Addition of excess pentafluorobenzene to the solution of the salt of the cation (II)(a) in SbF_5 in an attempt to alkylate the former by the generation of the diphenylmethyl cation was also unsuccessful. Even when the solution was held for 18 h at 25 °C or 5 h at 80 °C, subsequent hydrolysis led only to decafluorobenzophenone and pentafluorobenzene. Attempted alkylation of pentachlorobenzene by means of the cation (I)(a) in SbF_5 was also unsuccessful even on heating to 80 °C.

Experimental

The ^1H and ^{19}F NMR spectra of CCl_4 solutions of the neutral compounds were recorded using C_6F_6 and a hexamethyldisiloxane (9.96 τ) as internal standards and employing a Varian A56/60 instrument throughout. Solution concentrations of 15 - 30% were used. The UV spectra were recorded using a Unicam SP-700C instrument and employing ethanolic solutions of concentration 0.5×10^{-4} mol l^{-1} with a layer thickness of 0.5 cm. The IR spectra were recorded using a UR-10 spectrometer. The NMR, UV and IR spectra of all the compounds studied were in agreement with their predicted structures.

Preparation of 4-chloro-heptafluorotoluene (III)(d) (nc)

$NaNO_2$ (25 g) was added to a mixture consisting of 25 g of heptafluoro-*p*-toluidine [4] in 100 cm^3 of HF kept at −20 °C to −5 °C using continuous stirring. The resulting mixture was stirred for a further 3 h at this temperature and then cuprous chloride (prepared directly before use from 100 g of $CuSO_4 \cdot 5H_2O$ by the method of ref. 9) in 150 cm^3 of HCl (density 1.19) was added and the cooling discontinued. After 2 h the product was extracted with methylene chloride, the extract washed with water (500 cm^3) and steam-distilled. The organic part of the condensate was separated and dried with anhydrous $MgSO_4$. The solvent was removed by heating on a water bath, the residue distilled, and the fraction boiling at 137 - 138.5 °C collected when 14.1 g (52% yield) of compound (III)(d) was obtained. Analysis: Found: C, 33.3, 33.1; F, 52.7, 52.2; Cl, 14.0, 14.2%, mol. wt. (mass spectrum) 352, 354. C_7F_7Cl requires C, 33.1; F, 52.7; Cl, 14.1%, mol. wt. 352 (based on ^{35}Cl), 354 (based on ^{37}Cl). UV spectrum: 210 (3.92), 222 (3.92), 277 nm (3.46).

TABLE 3

Characteristics of polyfluorinated diphenyldifluoromethanes obtained by pouring salt solutions of polyfluorinated diphenylmethyl cations in antimony pentafluoride into hydrogen fluoride

Alkylating agent	Aromatic compound	Diphenyl-methane	Yield (%)	M.p./°C (ethanol)	Found (%)					Calculated (%)				
					C	H	F	Cl or Br	Mol. wt. (mass spectrum)	C	H	F	Cl or Br	Mol. wt.
(III)(a)	(XII)(a)	(VI)(a)	68	46 - 48 (49 - 50)[4]*										
(III)(a)	(XII)(b)	(VI)(b)(nc)	67	28 - 30.5	42.6 42.5	0.12 0.22	57.3 57.8		366	42.6	0.27	57.1		366
(III)(a)	(XII)(c)	(VI)(c)(nc)	81	27 - 28.5	44.3 44.0	0.80 0.71	55.6 55.3		380	44.2	0.79	55.0		380
(III)(b)	(XII)(b)	(VI)(d)(nc)	70	40.5 - 42	45.2 45.0	0.31 0.53	54.2 54.7		348	44.8	0.57	54.6		348
(III)(d)	(XII)(a)	(VI)(e)(nc)	81	47 - 48	38.7		51.5 51.6	9.06 8.76	400 402	39.0		52.2	8.86	400 (based on ^{35}Cl), 402 (based on ^{37}Cl)
III)(e)	(XII)(a)	(VI)(f)(nc)	62	68 - 69.5	34.4 34.4		46.7 46.9	18.1 17.9	444 446	35.0		47.0	18.0	444 (based on ^{79}Br), 446 (based on ^{81}Br)
III)(g)	(XII)(a)	(VI)(g)(nc)	85	45.5 - 47	39.3 39.0		61.1 60.9		434	38.7		61.3		434
III)(d)	(XII)(d)	(VI)(h)(nc)	74	55.5 - 56.5	37.5 37.7		45.2 45.6	17.2 17.2	416 420	37.4		45.6	17.0	416 (based on ^{35}Cl), 420 (based on ^{37}Cl)
III)(d)	(XII)(b)	(VI)(i)(nc)	77	36.5 - 38	40.5	0.12	49.6 49.2	9.46 9.75	382 384	40.6	0.26	49.7	9.28	382 (based on ^{35}Cl), 384 (based on ^{37}Cl)

