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A comparative study of physical properties of bis(trifluoromethylsulfonyl)dihalogenomethanes and bis(fluorosulfonyl)dihalogenomethanes

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Abstract

The reaction of bis(trifluoromethylsulfonyl)methane (**1**) with *N*-halogenosuccinimide leads to bis(trifluoromethylsulfonyl)dihalogenomethanes (halogen = chlorine (**2b**), bromine (**2c**), iodine (**2d**)). The related fluorine derivative **2a** was obtained by the electrochemical fluorination (ECF) of **1** in anhydrous HF. Spectral data (^{13}C, ^{19}F-NMR and mass spectra) and other hitherto unknown physical properties of bis(trifluoromethylsulfonyl)dihalogenomethanes (**2a–d**) are determined and compared with the data of the bis(fluorosulfonyl)-dihalogenomethanes (**3a–d**).

Keywords: Bis(trifluoromethylsulfonyl)dihalogenomethanes; Bis(fluorosulfonyl)dihalogenomethanes; Electrochemical fluorination (ECF); Bis(trifluoromethylsulfonyl)methane

1. Introduction

Bis(trifluoromethylsulfonyl)methane $H_2C(SO_2CF_3)_2$ (**1**) was first prepared by Gramstad and Haszeldine in 1956 by reacting methylmagnesium halides with trifluoromethanesulfonylfluoride [1] in diethylether. This synthesis was later improved by Koshar and Mitsch in 1973, replacing diethylether by tetrahydrofuran (THF) [2].

$$CF_3SO_2F \xrightarrow[2.\ HCl\ aq]{1.\ MeMgCl\,/\,THF} \underset{\mathbf{1}}{H_2C(SO_2CF_3)_2} \qquad (1)$$

Because of the very strong electron withdrawing effect of the two trifluoromethylsulfonyl groups [3] **1** is a very strong carbon acid with an estimated P_{Ka} about −1 [2]. Salts of this C–H-acid are easily prepared using metal hydroxides or carbonates like Ag_2CO_3 [2] or K_2CO_3 [4] in acetone or THF, respectively to obtain $M[HC(SO_2CF_3)_2]$ (M = Ag, K). Polyethylenoxide complexes with $Li[HC(SO_2CF_3)_2]$ show high ionic conductivities and an electrochemical stability window of approximately 4.5 V [5]. The dihalogenomethanebis(trifluoromethylsulfonylfluorides) (halogeno = chlorine (**2b**) and bromine (**2c**)) can be used as side-chain halogenation reagents for aromatic hydrocarbons such as toluene [2].

2. Results and discussion

Bis(trifluoromethylsulfonyl)methane (**1**) can easily be prepared by the method described by Koshar and Mitsch [2]. Whereas the original procedure [1] applied a large excess of Grignard-reagent (molar ratio methylmagnesiumchloride: trifluoromethanesulfonylfluoride 3:1), the same results (see Section 3) were obtained with a molar ratio of 2:1, which exactly corresponds to Eq. (1).

The reaction of *N*-halogenosuccinimides (NXS) in tetrachloromethane (halogeno = chlorine, bromine, iodine) with bis(trifluoromethylsulfonyl)methane **1** leads to the formation of the corresponding bis(trifluoromethylsulfonyl)dihalogenomethanes **2b–d** (halogeno = chlorine (**2b**), bromine (**2c**) and iodine (**2d**)) in good yields, except (**2d**).

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$$H_2C(SO_2CF_3)_2 \xrightarrow[-\text{NHS}]{\text{NXS / } CCl_4} X_2C(SO_2CF_3)_2 \quad (2)$$

1

X = Cl (**2b**), Br (**2c**), I (**2d**)

The chlorine **2b** and bromine derivatives **2c** have already been synthesized [2] by the reaction of **1** with elemental chlorine or bromine, but nevertheless only boiling points are published.

Electrochemical fluorination (ECF) of **1** in anhydrous HF gives bis(trifluoromethylsulfonyl)difluoromethane (**2a**). In contrast to the ECF of the related methanebis(sulfonylfluoride) (**3**) [6], which is carried out in 75% yield, only 25% **2a** is formed.

