

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

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Abstract

Trifluoromethanethio-(or seleno-)sulfonates ($\text{CF}_3\text{SO}_2\text{YR}$, $\text{Y}=\text{S}$, 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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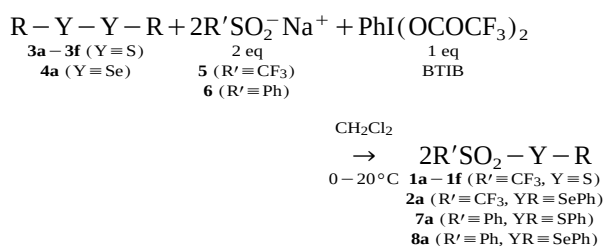
1. Introduction

Aryl selenosulfonates ($\text{ArSO}_2\text{SeAr}'$) 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 described since they are reported to be less reactive than the seleno analogs [1]. The reactivity of thioesters and selenoesters of triflic acid ($\text{CF}_3\text{SO}_2\text{SR}$ **1**, $\text{CF}_3\text{SO}_2\text{SeR}$ **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 sulfonates 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 sulfonates (especially **5**). All the results are summarized in Table 1.



Thus the reaction of disulfides (or diselenides), sulfonates 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 ₂ YR (%)
CF ₃	Ph	S	1a 87
CF ₃	Cl-C ₆ H ₄ -	S	1b 62
CF ₃	PhCH ₂	S	1c 82
CF ₃	<i>n</i> -C ₈ H ₁₇	S	1d 70
CF ₃	<i>c</i> -C ₆ H ₁₁	S	1e 80
CF ₃	<i>t</i> -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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