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## A Facile Method for the Preparation of Allylsulphonyldifluoro-acetates and -acetamides

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Sulphination of isopropyl bromodifluoroacetate **1a** and *N,N*-diethyl bromodifluoroacetamide **1b** with sodium dithionite gives compounds **2a** and **2b** respectively which upon cuprous bromide catalysed allylation gave the allylsulphonyldifluoro-acetates and -acetamides.

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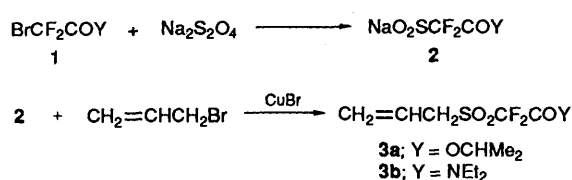
The perfluoroalkylsulphonyl moiety is one of the strongest neutral electron withdrawing groups known<sup>1</sup> and exhibits versatile reactivity.<sup>2</sup> Although a number of methods for the preparation of perfluoroalkyl sulphones have been documented,<sup>3</sup> there are few reports describing the preparation of  $\alpha$ -functionalized difluoromethylene sulphones. Herein, we describe a facile method for the preparation of allylsulphonyldifluoro-acetates and -acetamides.

The sulphination of perfluoroalkyl iodides with sodium dithionite was first reported by Huang and co-workers<sup>4</sup> and recently, we demonstrated the utility of this methodology in the preparation of the first example of a fluorinated mixed phosphonic/sulphonic acid.<sup>5</sup> We have now found that isopropyl bromodifluoroacetate **1a** and *N,N*-diethyl bromodifluoroacetamide **1b** react with sodium dithionite in the presence of sodium hydrogen carbonate in aqueous acetonitrile at 50 °C

**Table 1** Preparation of allylsulphonyldifluoro-acetates **3a** and -acetamides **3b**

Y	Allyl halides	Products <sup>a</sup> <b>3a</b> and <b>3b</b>	Isomeric ratio <sup>b</sup>	Yield <sup>c</sup> (%)
OPr <sup>i</sup>	CH <sub>2</sub> =CHCH <sub>2</sub> Br	CH <sub>2</sub> =CHCH <sub>2</sub> SO <sub>2</sub> CF <sub>2</sub> CO <sub>2</sub> Pr <sup>i</sup>	100	80
OPr <sup>i</sup>	MeCH=CHCH <sub>2</sub> Cl	MeCH=CHCH <sub>2</sub> SO <sub>2</sub> CF <sub>2</sub> CO <sub>2</sub> Pr <sup>i</sup>	52	87
		CH <sub>2</sub> =CHCHMeSO <sub>2</sub> CF <sub>2</sub> CO <sub>2</sub> Pr <sup>i</sup>	48	
OPr <sup>i</sup>	MeCHClCH=CH <sub>2</sub>	MeCH=CHCH <sub>2</sub> SO <sub>2</sub> CF <sub>2</sub> CO <sub>2</sub> Pr <sup>i</sup>	52	94
		CH <sub>2</sub> =CHCHMeSO <sub>2</sub> CF <sub>2</sub> CO <sub>2</sub> Pr <sup>i</sup>	48	
OPr <sup>i</sup>	Me <sub>2</sub> C=CHCH <sub>2</sub> Cl	Me <sub>2</sub> C=CHCH <sub>2</sub> SO <sub>2</sub> CF <sub>2</sub> CO <sub>2</sub> Pr <sup>i</sup>	78	97
		CH <sub>2</sub> =CHCMe <sub>2</sub> SO <sub>2</sub> CF <sub>2</sub> CO <sub>2</sub> Pr <sup>i</sup>	22	
NEt <sub>2</sub>	CH <sub>2</sub> CHCH <sub>2</sub> Br	CH <sub>2</sub> =CHCH <sub>2</sub> SO <sub>2</sub> CF <sub>2</sub> CONEt <sub>2</sub>	100	87
NEt <sub>2</sub>	CH <sub>2</sub> =CMeCH <sub>2</sub> Cl	CH <sub>2</sub> =CMeCH <sub>2</sub> SO <sub>2</sub> CF <sub>2</sub> CONEt <sub>2</sub>	100	78
NEt <sub>2</sub>	MeCH=CHCH <sub>2</sub> Cl	MeCH=CHCH <sub>2</sub> SO <sub>2</sub> CF <sub>2</sub> CONEt <sub>2</sub>	93	77
		CH <sub>2</sub> =CHCHMeSO <sub>2</sub> CF <sub>2</sub> CONEt <sub>2</sub>	7	
NEt <sub>2</sub>	MeCHClCH=CH <sub>2</sub>	MeCH=CHCH <sub>2</sub> SO <sub>2</sub> CF <sub>2</sub> CONEt <sub>2</sub>	93	91
		CH <sub>2</sub> =CHCHMeSO <sub>2</sub> CF <sub>2</sub> CONEt <sub>2</sub>	7	
NEt <sub>2</sub>	Me <sub>2</sub> C=CHCH <sub>2</sub> Cl	Me <sub>2</sub> C=CHCH <sub>2</sub> SO <sub>2</sub> CF <sub>2</sub> CONEt <sub>2</sub>	100	83