TABLE 3 *(continued)*

(III)(d)	(XII)(c)	(VI)(j)(nc)	69	69 - 70	42.3 42.1	0.79 0.69	47.6 48.1	9.22 9.29	396 398	42.4	0.76	47.9	8.95	396 (based on ^{35}Cl), 398 (based on ^{37}Cl)
(III)(e)	(XII)(e)[10]	(VI)(k)(nc)	78	74 - 75.5	30.9 31.2		37.5 38.1	30.5 30.8	504 508	30.8		37.6	31.6	504 (based on ^{79}Br), 508 (based on ^{81}Br)
(III)(e)	(XII)(b)	(VI)(l)(nc)	87	40.5 - 42.5	36.1 36.0		44.2 43.9	18.5 18.7	426 428	36.5	0.23	44.5	18.7	426 (based on ^{79}Br), 428 (based on ^{81}Br)
(III)(e)	(XII)(c)	(VI)(m)(nc)	94	82.5 - 83.5	38.6 38.6	0.78 0.87	43.9 43.7	18.9 18.4	440 442	38.1	0.68	43.1	18.1	440 (based on ^{79}Br), 442 (based on ^{81}Br)
(III)(b)	(XII)(c)	(VI)(n)(nc)	54	129/1 mm Hg (b.p.)	46.3 46.2	0.84 0.68	52.7 52.8		362	46.4	1.10	52.5		362
(III)(f)[4]	(XII)(c)	(VI)(o)(nc)	67	90.5 - 92	47.8 47.8	1.66 1.71	50.1 49.7		376	47.9	1.60	50.5		376
(III)(g)	(XII)(c)	(VI)(p)(nc)	74	33.5 - 35	41.9 42.0	0.91 0.81	57.5 57.4		430	41.9	0.70	57.4		430
(XIII)	(XII)(a)	(IX)(nc)	81	102 - 103.5	43.1 43.1		57.7 57.7		733** 735**	42.7		57.3		730

*Figures in brackets refer to literature references.

**The molecular weight of compound (IX) was determined using isothermal distillation.

Preparation of 4-bromo-heptafluorotoluene (III)(e) (nc)

4-*H*-Heptafluorotoluene (15.3 g)[4] and a solution consisting of 5 cm^3 of bromine in 6 cm^3 of 60% oleum was stirred for 64 h at 60 - 65 °C. The reaction mixture was poured into water and the oily layer which separated was washed with aqueous sodium bisulphate and then with water until it was no longer acidic. After drying over anhydrous $MgSO_4$, the oil was distilled, the fraction boiling at 152 - 153 °C being collected when 14.6 g (70% yield) of compound (III)(e) was obtained. Analysis: Found: C, 28.1, 28.0; F, 44.4, 44.6; Br, 27.0, 27.0%, mol. wt. (mass spectrum) 296, 298. C_7F_7Br requires C, 28.3, F, 44.8; Br, 27.0%, mol. wt. 296 (based on ^{79}Br), 298 (based on ^{81}Br). UV spectrum: 218 (3.93), 228 (3.79), 285 nm (3.26).

Preparation of 2,3,5,6-tetrafluorochlorobenzene (XII)(d)

4-Chlorotetrafluorobenzoic acid (IV)(d) (3.1 g) was decarboxylated by heating its solution in dimethylformamide [10]. Yield 2.2 g (87%), b.p. 123 - 123.5 °C (cited [11]: 123 - 123.5 °C).

Preparation of 4,4′-bis(trifluoromethyl)octafluorodiphenyl (XIII) (nc)

[redacted] heated in a sealed ampoule for 80 h at 190 - 200 °C. On extraction, 1.0 g (87%) of (XIII), m.p. 101 - 102 °C (ethanol) was obtained. Analysis: Found: C, 38.3, 38.2; F, 61.4, 61.3%, mol. wt. (mass spectrum) 434. $C_{14}F_{14}$ requires C, 38.7; F, 61.3%, mol. wt. 434. UV spectrum: 235 (4.29), 285 nm (3.78).

