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Journal of Fluorine Chemistry 122 (2003) 251-253

**JOURNAL OF** FLUORINE GUEMISTEY

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Short communication

# The application of novel methodology for the synthesis of o-, m-, and p-(SF<sub>5</sub>-perfluoroethyl) benzene derivatives

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Received 6 January 2003; received in revised form 5 March 2003; accepted 5 March 2003

#### Abstract

The reaction of *o*-, *m*-, and p-F<sub>2</sub>C=CFC<sub>6</sub>H<sub>4</sub>X with SF<sub>5</sub>Br produces an intermediate adduct, F<sub>5</sub>SCF<sub>2</sub>CFBrC<sub>6</sub>H<sub>4</sub>X, which, on treatment with AgBF<sub>4</sub>, affords the first useful, high yield preparation of *o*-, *m*-, and p-F<sub>5</sub>SCF<sub>2</sub>CF<sub>2</sub>C<sub>6</sub>H<sub>4</sub>X.  $\bigcirc$  2003 Elsevier Science B.V. All rights reserved.

Keywords: SF5-fluoroalkyl aromatics; Sulfur hexafluoride derivatives; Trifluorostyrenes

## 1. Introduction

The properties of organic compounds are often significantly enhanced or modified by the incorporation of perfluoroalkyl groups [1-3]. Although a large body of work has been published with compounds containing perfluoroalkyl groups, only a small number of compounds containing an  $F_5S$ -group or  $F_5S(CF_2)_n$ -groups has been prepared and investigated, even though useful properties that range from liquid crystals to pesticides to dielectrics are enhanced by incorporation of the F<sub>5</sub>S-moiety [4]. In the liquid crystal field, the F<sub>5</sub>S-group as a polar terminal group has produced a new class of liquid crystals that have both very strong dielectric anisotropy and moderately high clearing points [5]. The first reported organic superconductor contained an  $F_5S$ -group [6]. Since this initial report, a number of  $F_5S$ containing materials ranging from superconductivity to metallic conductivity to semiconductivity have been reported [7,8]. Polymeric F<sub>5</sub>S-containing imides with low dielectric constants (2.51-3.00) have potential use in the electronics industry [9]. When the surfactant properties of the F<sub>5</sub>S-group have been compared to similar F<sub>3</sub>C-containing analogs, the F<sub>5</sub>S-group has been found to be superior for lowering aqueous surface tension [10], and polymers containing the F<sub>5</sub>S-moiety have exhibited fluorinated surfaces with low wettability [11,12].

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There are many known meta-, para- and several orthoderivatives of  $SF_5C_6H_5$  [13–15]. However, only a relatively small number of *meta*-F<sub>5</sub>SCF<sub>2</sub>CF<sub>2</sub>C<sub>6</sub>H<sub>4</sub>X derivatives has been prepared; there are no known ortho- or para-derivatives [16,17]. In our laboratories, we have developed several synthetic pathways for preparing F<sub>5</sub>SCF<sub>2</sub>CF<sub>2</sub>C<sub>6</sub>H<sub>5</sub> [17,18]; the first method involves a multistep procedure for making  $F_5SCF_2CF_2I(1)$ , which in turn is reacted with benzene while the second method is a two-step process in which SF<sub>5</sub>Br is reacted with  $CF_2 = CFC_6H_5$  and the addition product is then treated with AgBF<sub>4</sub>. With F<sub>5</sub>SCF<sub>2</sub>CF<sub>2</sub>C<sub>6</sub>H<sub>5</sub> (2), electrophilic aromatic substitution reactions occur giving exclusively meta derivatives. When aromatic compounds other than benzene, such as toluene, are reacted with (1), only very low yields of F<sub>5</sub>SCF<sub>2</sub>CF<sub>2</sub>-aryl products are obtained. Consequently, this pathway did not lead to ortho- and paraanalogs.

#### 2. Results

The above limitations prompted us to seek a new, more general route to the functionalized  $F_5SCF_2CF_2C_6H_4X$  (*o*, *m*, *p*) derivatives. The recent report of a low-cost general route for the preparation of *o*-, *m*-, and *p*-trifluorostyrene derivatives [19] (Scheme 1) suggested a general entry into the preparation of *o*-, *m*-, and *p*-SF<sub>5</sub>CF<sub>2</sub>CF<sub>2</sub>C<sub>6</sub>H<sub>4</sub>X (Scheme 2). Since the substituent in the styrene precursor can be *ortho*, *meta*, or *para*, the F<sub>5</sub>S-analogs (4) can contain a variety of *ortho*, *meta* or *para* atoms or groups. Interestingly, no deactivating effect of ortho substituents in either reaction

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$$CF_{3}CH_{2}F + 2 LDA \xrightarrow{ZnCl_{2}} [F_{2}C=CFZnCl] \xrightarrow{R-C_{6}H_{4}X} F_{2}C=CFC_{6}H_{4}-R_{6}$$

Scheme 1. The preparation of trifluorostyrene derivatives [19].

$$F_2C=CFC_6H_4X + F_5SBr \xrightarrow{sunlamp} F_5SCF_2CFBrC_6H_4X$$
  
 $CH_2Cl_2/0^{\circ}C \xrightarrow{3}$ 

$$3 + AgBF_4 \xrightarrow{CH_2Cl_2} F_5SCF_2CF_2C_6H_4X$$

Scheme 2. The preparation of F<sub>5</sub>SCF<sub>2</sub>CF<sub>2</sub>C<sub>6</sub>H<sub>4</sub>X derivatives.

scheme was observed. Tables 1 and 2 summarize these results.

For both reaction steps, a range of reactivities was found—estimated by reaction times and temperatures for complete reaction. The addition of  $SF_5Br$  to the trifluoros-

Table 1 Preparation of  $F_5SCF_2CFBrC_6H_4X$  (3)

Entry	$F_2C=\!\!CFC_6H_4X+F_5SBr \xrightarrow{h\nu}_{CH_2Cl_2/0^\circ C} {\bf 3}$			
	X	Conditions	Yield of $3 (\%)^{a,b}$	
1	<i>m</i> -Br	18 h	53	
2	<i>p</i> -Br	25 h	53	
3	p-Cl	20 h	52	
4	$p-CH_3$	48 h	41	
5	$p-CF_3$	20 h	$22^{\rm c}$	
6	$p-NO_2$	51 h	80	
7	o-F	17 h	82	
8	o-CF3	18 h	74	
9	o-CH(CH <sub>3</sub> ) <sub>2</sub>	18 h	67	

<sup>a</sup> Isolated yield of **3**.

<sup>b</sup> All products gave satisfactory <sup>19</sup>F, <sup>1</sup>H NMR and HRMS data consistent with the assigned structure.

<sup>c</sup> Low yield due to volatility of product.

Table 2 Preparation of  $F_5SCF_2CF_2C_6H_4X$  (4)

Entry	$3 + \mathrm{AgBF}_{4} \stackrel{\mathrm{CH}_{2}\mathrm{C}}{\rightarrow}$	$3 + \mathrm{AgBF}_{4} \xrightarrow{\mathrm{CH}_{2}\mathrm{Cl}_{2}} 4$			
	X	Conditions	Yield of $4 (\%)^{a,b}$		
1	<i>m</i> -Br	44 h/RT	99		
2	<i>p</i> -Br	21 h/0 $^{\circ}C \rightarrow RT$	98		
3	p-Cl	20 h/0 $^\circ C \rightarrow RT$	97		
4	p-CH <sub>3</sub>	2/3 h/80 °C	38 <sup>c</sup>		
5	p-CF <sub>3</sub>	28 h/100 °C	96		
6	p-NO <sub>2</sub>	46 h/138 °C <sup>d</sup>	67		
7	o-F	22.5 h/0 °C	93		
8	o-CF <sub>3</sub>	3 h/100 °C	99		
9	o-CH(CH3)2	4.5 h/–78 $^\circ C \rightarrow RT$	89		

<sup>a</sup> Isolated yield of 4.

<sup>b</sup> All products gave satisfactory <sup>19</sup>F, <sup>1</sup>H NMR and HRMS data consistent with the assigned structure.