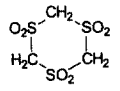
$$H_2C(SO_2CF_3)_2 \xrightarrow[HF]{e^{\ominus}} F_2C(SO_2CF_3)_2 + CF_3SO_2F \quad (3) \quad (3)$$

1 **2a**

25% 5%

Furthermore no monofluorinated product, e.g., fluoromethanebis(sulfonylfluoride) $FHC(SO_2F)$ could be detected in the case of the ECF of **3** [6]. The reason for this small yield can be the decomposition of the starting material during the electrofluorination. Only trifluoromethanesulfonylfluoride could be isolated in 5% yield. The ECF-cell, made of stainless steel, and the nickel-electrodes showed dramatic corrosion after the experiment.

2a was first obtained in traces by the treatment of **4** with elemental fluorine [7].



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All dihalogeno compounds, except iodine (**2d**), are clear colourless, in the case of **2c** light yellow, liquids with densities around 1.7–1.8 g ml^{-1}. These liquids are very volatile, especially the bromine **2c** and chlorine **2b** compounds are very difficult to isolate via distillation in vacuum. **2b** and **2c** react easily and quantitatively with aqueous potassium iodide solution to give elemental iodine, indicating partial positive charged chlorine and bromine, respectively.

In addition to NMR- and mass-spectroscopy and determination of physical properties for **2a** DSC investigations were also carried out. The DSC-experiments (recorded with 10 K min^{-1}) yield one precrystallization peak at −125.2°C (enthalpy: −7.0 kJ mol^{-1}) and one melting peak at −71.5°C (enthalpy: 10.6 kJ mol^{-1}) (Fig. 1).

The ^{19}F-NMR signal of the SO_2CF_3 groups **2a–d** is shifted to higher field within the sequence Hal = F, Cl, Br, I. In the case of the bis(fluorosulfonyl)dihalogenomethanes (halogen = F (**3a**), Cl (**3b**), Br (**3c**), I (**3d**)) a similar sequence

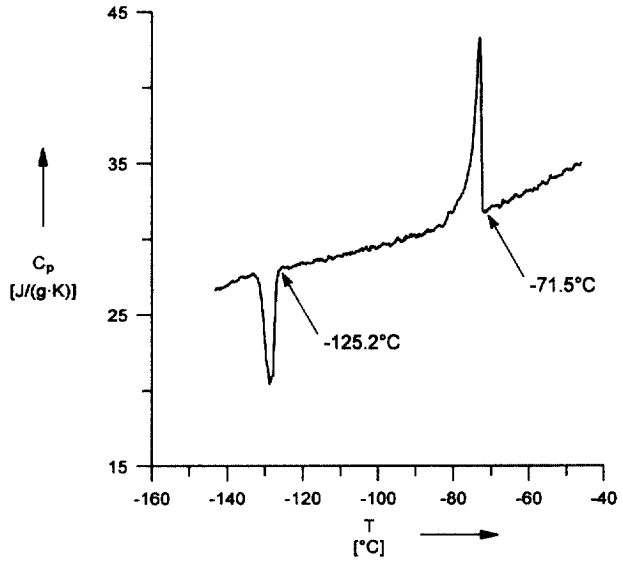

Fig. 1. DSC-diagram of bis(trifluoromethylsulfonyl)difluoromethane **1**.

Table 1
^{19}F-NMR data of **2a–d** and **3a–d**

Compound	^{19}F-NMR shifts [ppm]			
	X = F (a)	X = Cl (b)	X = Br (c)	X = I (d)
$X_2C(SO_2CF_3)_2$ (2)	−68.96	−65.01	−63.51	−61.06
$X_2C(SO_2F)_2$ (3)	47.63	41.04	40.72	40.01

for the shift of the SO_2F group is observed, but the influence of Cl, Br and I is less significant than for **2b–d** (Table 1).

