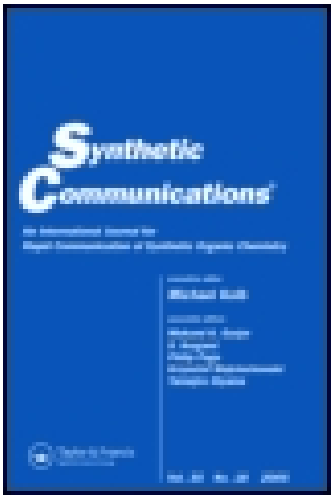

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A Novel Convenient Synthesis of Selenosulfonates

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A NOVEL CONVENIENT SYNTHESIS OF SELENOSULFONATES

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Abstract: Sodium sulfonate reacts smoothly with areneselenium cations, which are produced in situ by reacting diaryl diselenides with peroxydisulphate, to give selenosulfonates in good yields.

Selenosulfonates ($ArSeSO_2Ar^1$) are very important synthetic intermediates. They can readily undergo electrophilic and free radical additions to olefins[1-3], allenes[4], acetylenes[5-8] and diazomethane[9] to give various unsaturated sulfones after oxidative elimination of the areneseleno group, and these processes have been named "selenosulfonations". So it is necessary to find a more convenient synthesis of selenosulfonates.

In 1947, O. Foss[10] first discovered the synthesis of selenosulfonates from areneselenenyl bromides and sulfinates. But using this method, only two kinds of selenosulfonates were obtained. Recently, with the wide applications of the selenosulfonates, several synthetic methods of selenosulfonates have been reported. In all these methods, benzeneseleninic acid ($PhSeO_2H$) was used to react with many different

compounds, such as sulfinates[11], sulfonhydrazides, or seleneny1 halides[12]. But all of these materials are difficult to prepare, and all of these reactions take place at low temperature.

Recently it was reported that diaryl diselenides, which were easily obtained from reacting selenium powder with the corresponding Grignard reagents, can be oxidized to give electrophilic areneselenium cations[13]. The areneselenium cations are active intermediates. They can undergo electrophilic addition reactions with olifins[13–15] and acetylenes[16]. Considering that sodium sulfonate is a good nucleophilic reagent, it could react with areneselenium cations to afford a novel convenient synthesis of selenosulfonates. The experimental results show that diaryl diselenides and ammonium peroxydisulphate in methanol under refluxing produces areneselenium cations in situ. Then they can react smoothly with sodium sulfonate under phase transfer conditions to give selenosulfonates in excellent yields.

$$\underset{1}{\mathrm{ArSeSeAr}} + \mathrm{S_2O_8^{2-}} \xrightarrow[\text{reflux}]{\mathrm{MeOH}} 2\mathrm{ArSe^+} + 2\mathrm{SO_4^{2-}}$$

$$\underset{2}{\mathrm{ArSe^+}} + \mathrm{Ar'SO_2^-} \xrightarrow[\text{r. t.}]{\mathrm{MeOH/TEBA}} \underset{3}{\mathrm{ArSeSO_2Ar'}}$$

Ar	Ar'	Ar	Ar'
3a: C_6H_5	C_6H_5	3d: 4—ClC_6H_4	C_6H_5
3b: C_6H_5	4—$CH_3C_6H_4$	3e: 4—ClC_6H_4	4—$CH_3C_6H_4$
3c: C_6H_5	4—ClC_6H_4	3f: 4—ClC_6H_4	4—ClC_6H_4

The advantages of this method are milder conditions, simpler manipulation, easilier obtained materials and better yields, compared with the previous methods.

The possible mechanism of this reaction is that diaryl diselenide could be converted into electrophilic selenenylating reagent by treating with peroxydisulphate, then arenenselenium cations attack sulfinates to give selenosulfonates.

EXPERIMENTAL

The IR spectra were recorded on Perkin Elmer 683 spectrophotometer. The ^{1}H- NMR spectra were recorded on Varian Em- 360A Fx-90Q. The microelemental analyses were carried out on Carlo Erba. Melting points were uncorrected.

Diaryl diselenides were prepared as described[17].

Sodium sulfonates were prepared as described[18].

General procedure: Diaryl diselenide (0. 5mmol) and ammonium peroxydisulfate (0. 55mmol) in 10ml methanol was refluxed for 1-1. 5hrs. After cooling, the sulfonate (1mmol) and 0. 1g TEBA was added and the mixture was stirred at room temperature for more than 6hrs. The process of the reaction was monitored by TLC. Then 20ml dichloromethane was added to the reaction mixture and the solution was washed twice with 20ml water. The separated organic layer was dried over anhydrous magnesium sulfate. After removal of solvent, careful addition of hexane to the crude product resulted in crystallization of the pure selenosulfonates.

3a: yield 77%; m. p. 55. 5—56. 5℃ (lit[12] 56—58℃); IR (KBr) υ_{max}: 1100, 1435; NMR ($CDCl_3$) δ: 7. 7—7. 3 (m, 10H).

3b: yield 81%; m. p. 77—79℃ (lit[12] 77—78℃); IR (KBr) υ_{max}: 1140, 1325; NMR ($CDCl_3$) δ: 7. 5—7. 1 (m, 9H).

3c: yield 87%; m. p. 98—100℃ (lit[12] 99—100℃); IR (KBr) υ_{max}: 1150, 1320; NMR ($CDCl_3$) δ: 7. 9—7. 3 (m, 9H).

3d: yield 83%; m. p. 81—83℃; IR (KBr) υ_{max}: 1140, 1325; NMR ($CDCl_3$) δ: 7. 5—7. 2 (m, 9H); $C_{12}H_9ClO_2SSe$, Calcd. C: 43. 37, H: 2. 71. Found, C: 43. 16, H: 2. 68

3e: yield 85%; m. p. 100—102℃; IR (KBr) υ_{max}: 1135, 1310; NMR ($CDCl_3$) δ: 7. 5—7. 1 (m, 8H), 2. 4 (s, 3H); $C_{13}H_{11}ClO_2SSe$, Calcd. C: 45. 15, H: 3. 18, Found, C: 44. 83, H: 3. 30.

3f: yield 87%; m. p. 119—121℃; IR (KBr) υ_{max}: 1140, 1320; NMR ($CDCl_3$) δ: 7. 9—7. 1 (m, 8H); $C_{12}H_8ClO_2SSe$, Calcd. C: 42. 62, H: 2. 19, Found, C: 42. 60, H: 2. 33.

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