Electrochemical Reduction of Carbon Diselenide and Preparation of 4,4′,5,5′-Tetra(selenomethoxy)tetraselenafulvalene

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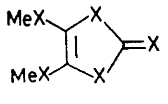
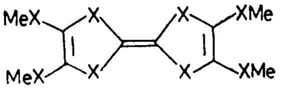
Summary Carbon diselenide has been electrochemically reduced and methylated to form 4,5-di(selenomethoxy)-1,3-diselenole-2-selone from which 4,4′,5,5′-tetra(selenomethoxy)tetraselenafulvalene was prepared.

Recent interest in electrically conducting metal-like organic charge-transfer salts[1] has led to synthetic attempts, including electrochemical methods,[2] to prepare new sulphur-[3] and selenium-[4]containing, electron-rich heterocyclic donor molecules. The electrochemical reduction of carbon disulphide has been studied[5,6] and its methylated reduction product (**1**) has been converted into the tetrathiafulvalene (**2**).

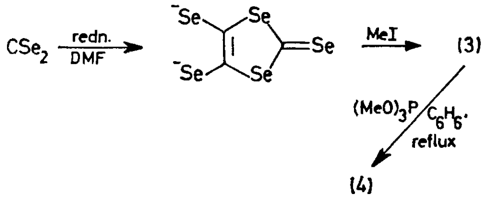


(**1**), X = S
(**3**); X = Se



(**2**); X = S
(**4**); X = Se

We report here, for the first time, the electrochemical reduction of carbon diselenide to yield the novel heterocyclic system (**3**) and the subsequent preparation of the tetraselenafulvalene (**4**).



The cyclic voltammogram of CSe_2 in dimethylformamide (DMF) at a platinum electrode (Figure) shows a broad reduction peak[†] at −1·65 V (*cf.*[6] CS_2: −1·96 V, Pt, DMF). Bulk electrolysis at −1·65 V afforded only a trace of (**3**); however, at −1·35 V, (**3**) was obtained in 55% yield (based on coulombs passed), m.p. 79—80 °C, δ (CCl_4, relative to $SiMe_4$) 2·44, λ_{max} (C_6H_{12}) 250 (ε 7300), 300 (2600), and 430 (4800) nm, ν_{max} (CCl_4) C=Se 10·8 μm. Considerable fouling of the working electrode prevented higher conversion and acquisition of coulometric data.

[†] All potentials are peak potentials and are referenced to the aqueous standard colomel electrode (SCE).

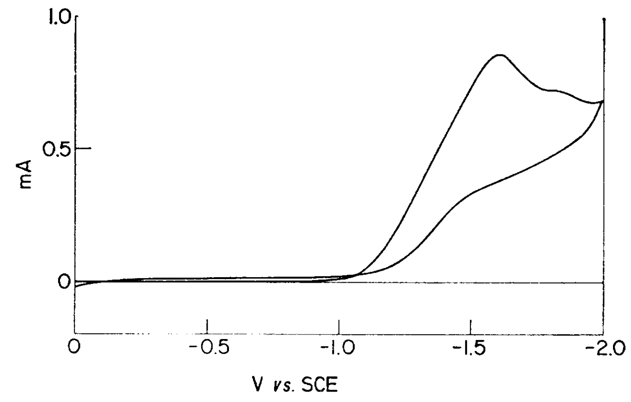


Figure. Cyclic voltammogram of carbon diselenide in DMF.

Compound (**3**) can be directly coupled to the heterofulvalene (**4**) by treatment with $(MeO)_3P$ because of the presence of the selenocarbonyl bond.[4a,b,7] This is in contrast to the analogous sulphur system (**1**) which fails to react under similar conditions necessitating a multi-step procedure to give the respective heterofulvalene. Reaction of (**3**) with $(MeO)_3P$ in refluxing benzene for 5 h gave (**4**) in 10% yield as a reddish-brown solid, m.p. 112—113 °C, δ (CCl_4, relative to $SiMe_4$) 2·35, λ_{max} (MeCN) 280, 308, and 430 nm; ν_{max} (CCl_4) 7·05 m, 7·35w, 7·85w, and 10·95s μm; M^+, *m/e* 772 (based on ^{80}Se).

Cyclic voltammograms of (**4**) exhibited two reversible oxidation waves at +0·58 and +0·81 V (Pt anode, MeCN, 0·1 M Et_4NClO_4) which show it to be more difficult to oxidize than the corresponding sulphur analogue (**2**). This behaviour is consistent with previous results on tetraselenafulvalene and tetrathiafulvalene.[8]

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