Preparation of 4-trifluoromethyltetrafluorobenzoic acid (XIV)

A mixture consisting of 2 g of 1,2-dibromoethane and 3 g of compound (III)(d) were added dropwise to a continuously stirred mixture consisting of 3 g of magnesium turnings in 150 cm^3 of absolute tetrahydrofuran. The reaction mixture was heated to boiling for 20 min and then cooled with ice. After cooling, a further 23 g of (III)(d) were added over a period of 1.5 h. The mixture was stirred for a further 1 h and then CO_2 was bubbled through for 5 h while the solution was cooled externally with ice. The resulting solution was poured into water, acidified with sulphuric acid, the oily layer separated and dried over P_2O_5. Sublimation and subsequent crystallisation from toluene gave 12.6 g (52%) of the acid (XIV), m.p. 107 - 108.5 °C (cited [12]: 107.5 - 110.5 °C).

*Preparation of perfluoro-*p*-xylene (III)(g)*

The acid (XIV) (5.5 g) and 6 cm^3 of SF_4 were heated at 180 - 200 °C in a steel bomb for 24 h. The product was steam-distilled, separated and dried with anhydrous $MgSO_4$. Distillation gave 5 g of (III)(g), b.p. 122 - 122.5 °C (cited [13]: 121 - 122 °C).

The typical syntheses of perfluorinated benzoic acids, diarylketones and diaryldifluoromethanes are described below.

Preparation of pentafluorobenzoic acid (IV)(a)

Octafluorotoluene (4.2 g) was dissolved in 19.9 g of SbF_5 at 20 - 25 °C and the solution poured onto ice when 0.8 g of unreacted octafluorotoluene was separated. The product was extracted from the aqueous solution with ether, the extract dried with anhydrous $MgSO_4$ and the ether evaporated. After this procedure, 1.8 g of acid (IV)(a) was obtained (66% yield based on amount of octafluorotoluene reacted). The melting points (toluene) and yields of the other acids obtained are listed in Table 1.

Preparation of decafluorobenzophenone (V)(a)

Pentafluorobenzene (1.3 g) was added to a continuously stirred solution consisting of 1.3 g of octafluorotoluene in 8.0 g of SbF_5 at 20 - 25 °C. The mixture was poured onto ice, the solid filtered, washed with water to separate the acid and dried over P_2O_5. 1.8 g (93%) of ketone (V)(a) was obtained.

The characteristics of the other ketones obtained are listed in Table 2.

Preparation of decafluorodiphenyldifluoromethane (VI)(a)

A solution of the salt of the ion (II)(a), prepared by successively dissolving 0.9 g of perfluorotoluene and 0.9 g of pentafluorobenzene in 4.0 g of SbF_5, was poured into 50 cm^3 of distilled HF. The reaction mixture was poured onto ice, the solid filtered, washed with water to separate the acid and dried over P_2O_5. Sublimation gave 1.1 g (68%) of decafluorodiphenyldifluoromethane (VI)(a).

In the case of 4-methyl-4′-*H*-octafluorodiphenyldifluoromethane, after pouring onto ice an oil was obtained which was extracted with ether, the ethereal extracts washed with 10% NaOH (until neutral) then with water and dried with $MgSO_4$. The ether was evaporated, the residue distilled in vacuum, the fraction b.p. 129 °C/1 mmHg being collected.

The characteristics of the diphenyldifluoromethanes so obtained are listed in Table 3.

Preparation of perfluoro-4,4′-di(benzoyl)diphenyl (VIII) (nc)

Compound (XIII) (0.4 g), 0.3 g of (III)(a) and 8.0 g of SbF_5 were heated at 70 °C for 1 h giving a homogeneous solution. After cooling to 20 °C the solution was subjected to a treatment similar to that described above for (V)(a).

Preparation of perfluoro-4,4′-di(benzyl)diphenyl (IX) (nc)

Compound (XIII) (1.1 g), 1.4 g of (III)(a) and 16.0 g of SbF_5 were heated at 70 °C for 1 h giving a homogeneous solution. After cooling to 20 °C, the solution was poured into HF, and then treated further as described above for (VI).

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