Comparison of the ^{13}C-NMR-resonances of the α-carbons of **2a–d** and **3a–d** shows a low field shift when going from SO_2F to SO_2CF_3 group. This can be explained by the higher electron withdrawing effect of the SO_2CF_3 group. Fig. 2 shows the correlation between the ^{13}C-NMR-shift and the

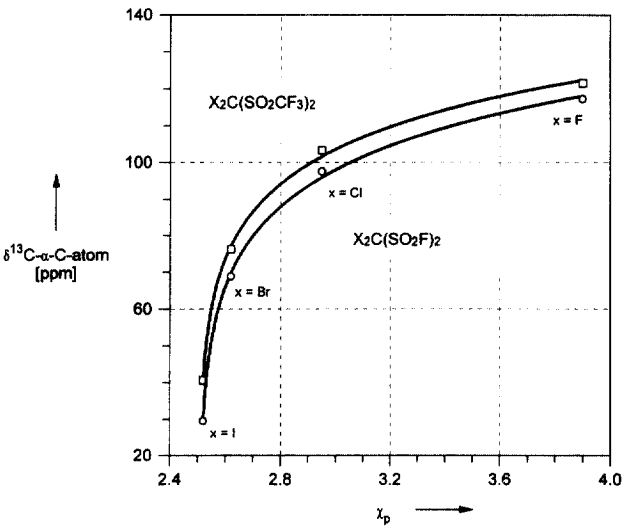

Fig. 2. Correlation between the electronegativity and the ^{13}C-NMR-shift of **2a–d** and **3a–d**.

Table 2
^{13}C-NMR-data of the α-C-Atom and electronegativity of **2a–d** and **3a–d**

X	Electronegativity (Mulliken–Jaffée)	^{13}C-NMR shifts [ppm]	
		$X_2C(SO_2CF_3)_2$ (**2**)	$X_2C(SO_2F)_2$ (**3**)
F (**a**)	3.90	121.48	117.17
Cl (**b**)	2.95	103.25	97.57
Br (**c**)	2.62	76.25	65.83
I (**d**)	2.52	40.60	29.55

electronegativity (Mulliken–Jaffée). The difference between the ^{13}C-NMR shift of $X_2C(SO_2CF_3)_2$ **2a–d** and $X_2C(SO_2F)_2$ **3a–d** decreases with increase of the electronegativity of the substituent X (Table 2). The $^1J_{CF}$-coupling constant of **2a** (351 Hz) is a typical value for the $^1J_{CF}$-coupling constant of carbonylfluorides, in which carbon has a planar moiety [8].

3. Experimental details

3.1. Apparatus

The electrochemical fluorination cell and its use were described in previous papers [9,10].

3.2. Analytical procedures

IR spectra were recorded from 4000–225 cm^{-1} on a Nicolet 20 DXB instrument. NMR-spectra were taken on a Bruker WP 80 SY (75.4 MHz ^{19}F), and a Bruker WM 500 (500.1 MHz ^{1}H, 125.8 MHz ^{13}C and 470.6 MHz ^{19}F) in acetonitrile-d_3 CD_3CN (^{13}C) as internal and C_6F_6 (^{19}F) as external standard, respectively. Mass spectra data were determined with Varian MAT 311A (EI, 70 eV) and AMD Intektra DP10 V 0.86 as data system.

3.3. Bis(trifluoromethylsulfonyl)methane (1)

A total of 225 g trifluoromethanesulfonylfluoride (obtained by ECF, see Ref. [1]) were bubbled into a 1200 ml ice cooled 2.5 molar solution of methylmagnesiumchloride in THF over 250–300 min. The temperature should not go over 20°C. After addition of trifluoromethanesulfonylfluoride, further stirring of the suspension for about 1 h at 60°C was necessary to complete the reaction. The suspension is cooled down to room temperature and 50–60 ml 3 M hydrochloric acid were added with caution, especially the first 3 ml. After evaporation of the solvent the remaining solid is dissolved in 1500 ml 3 M hydrochloric acid and stirred for 4 h. The two-phase-liquid was extracted with diethylether (400 ml, 4 times). After combining the ether phases and removing the solvent, the remaining red oily liquid was distilled under vacuum. A colourless, waxy solid was obtained.

