Tetraformyltetraselenafulvalene (TFTSeF): Synthesis and Some Uses as a Precursor of Polyfunctionalized Tetraselenafulvalenes

Marc Sallé,[a] Alain Gorgues,[a]* Jean-Marc Fabre,[b] Klaus Bechgaard,[c] Michel Jubault,[a] and Fernand Texier[a]

[a] *Laboratoire de Synthèse Organique et d'Electrochimie (LSOE), Université d'Angers, 2 bd Lavoisier, 49045 Angers Cédex, France*

[b] *Laboratoire de Chimie Structurale Organique, