Tetralithiation of Tetraselenafulvalene: a New Synthesis of Tetrasubstituted Tetraselenafulvalenes

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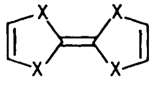
Tetraselenafulvalene reacts with four equivalents of lithium di-usopropylamide (LDA) at −80 °C to give a tetralithio derivative; reaction of the latter with some representative electrophiles gave tetrasubstituted tetraselenafulvalenes in preparatively useful yields.

The intense interest in the metallic properties of the cation radical salts of tetrathiafulvalene (TTF) (**1**) has been extended to the analogous salts of tetraselenafulvalene (TSeF) (**2**).[1] In recent years, low temperature superconductivity has been observed in various salts of both bis-ethylenedithio TTF[2] and tetramethyl TSeF.[3]

Fully substituted TTFs and TSeFs are generally prepared by coupling reactions from substituted 1,3-dithioles or 1,3-diselenoles.[4] The direct reaction of TTF or TSeF with electrophilic reagents leads to oxidation rather than substitution. However, TTF is readily converted to a tetralithio derivative which affords tetrasubstituted TTFs on reaction with electrophiles.[5]

Our recent simplified synthesis of TSeF has made this compound available by a practical and economic route,[6] and we now report our observations on its conversions to tetrasubstituted derivatives *via* its tetralithio derivative.

Treatment of TSeF with n-butyl-lithium under conditions employed for TTF[5b] led to total destruction of the molecule. Mass spectrometry indicated the formation of compounds (**3**) and (**4**), resulting from anionic attack at carbon or selenium rather than lithium–hydrogen exchange. In contrast, reaction of TSeF with LDA (4 equiv.) at −80 to −100 °C, followed by addition of excess electrophile (Ph_2S_2, Ph_2Se_2, $ClCO_2Me$, or CO_2), afforded the corresponding tetrasubstituted TSeFs (**5**)—(**8**).[†‡§] To the LDA prepared from *N,N*-di-isopropylamine (0.147 ml; 1.02 mmol) in 5 ml THF and n-BuLi (0.5 ml; 2.5 M, 1.02 mmol) at −80 °C was added TSeF (**2**) (100 mg;



(**1**) X = S
(**2**) X = Se

[†] Compound (**5**), a purplish pink solid, was prepared in 44% yield, m.p. (decomp.) 140 °C; $\lambda_{max.}$ [EtOH, nm (log ε)] 386 (2.90), 277 (3.72), 2.41 (3.90), 216 (3.92); i.r. (KBr) ν 1573, 1460, 1170, 1060, 1020, 992, 900, 825, 730, 680 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$, Me_4Si as reference) 7.41, 7.36 (Ar*H*).

Compound (**6**), a purple pink solid, was prepared in 52% yield, m.p. (decomp.) 155 °C; $\lambda_{max.}$ [EtOH, nm (log ε)] 3.88 (3.21), 297 (3.82), 2.19 (4.14); i.r. (KBr) ν 1575, 1460, 1430, 1170, 1060, 1020, 992, 900, 823, 730, 680 cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$) 7.54, 7.32 (Ar*H*).

Compound (**7**), shiny dark purplish black crystals, was prepared in 40% yield; m.p. (decomp.) 145 °C; i.r. (KBr) compared well with the sample prepared earlier in this lab[7]; ^{1}H n.m.r. δ ($CDCl_3$) 3.83 (s, O*Me*).

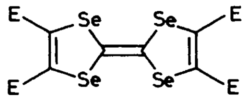
Compound (**8**), black shiny crystalline solid, was prepared in 28% yield, m.p. (decomp.) >300 °C; $\lambda_{max.}$ [EtOH, nm, (log ε)] 360 (3.59), 322 (3.81), 277 (3.92), 205 (4.11); the i.r. spectra of (**8**) compared well with the i.r. spectra of the hydrolysis product of (**7**).[‡,§]

[‡] In one report on the lithiation of TTF[5b] it was mentioned that TSeF could be similarly lithiated and converted to monoethyl TSeF and monocarboxy TSeF, although no experimental details or yields were given.

[§] Satisfactory elemental analyses were obtained for all new compounds.

BuCH=CH—SeBu
(3)

BuSe—CH=CH—SeBu
(4)



(5) E = —SPh
(6) E = —SePh
(7) E = —CO_2Me
(8) E = —CO_2H

0.255 mmol) through an L-shaped tube which was already attached to the round-bottomed flask under N_2. As soon as the whole of T.Se.F. went into solution (*ca.* 10—15 min), the electrophile (**2**) (1.2 mmol) was added at −80 °C and stirred at this temperature for 15 min and allowed to come to room temp. (*ca.* 30 min). Water was added to this mixture and the resulting solution was extracted in CH_2Cl_2 (3 × 10 ml). The organic layer was washed (H_2O), dried (Na_2SO_4) and evaporated. The residue was purified by chromatography on a column of silica gel using hexane–benzene (5:1) as the eluting solvent.

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