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A new synthesis of thioesters and selenoesters of triflic acid under oxidative conditions

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Abstract

Trifluoromethanethio-(or seleno-)sulfonates (CF_3SO_2YR, Y = S, Se) are easily obtained in one step at 0–20 °C from disulfides (or diselenides), sodium trifluoromethanesulfinate and [bis-(trifluoroacetoxy)iodo]benzene (BTIB). © 1997 Elsevier Science S.A.

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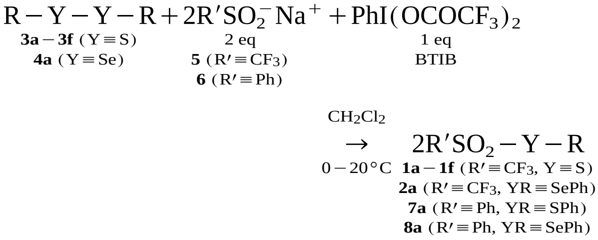
1. Introduction

Aryl selenosulfonates ($ArSO_2SeAr'$) are very useful synthetic tools since they are powerful electrophilic selenylating agents and can undergo electrophilic or free radical additions to unsaturated substrates [1]. Thiosulfonates are less decribed since they are reported to be less reactive than the seleno analogs [1]. The reactivity of thioesters and selenoesters of triflic acid (CF_3SO_2SR **1**, CF_3SO_2SeR **2**) is presently under study in our laboratory: these compounds are much more potent electrophiles than the non-fluorinated analogs and can undergo ‘thiosulfonation’ as well as ‘selenosulfonation’ processes under mild conditions. They are also valuable sources of trifluoromethyl radicals (full papers in preparation). We have recently published a simple one-pot preparation of these reagents from disulfides **3** (or diselenides **4**), sodium trifluoromethanesulfinate **5** and bromine [2]. Though very satisfactory with dialkyl dichalcogenides, this technique delivers only medium yields with aromatic disulfides. Thus, more efficient ways were needed to activate these latter substrates towards **5**. A few years ago, non-fluorinated selenosulfonates were obtained from alkaline sulfinates and selenenyl cations generated by oxidation of diselenides with ammonium peroxydisulfate [3] or [bis-(trifluoroacetoxy)iodo]benzene (BTIB) [4]. Owing to the fact that **5** is oxidized to trifluoromethyl radical by peroxydisulfate anions [5], the former technique should not be adapted to the preparation of trifluoromethaneselenosulfonates **2** but the reaction of **4**, **5** and BTIB could constitute a good access to **2**.

2. Results and discussion

Indeed, when a suspension of diphenyl diselenide **4a** and **5** (2 equivalents) in dichloromethane was treated with BTIB (1 equivalent) at 0 °C then stirred at room temperature for 2 h, **2a** was obtained in a good yield (82%), far better than the yield previously obtained from **4a**, **5** and bromine (55%) [2]. It must be noted that a larger excess of **5** (4 equivalents, according to the molar ratio given in the literature [4]) did not modify the yield of **2a**. This effect, which we did not observe for the reaction of sodium benzenesulfinate with diphenyl diselenide and BTIB (4 eq. $PhSO_2Na$, yield 81% [4]; 2 eq. $PhSO_2Na$, yield 67%), was probably due to a higher solubility of **5** compared with $PhSO_2Na$.

Moreover, the same method has been successfully extended to the preparation of thiosulfonates from disulfides **3**, BTIB and sulfinates (especially **5**). All the results are summarized in Table 1.



$$\underset{\substack{\mathbf{3a}-\mathbf{3f}\ (Y\equiv S)\\ \mathbf{4a}\ (Y\equiv Se)}}{R-Y-Y-R} + \underset{\substack{2\ \text{eq}\\ \mathbf{5}\ (R'\equiv CF_3)\\ \mathbf{6}\ (R'\equiv Ph)}}{2R'SO_2^-Na^+} + \underset{\substack{1\ \text{eq}\\ \text{BTIB}}}{PhI(OCOCF_3)_2} \xrightarrow[0-20^\circ C]{CH_2Cl_2} \underset{\substack{\mathbf{1a}-\mathbf{1f}\ (R'\equiv CF_3,\ Y\equiv S)\\ \mathbf{2a}\ (R'\equiv CF_3,\ YR\equiv SePh)\\ \mathbf{7a}\ (R'\equiv Ph,\ YR\equiv SPh)\\ \mathbf{8a}\ (R'\equiv Ph,\ YR\equiv SePh)}}{2R'SO_2-Y-R}$$

Thus the reaction of disulfides (or diselenides), sulfinates and BTIB offers, on the laboratory scale, a very convenient access to thiosulfonates and selenosulfonates, especially when aromatic dichalcogenides are used. This process has

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Table 1
Preparation of thiosulfonates and selenosulfonates from sulfinates, BTIB and dichalcogenides

R′	R	Y	Isolated yield $R'SO_2YR$ (%)
CF_3	Ph	S	**1a** 87
CF_3	Cl–C_6H_4–	S	**1b** 62
CF_3	$PhCH_2$	S	**1c** 82
CF_3	*n*-C_8H_{17}	S	**1d** 70
CF_3	*c*-C_6H_{11}	S	**1e** 80
CF_3	*t*-Bu	S	**1f** unstable
CF_3	Ph	Se	**2a** 82
CF_3 (4 eq.)	Ph	Se	**2a** 80
Ph	Ph	S	**7a** 60
Ph	Ph	Se	**8a** 67

been shown very fruitful for the preparation of thioesters and selenoesters of triflic acid. Nevertheless, because of the rather high price of BTIB and the by-production of iodobenzene and trifluoroacetic acid, this method is probably not as easy to scale-up as the technique, using bromine, which we previously described [2].

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