<sup>c</sup> Low yield due to loss in the filtration process.

<sup>d</sup> Boiling xylene (solvent).

tyrenes proceeded faster with alkyl or halogen substituents  $(p-CH_3, o-CH(CH_3)_2, o-F, m-Br, p-Br, and p-Cl)$  and less readily with electron withdrawing substituents  $(o-CF_3, p-CF_3, and p-NO_2)$ . Similar reactivity patterns were found in the conversion of **3** to **4**.

In conclusion, we have developed a simple, general route to  $F_5SCF_2CF_2C_6H_4X$  derivatives, where X can be a variety of *o*, *m*, and *p* atoms or groups. This methodology avoids  $S_2F_{10}$ , and since  $S_2F_{10}$  is prepared from  $SF_5Br$ , saves one additional step, avoids the use of  $C_2F_4$ , and provides entry to any pattern of aromatic substitution.

#### 3. Experimental

The reactant  $SF_5Br$  was prepared using  $SF_4$ ,  $BrF_3$ ,  $Br_2$ , and CsF [20].

A typical experimental procedure is described below.

The reactions were carried out in a 30 ml Carius tube equipped with a Kontes PTFE valve and a PTFE coated stirring bar. After evacuation, the Carius tube was filled with argon. The trifluorostyrene derivative, dissolved in pentane (1-2 g of the styrene in 3-5 ml pentane), and  $CH_2Cl_2$  (5 ml) were added to the Carius tube. After cooling to -196 °C, the vessel was evacuated and up to 2 mol-equivalents of SF5Br were added via vacuum transfer. The Carius tube was then placed in a 0 °C circulating water bath under three 90 W sun lamps at a distance of 15-20 cm. Completion of the reaction was marked by a change of color from light yellow to redbrown. The absence of a vinyl stretching frequency (1756- $1790 \text{ cm}^{-1}$ ) in the infrared spectrum confirmed the total consumption of the trifluorostyrene derivative. The pentane and CH<sub>2</sub>Cl<sub>2</sub> were removed by rotary evaporation and the product isolated by silica gel chromatography (hexane as eluant). Hexane and any residual solvents were removed under vacuum to give the pure product (3). For example, 1.0 g (5.7 mmol) o-F-trifluorostyrene in 3 ml pentane, 5 ml CH<sub>2</sub>Cl<sub>2</sub>, and 1.53 g (7.4 mmol) SF<sub>5</sub>Br were added to a 30 ml Carius tube. The mixture was irradiated for 17 h at 0 °C. The product was isolated by silica gel chromatography; yield was 82%.

To a 30 ml Carius tube equipped with a Kontes Teflon valve and a Teflon coated stirring bar, was added AgBF<sub>4</sub>. Anhydrous CH<sub>2</sub>Cl<sub>2</sub> (5 ml) was transferred to the Carius tube under vacuum, and a ~0.5 molar equivalent amount of **3** was added under an argon atmosphere. The reaction mixture was usually stirred at room temperature or with heating (cf. Table 2). When GC–MS analysis indicated total consumption of **3**, the reaction mixture was cooled to room temperature, the solid phase removed by vacuum filtration and the solid washed with 2–3 ml of CH<sub>2</sub>Cl<sub>2</sub>. The CH<sub>2</sub>Cl<sub>2</sub> fractions

were combined and separated by silica gel chromatography—solvent removed under vacuum to give pure **4**, identified by IR, <sup>19</sup>F and <sup>1</sup>H NMR and HRMS. For example, 0.98 g (2.6 mmol) of the above *o*-F adduct, 5.2 ml CH<sub>2</sub>Cl<sub>2</sub>, and 0.89 g (4.6 mmol) AgBF<sub>4</sub> were added to a 30 ml Carius tube under an argon atmosphere. The reaction mixture was stirred for 22.5 h at 0 °C; the solid phase was removed by vacuum filtration and washed with small amounts of CH<sub>2</sub>Cl<sub>2</sub>. The filtrate was passed through a short column of silica gel in order to remove any polar constituents and the eluate was concentrated under vacuum at -24 °C. The yield of the product was 93%.