<sup>a</sup> All products gave satisfactory <sup>19</sup>F, <sup>1</sup>H NMR, IR and MS spectroscopic data. <sup>b</sup> Isomeric ratio was determined by <sup>19</sup>F NMR spectroscopy. <sup>c</sup> Isolated yields.



isolated yields, respectively. In the presence of a catalytic amount of cuprous bromide, reaction of **2** with allyl bromide in DMF at 40 °C gave allylsulphonyldifluoro-acetate **3a** or -acetamide **3b** in good yields. With substituted allyl halides, the products resulting from both α- and γ-attack were observed.

Allylation of the acetamide **2b** exhibited better regioselectivity with substituted allyl halides than did **2a**. Treatment of **2b** with 1-chlorobut-2-ene gave 93% of but-2-enylsulphonyl(difluoro)-acetamide, only 7% of its regioisomer being observed. Reaction of **2b** with 1-chloro-3-methylbut-2-ene gave regiospecific formation of the (*N,N*-diethylaminocarbonyldifluoromethylsulphonyl)-substituted alkene *via* attack at the least hindered carbon. These results are summarized in Table 1.

### Experimental

In a typical experimental procedure, a two-necked flask fitted with a rubber septum, a stir bar and a condenser topped with a nitrogen inlet was charged with **2a** (1.8 g, 8 mmol),<sup>6</sup> cuprous bromide (0.3 g, 2.1 mmol) and DMF (8 cm<sup>3</sup>). Allyl bromide (1.2 g, 10 mmol) was added *via* syringe and the reaction mixture was stirred at 40 °C for 6 h. The mixture was poured into water and dichloromethane, the solids removed by filtration, the organic layer separated, washed with water and dried (MgSO<sub>4</sub>). After evaporation of dichloromethane, the residue was distilled at

reduced pressure to give **3a** (1.5 g, 80%); b.p. 112–113 °C/2 mmHg; δ<sub>F</sub>(CFCl<sub>3</sub>; CDCl<sub>3</sub>) –109.5(s); δ<sub>H</sub>[(CH<sub>3</sub>)<sub>4</sub>Si] 5.88–5.82 (1 H, m), 5.60–5.54 (2 H, m), 5.26 (1 H, hept, *J* 6.2), 4.02 (2 H, dt, *J* 6.1, *J* 1.0)\* and 1.38 (6 H, d, *J* 6.4); δ<sub>C</sub>[CDCl<sub>3</sub>; (CH<sub>3</sub>)<sub>4</sub>Si] 157.98 (t, *J* 27), 126.91, 121.18, 113.90 (t, *J* 2.99.4), 74.23, 54.89 and 21.32; ν<sub>max</sub>/cm<sup>-1</sup> 2980(m), 1760(s), 1640(m), 1360(s), 1305(s), 1150–1200(vs) and 1100(s); *m/z* 241 (M<sup>+</sup> – 1, 0.1%), 136 (24.8), 116 (18.3), 91 (27.5), 43 (81.5) and 41 (100).

The ready availability of precursors and catalyst, the simplicity of the experimental procedure, the mild reaction conditions, and the potential for further elaboration of the allylation products make this preparation a convenient and useful route to allylsulphonyldifluoro-acetates and -acetamides.

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- 2a** was prepared by a modification of Huang's procedure.

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\* *J* values are given in Hz throughout.

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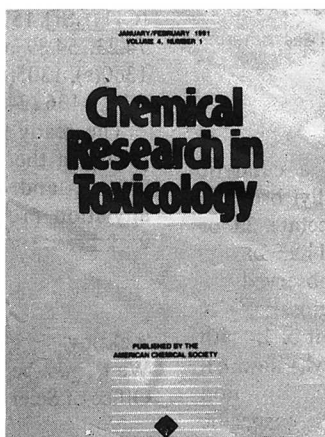
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