New Synthesis of Substituted Diselenadithiafulvalenes (DSDTF) and Tetraselenafulvalenes (TSF)

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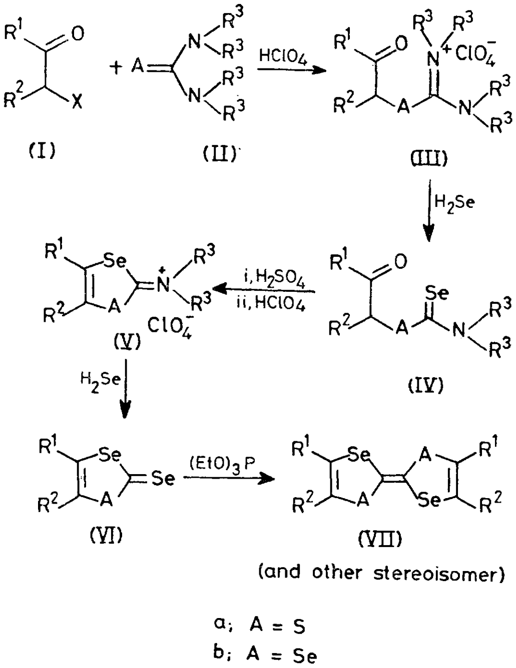
Summary A new general synthesis of substituted diselenadithiafulvalenes (DSDTF) (VIIa) and tetraselenafulvalenes (TSF) (VIIb) is illustrated by the synthesis of hexamethylenediselenadithiafulvalene (HMDSDTF) (VIII).

THE study of charge-transfer salts prepared from tetra-alkyl-substituted diselenadithiafulvalenes[1] and tetraselenafulvalenes[2] has provided valuable information regarding the effect of interchain coupling (dimensionality) on the electrical and magnetic properties of quasi-one-dimensional organic 'metals'.[3] We report here on an alternative synthesis of these compounds that starts with readily available materials and proceeds with reasonably good yields in all steps. The new synthetic method is illustrated by the preparation of dithiadiselena π-donors, as outlined in the Scheme; the corresponding tetraselena-compounds can be made starting from the selena-urea (IIb).

2-Chlorocyclopentanone (I; $R^1R^2 = [CH_2]_3$; X = Cl) and 1,1,3,3-tetramethylthiourea (IIa; R^3 = Me) were allowed to react at room temperature to give a 70% yield of the thiouronium perchlorate (IIIa), δ (CD_3OD, Me_4Si) 1·6—2·7 (m, 6H), 3·3 (s, 12H), and 4 (t, 1H, *J* 9 Hz); ν (KBr) 3400m, 2880m, 1730s, 1580s, 1500s, 1440s, 1390s, 1250s, 1200s, and 1000—1180vs cm^{-1}. Treatment of an aqueous solution of (IIIa) with H_2Se produced a 75% yield of (IVa), *m/e* (70 eV) 251 (M^+) and 136 [$\{S–C(:Se)–NMe_2\}^{+\cdot}$]; δ ($CDCl_3$, Me_4Si) 1·8—



SCHEME. X, Halogen; R^1 and R^2, alkyl.

3·0 (m, 6H), 3·4 (s, 3H), 3·7 (s, 3H), and 5 (t, 1H, *J* 9 Hz); ν (KBr) 2900m, 1690s, 1470s, 1420s, 1225s, 1120m, 1100m, 995m, and 815s cm^{-1}. Ring closure and dehydration of (IVa) to form (Va) was effected by conc. H_2SO_4. Compound (Va) was isolated in 90% yield as the perchlorate salt by the addition of $HClO_4$ to the reaction mixture [(Va): δ (CD_3OD, Me_4Si) 2·45 (m, 2H), 2·95 (m, 4H), and 3·55 (s, 6H); ν (KBr) 3460m, 3400m, 2905m, 2650m, 1600s, 1560s, 1445m, 1405s, 1310m, 1240s, and 950—1200vs cm^{-1}]. Treatment of an MeOH–H_2O solution of (Va) with H_2Se gave a 90% yield of (VIa), *m/e* (70 eV) 238 (M^+); δ (C_6D_6, Me_4Si) 1·55 (2H, m, *J* 6·3 Hz) and 1·83 (4H, m, *J* 6·3 Hz); ν (KBr) 2860w, 1425w, 960w, 905s, 805m, and 500m cm^{-1}. Compound (VIa), when heated with an excess of triethyl phosphite, gave a 50% yield of the known compound (VIIa), m.p. >240 °C (decomp.), together with its other stereoisomer.[1b]†

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† Satisfactory elemental analyses were obtained for (VIa) and (VIIa). Four-probe d.c. conductivity measurement on a single crystal of the tetracyanoquinodimethane (TCNQ) salt of (VIIa) gave the following results: $\sigma_{RT} = 900\ \Omega^{-1}\ \mathrm{cm}^{-1}$; $\sigma_{\max}/\sigma_{RT} = 4$; and $T_{\max} = 76$ K. The previously reported compaction conductivity (ref. 1b) for the TCNQ salt of (VIIa) was 100 Ω^{-1} cm^{-1}.

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