## Acknowledgements

We (PSU, UI) are grateful to the National Science Foundation (CHE-9904316 and CHE-9820769) for support of this work. We wish to thank Jeff Morré (Mass Spectrometry Laboratory, Oregon State University, Corvallis, Oregon) for obtaining the high resolution mass spectra (HRMS).

### References

- R.E. Banks, B.E. Smart, J.C. Tatlow (Eds.), Organofluorine Chemistry—Principles and Commercial Applications, Plenum Press, New York, London, 1994.
- [2] J. McCarthy, Utility of Fluorine in Biologically Active Molecules, in: Proceedings of the Presentation at the 219th National American Chemical Society Meeting, San Francisco, CA, 2000, p. 1.

- [3] J.T. Welch, Tetrahedron 43 (1987) 3123.
- [4] R. Winter, G.L. Gard, Functionalization of pentafluoro- $\lambda^6$ -sulfanyl (SF<sub>5</sub>) olefins and acetylenes, in: J.S. Thrasher, S.H. Strauss (Eds.), Inorganic Fluorine Chemistry Towards the 21st Century, ACS Symposium Series #555, Washington, DC, 1994 (Chapter 8).
- [5] P. Kirsch, M. Bremer, A. Taugerbeck, T. Wallmichrath, Angew. Chem., Int. Ed. Engl. 40 (2001) 1480.
- [6] U. Geiser, J.A. Schlueter, H.H. Wang, A.M. Kini, P.P. Sche, H.I. Zakowicz, M.L. Van Zile, J.D. Dudek, J.M. Williams, J. Renn, M.H. Whangbo, P.G. Nixon, R.W. Winter, G.L. Gard, J. Am. Chem. Soc. 118 (1996) 9996.
- [7] J.A. Schlueter, B.H. Ward, U. Geiser, H.H. Wang, A.M. Kini, J.P. Parakka, E. Morales, H.J. Koo, M.H. Whangbo, R.W. Winter, J. Mohtasham, G.L. Gard, Chem. Mater. 11 (2001) 2008.
- [8] B.H. Ward, J.A. Schlueter, U. Geiser, H.H. Wang, E. Morales, J.P. Parakka, S.Y. Thomas, J.M. Williams, P.G. Nixon, R.W. Winter, G.L. Gard, H.-J. Koo, M.H. Whangbo, Chem. Mater. 12 (2000) 343.
- [9] T.L. St. Clair, A.K. St. Clair, J.S. Thrasher, US Patent 5,220,070 (1993).
- [10] J.C. Hansen, P.M. Savu, US Patent 5,286,352 (1994).
- [11] R. Winter, P.G. Nixon, G.L. Gard, D.G. Castner, N.R. Holcomb, Y-H. Hu, D.W. Grainger, Chem. Mater. 11 (1999) 3044.
- [12] P.G. Nixon, R. Winter, D.G. Castner, N.R. Holcomb, D.W. Grainger, G.L. Gard, Chem. Mater. 12 (2000) 3108.
- [13] W.A. Sheppard, J. Am. Chem. Soc. 84 (1962) 3064.
- [14] R.D. Bowden, P.J. Comina, M.P. Greenhall, B.M. Kariuki, A. Loveday, D. Philp, Tetrahedron 56 (2000) 3399.
- [15] A.M. Sipyagin, C.P. Bateman, Y.-T. Tan, J.S. Thrasher, J. Fluorine Chem. 112 (2001) 287.
- [16] A.M. Hodges, R.W. Winter, S.W. Winner, D.A. Preston, G.L. Gard, J. Fluorine Chem. 114 (2002) 3.
- [17] R.W. Winter, S.W. Winner, D.A. Preston, J. Mohtasham, J.A. Smith, G.L. Gard, J. Fluorine Chem. 115 (2002) 101.
- [18] R.W. Winter, G.L. Gard, J. Fluorine Chem. 118 (2002) 157.
- [19] R. Anilkumar, D.J. Burton, Tetrahedron Lett. 43 (2002) 2731.
- [20] R. Winter, R.J. Terjeson, G.L. Gard, J. Fluorine Chem. 89 (1998) 105.