Yield: 160.0 g (77%). m.p.: 36°C (Lit. [2] 35°C). b.p.: 74–75°C (5 Torr) (Lit. [2] 99–101°C (25 Torr)). ^{1}H-NMR ($CDCl_3$, 500.1 MHz, TMS) $\delta = 5.02$. ^{13}C-NMR ($CDCl_3$, 125.76 MHz, $CDCl_3$) $\delta = 64.04$ (s), 118.75 (qua, $^1J_{CF} = 327.5$ Hz). ^{19}F-NMR ($CDCl_3$, 470.59 MHz, C_6F_6 extern) $\delta = -77.41$ (s). MS (EI, 70 eV, 112°C): $m/e = 211$ (11%, $M - SO_2^{+\bullet}$), 147 (11%, $F_3CSO_2{-}CH_2^{+\bullet}$), 133 (15%, $F_3CSO_2^{+\bullet}$), 131 (25%, $F_3CSO{-}CH_2^{+\bullet}$), 117 (12%, $F_3CSO^{+\bullet}$), 69 (100%, $CF_3^{+\bullet}$), 62 (10%, $SO_2CH_2^{+\bullet}$), 48 (7%, $SO^{+\bullet}$) and other fragments.

3.4. Bis(trifluoromethylsulfonyl)difluoromethane (2a)

A total of 200 g anhydrous hydrogen fluoride were introduced into the ECF cell (volume 280 ml) and dried for about 30 h by passing current to remove moisture and to condition the Ni-electrodes. Cell voltage of 4.5–4.8 V was maintained for this drying process. The temperature of the cell was held at 0°C. The temperature of the condenser was maintained at −30°C in this experiment. After the drying procedure, 15% (w/w) solution of **1** in anhydrous hydrogen fluoride was transferred into the cell.

Electrolysis was carried out under galvanostatic conditions (current density: 0.80 A dm^{-2}). The cell voltage was maintained between 4.8–5.3 V. Subsequent addition of the starting material was done after passing 130% of theoretical current. Perfluoro compound formed during the electrochemical fluorination was removed periodically through the bottom valve of the ECF cell. The electrofluorination was stopped after nearly 0.5 mol of compound had been electrolyzed. The perfluorinated materials obtained were separated from the hydrogen fluoride phase, washed with cold water, 2% sodium hydrogen carbonate solution and again with water and finally dried using anhydrous sodium sulfate. After filtration the clear and colourless liquid was distilled.

Yield: 39.5 g (25%). m.p.: −71.5°C. b.p.: 102–103°C. Density (25°C): 1.693 g ml^{-1}. n_D^{20}: 1.3402. Viscosity (m Pa): 1.40. ^{13}C-NMR (CD_3CN, 125.8 MHz) $\delta = 120.05$ (tri-qua, $^1J_{CF} = 331.1$ Hz, $^3J_{CF} = 3.0$ Hz, CF_3) 121.48 (sep-tri, $^1J_{CF} = 350.6$ Hz, $^3J_{CF} = 3.0$ Hz, CF_2)-^{19}F-NMR (CD_3CN, 75.4 MHz): $\delta = -93.84$ (sep, $^4J_{FF} = 8.0$ Hz, 2F), −68.96 (t, $^4J_{FF} = 7.7$ Hz, 6F)-IR (KBr-Film): $\tilde{\nu} = 1425$ sst, 1242 sst, 1228 sst, 1202 st, 1185 m, 1110 sst, 902 s, 871 m, 627 s, 611 m, 585 st, 543 m, 519 m, 502 st, 442 s-MS (EI, 70 eV, 25°C): $m/e = 316$ (<1%, $M^{+\bullet}$), 183 (0.3%, $F_3C{-}SO_2{-}CF_2^{+\bullet}$), 167 (0.3%, $F_3C{-}SO{-}CF_2^{+\bullet}$), 133 (8%, $F_3C{-}SO_2^{+\bullet}$), 117 (25%, $F_3C{-}SO^{+\bullet}$), 69 (100%, $F_3C^{+\bullet}$), 64 (5%, $SO_2^{+\bullet}$), 50 (5%, $CF_2^{+\bullet}$), 48 (16%, $SO^{+\bullet}$) and other fragments.

