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The preparation of bis(pentafluorophenyl)iodine(III) sulphonates from the reactions of iodine(III) compounds with pentafluorobenzene in strong acids*

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Abstract

Bis(pentafluorophenyl)iodine trifluoromethanesulphonate and bis(pentafluorophenyl)iodine 2,4,6-trinitrobenzenesulphonate can be prepared in approximately 80% yield from the reactions of iodine tris(trifluoroacetate), pentafluorobenzene and the corresponding sulphonic acid in trifluoroacetic acid. The ^{19}F NMR data and vibrational spectra have been compared with those of related compounds.

Introduction

A variety of synthetic methods for the preparation of diaryliodine ions has been developed since Hartmann and Meyer prepared the mono(*p*-iodophenyl) phenyliodine cation in 1894 [1]. The description of a great number of these compounds is summarized in several reviews, e.g. refs. 2 and 3. Although many perfluoroorganoiodine cations are well characterized [4–7], only spectroscopic evidence has been provided for bis(perfluoroorgano)iodine derivatives [8–13]. In the meantime, we have developed two different pathways for the synthesis of bis(pentafluorophenyl)iodine tetrafluoroborates. Thus, $[I(C_6F_5)_2][BF_4]$ can be prepared either by the reaction of $[Xe(C_6F_5)][BF_4]$ with C_6F_5I [12] or by the reaction of $I(C_6F_5)F_2$ with $B(C_6F_5)_3$ in the presence of BF_3 [13].

In this paper the synthesis of $[I(C_6F_5)_2][OSO_2R]$ ($R=CF_3$, 2,4,6-$(NO_2)_3$-C_6H_2) from iodine tris(trifluoroacetate) and pentafluorobenzene is described.

Results and discussion

Bis(pentafluorophenyl)iodine sulphonates can be synthesized by combining two methods for the preparation of diorganoiodine ions worked out

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*Dedicated to Prof. Dr L. M. Yagupol'skii on the occasion of his 70th birthday.

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by Umemoto *et al.* [6] and Beringer *et al.* [14]. Iodine tris(trifluoroacetate) reacts readily with pentafluorobenzene in trifluoroacetic acid in the presence of trifluoromethanesulphonic acid or 2,4,6-trinitrobenzenesulphonic acid to yield the corresponding bis(pentafluorophenyl)iodine sulphonate.

$$I(OCOCF_3)_3 + 2C_6F_5H + HOSO_2R \longrightarrow [I(C_6F_5)_2][OSO_2R] + 3CF_3COOH$$

$[R = CF_3,\ 2,4,6\text{-}(NO_2)_3C_6H_2]$

In the absence of the sulphonic acid, no reaction takes place. If only catalytic amounts of $HOSO_2R$ are added, the conversion is incomplete. These results are comparable to those published by Umemoto *et al.* [6].

In considering these results, the following reaction sequence may be proposed. In an initial step, one trifluoroacetate group of $I(OCOCF_3)_3$ is replaced by the sulphonate group. The resulting $[I(OCOCF_3)_2][OSO_2R]$ is the reactive species which attacks pentafluorobenzene in an electrophilic manner to form $I(C_6F_5)(OCOCF_3)_2$. A repetition of this sequence, followed by a substitution of the trifluoroacetate group by the sulphonate group, finally yields $[I(C_6F_5)_2][OSO_2R]$.

$$I(OCOCF_3)_3 + HOSO_2R \longrightarrow [I(OCOCF_3)_2][OSO_2R] + CF_3COOH$$

$$[I(OCOCF_3)_2][OSO_2R] + C_6F_5H \longrightarrow I(C_6F_5)(OCOCF_3)_2 + HOSO_2R$$

$$I(C_6F_5)(OCOCF_3)_2 + HOSO_2R \longrightarrow I(C_6F_5)(OCOCF_3)(OSO_2R) + CF_3COOH$$

$$I(C_6F_5)(OCOCF_3)(OSO_2R) + C_6F_5H \longrightarrow [I(C_6F_5)_2][OSO_2R] + CF_3COOH$$

$$I(OCOCF_3)_3 + 2C_6F_5H + HOSO_2R \longrightarrow [I(C_6F_5)_2][OSO_2R] + 3CF_3COOH$$

$[I(C_6F_5)_2][OSO_2R]$ decomposes at approximately 250 °C evolving elemental iodine.

The ^{19}F NMR spectra recorded in different solvents (Table 1) show that bis(pentafluorophenyl)iodine sulphonates are dissolved as ions with a strong cation–anion interaction. The resonances of the 4-fluorine atom, and also of the 3,5-fluorine atoms, are deshielded in comparison to non-ionic derivatives, e.g. $I(C_6F_5)F_2$. The similarity of the chemical shifts of $[Xe(C_6F_5)][BF_4]$, $[Te(C_6F_5)_3][BF_4]$ or $[I(C_6F_5)_2][BF_4]$ [12, 13] and $[I(C_6F_5)_2][OSO_2R]$ suggests a partially ionic equilibrium according to:

$$[I(C_6F_5)_2][OSO_2R] \rightleftharpoons [I(C_6F_5)_2]^+ + OSO_2R^-$$

The stability of the cation may be explained by its mesomeric structures.

