A General Method for the Synthesis of Alkylenedithio- and Bis(alkylenedithio)-tetraselenafulvalenes

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1. Synthesis of tetraselenafulvalene (TSF) from 1,2,3-selenadiazole.¹

Methylene-1,3-diselenole. To a solution of 1,2,3-selenadiazole² (5.0 g, 37.5 mmol) in DMF-*t*-BuOH (100 mL:16 mL) was slowly added potassium *t*-butoxide (4.12 g, 37.5 mmol) in portions at 0 °C. After the reaction mixture was further stirred at room temperature for 30 min, the mixture was poured into ice-cooled water (500 mL), and the resulting precipitate was collected by filtration and dried in vacuo to give practically pure methylene-1,3-diselenole (2.68 g, 68 % yield) as colorless leaflets. The filtrate was extracted with hexane (100 mL × 3), and the extract was dried over Na₂SO₄. Evaporation of the solvent gave an additional crop of the product (1.29 g, 32% yield). The crude product was used in the next reaction without further purification.

Tetraselenafulvalene (TSF). To a solution of methylene-1,3-diselenole (500 mg, 2.35 mmol) and morpholine (1.3 mL) in DMF (12 mL) was slowly added a DMF (20 mL) solution of iodine (1.25 g, 4.9 mmol) at room temperature. The resulting reaction mixture was stirred additionally for 30 min and then diluted with water (200 mL). The mixture was extracted with carbon disulfide (20 mL $\times$ 3), and the extract was successively washed with aqueous sodium thiosulfate solution and water, dried over Na₂SO₄, and concentrated. The residue was purified by column chromatography on silica gel eluted with carbon disulfide to give TSF as a red solid (*R*_f 0.5, 120 mg). mp 132 °C.

2. References

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