3.5. Bis(trifluoromethylsulfonyl)dihalogenomethanes (2b–d)

3.5.1. General procedure

To a suspension of 52 mmol *N*-halogenosuccinimide in 20 ml tetrachloromethane was added a solution of 7.0 g (25 mmol) **1** in 10 ml tetrachloromethane. This suspension was

refluxed at 80°C (in the case of *N*-iodosuccinimide warmed up to 40°C) for about 1 h. After cooling down to 0°C the solid (*N*-succinimide) was filtered. The solvent of the remaining solution was evaporated in vacuum (200 Torr).

Products **2b** and **2c** were distilled in vacuum (5 Torr) trapping the compounds at −20°C, because of the high volatility. **2d** was recrystalized from chloroform/*n*-pentane giving very light sensitive yellow crystals.

3.5.2. Bis(trifluoromethylsulfonyl)dichloromethane (2b)

Starting material: 7.0 g *N*-chlorosuccinimide. Yield: 6.6 (76%). b.p.: 58–59°C (5 Torr) (Lit. [2] 95.0–95.5°C (40 Torr)). ^{13}C-NMR ($CDCl_3$, 125.76 MHz, $CDCl_3$) $\delta = 103.25$ (sep, $^3J_{CF} = 3.0$ Hz), 120.23 (qua, $^1J_{CF} = 333.9$ Hz). ^{19}F-NMR ($CDCl_3$, 470.59 MHz, C_6F_6 extern) $\delta = -65.01$ (s). MS (EI, 70 eV, 112°C) $m/e = 215$ (11%, $Cl_2CSO_2CF_3^{+\bullet}$), 117 (98%, $F_3CSO^{+\bullet}$), 82 (32%, $Cl_2C^{+\bullet}$), 69 (100%, $CF_3^{+\bullet}$), 51 (23%, $SF^{+\bullet}$) and other fragments.

3.5.3. Bis(trifluoromethylsulfonyl)dibromomethane (2c)

Starting material: 9.3 g *N*-bromosuccinimide. Yield: 8.5 g (78%). b.p.: 87–88°C (5 Torr) (Lit. [2] 107–108°C (17 Torr)). ^{13}C-NMR ($CDCl_3$, 125.76 MHz, $CDCl_3$) $\delta = 76.25$ (sep, $^3J_{CF} = 3.2$ Hz), 119.59 (qua, $^1J_{CF} = 334.1$ Hz). ^{19}F-NMR ($CDCl_3$, 470.59 MHz, C_6F_6 extern) $\delta = -63.51$ (s). MS (EI, 70 eV, 112°C) $m/e = 438$ ($< 0.1\%$, $M^{+\bullet}$), 305 (14%, $Br_2CSO_2CF_3^{+\bullet}$), 172 (13%, $Br_2C^{+\bullet}$), 117 (64%, $F_3CSO^{+\bullet}$), 69 (100%, $CF_3^{+\bullet}$) and other fragments.

3.5.4. Bis(trifluoromethylsulfonyl)diiodomethane (2d)

Starting material: 5.9 g *N*-iodosuccinimide in 10 ml CCl_4, 3.5 g **1** in 5 ml CCl_4. Yield: 2.6 g (39%). m.p.: 185°C with decomposition. ^{13}C-NMR ($CDCl_3$, 125.76 MHz, $CDCl_3$) $\delta = 40.60$ (sep, $^3J_{CF} = 2.7$ Hz), 116.87 (qua, $^1J_{CF} = 334.3$ Hz). ^{19}F-NMR ($CDCl_3$, 470.59 MHz, C_6F_6 extern) $\delta = -61.06$ (s). MS (EI, 70 eV, 140°C) $m/e = 532$ (1%, $M^{+\bullet}$), 399 (17%, $I_2CSO_2CF_3^{+\bullet}$), 254 (70%, $I_2^{+\bullet}$), 127 (76%, $I^{+\bullet}$), 69 (100%, $CF_3^{+\bullet}$), 117 (65%, $F_3CSO^{+\bullet}$) and other fragments.

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