This presumption is also based on a comparison of the vibrational spectra of the isoelectronic bis(pentafluorophenyl)tellurium and sodium trifluoromethane sulphonate (Table 2). A comparison of the vibrational frequencies shows an obvious similarity between $[I(C_6F_5)_2]^+$ and $Te(C_6F_5)_2$ [15]. The absorption bands of the trifluoromethane sulphonate are more similar to

TABLE 1

^{19}F NMR data (δ, ppm) for $[I(C_6F_5)_2][OSO_2R]$ in various solvents and in comparison to the pentafluorophenyl derivatives of xenon and tellurium

$R = CF_3$:

Solvent	δ(2,6-F)	δ(3,5-F)	δ(4-F)	$\delta(CF_3)$
CF_3COOH	−120.80	−157.26	−142.24	−75.60
glyme	−122.02	−157.93	−143.89	−75.65
CH_2Cl_2[a]	−117.9	−153.8	−136.1	−72.0
CH_3CN	−120.76	−154.16	−141.95	−75.65
H_2O	−122.32	−156.79	−142.80	−75.63

[a]Broad lines.

$R = 2,4,6\text{-}(NO_2)_3C_6H_2$:

Solvent	δ(2,6-F)	δ(3,5-F)	δ(4-F)
CF_3COOH	−122.26	−157.49	−142.00

In comparison (solvent = CH_3CN) [13]:

Compound	δ(2,6-F)	δ(3,5-F)	δ(4-F)	$\delta(BF_4^-)$
$[I(C_6F_5)_2][BF_4]$	−120.6	−155.6	−141.5	−149.7
$[Xe(C_6F_5)][BF_4]$	−125.2	−154.8	−142.0	−149.9
$[Te(C_6F_5)_3][BF_4]$	−122.5	−155.9	−141.1	−149.8

those of $NaOSO_2CF_3$ than to those of $I(OSO_2CF_3)_3$ and related compounds [16–18].

These results show that it is possible to obtain $[I(C_6F_5)_2][OSO_2R]$ on a convenient manner in good yields.

Experimental

The ^{19}F NMR spectra were recorded on a Bruker FT-NMR spectrometer AMX 300 at 282.4 MHz. CCl_3F was used as an external standard. A negative chemical shift denotes a resonance occurring to low frequency (high field) of the reference compound.

Infrared spectra were recorded on a Perkin-Elmer PE 580 B spectrometer using KBr pellets. Raman spectra were run on a Coderg T 800 spectrometer equipped with an Ar^+ laser (Spectra Physics) operating at 514.5 nm.

C_6F_5H was purchased from Johnson Matthey (Alfa Products) and $HOSO_2CF_3$ from Merck-Schuchardt. CF_3COOH was received as a gift from Solvay, Fluor und Derivative, Hannover (Germany) and $HOSO_2\text{-}2,4,6\text{-}(NO_2)_3C_6H_2$ as a gift from Prof. Dr F. Huber, Dortmund. $I(OCOCF_3)_3$ was prepared according to a reported procedure [19].

TABLE 2

Vibrational frequencies (cm^{-1}) of $[I(C_6F_5)_2][OSO_2CF_3]$, $Te(C_6F_5)_2$ and $NaOSO_2CF_3$

$[I(C_6F_5)_2][OSO_2CF_3]$		$Te(C_6F_5)_2$		$NaOSO_2CF_3$	
IR	Raman	IR [15]	Raman	IR [16]	Raman [16]
1640	1640	1637	1640		
1515	1525	1508	1520		
1500		1484			
	1425		1405		
1385		1383			
	1330				
1285				1280	1285
1235	1235			1232	1230
1170	1150		1145	1168	1188
	1125		1125		
1100		1083	1090		
1030	1035			1036	1038
985	975	971	975		
810	810	793	800		
	775				776
	740				
	625		625	630	
	620				
	590		590	591	580
	530			531	520
	495		495	515	
	445		450		
	395		395		
	355		360	351	353
	320			319	321
	285		280		
	215		205		208
	175		180		
	145		140		
	(125)		(125)		

General procedure

$I(OCOCF_3)_3$ was suspended in CF_3COOH at 0 °C. C_6F_5H was added and the reaction mixture stirred for *c.* 1 h. After adding $HOSO_2R$, the reaction mixture was warmed up to room temperature and stirred for 72 h. After evaporating all volatile compounds *in vacuo*, $[I(C_6F_5)_2][OSO_2R]$ remains as a white to pale yellow solid in *c.* 80% yield. The condensate contained small amounts of C_6F_5I and unreacted C_6F_5H.

$[I(C_6F_5)_2][OSO_2CF_3]$: 1.2 ml C_6F_5H (10.8 mmol), 2.33 g $I(OCOCF_3)_3$ (5.00 mmol), 0.5 ml $HOSO_2CF_3$ (5.4 mmol), 10 ml CF_3COOH. Yield, 2.47 g $[I(C_6F_5)_2][OSO_2CF_3]$ (4.05 mmol) (81%).

$[I(C_6F_5)_2][OSO_2\text{-}2,4,6\text{-}(NO_2)_3C_6H_2]$: 0.6 ml C_6F_5H (5.4 mmol), 1.16 g $I(OCOCF_3)_3$ (2.5 mmol), 0.70 g $HOSO_2\text{-}2,4,6\text{-}(NO_2)_3C_6H_2$ (2.4 mmol), 5 ml

CF_3COOH. Yield, 1.41 g $[I(C_6F_5)_2][OSO_2\text{-}2,4,6\text{-}(NO_2)_3C_6H_2]$ (1.87 mmol) (75%).

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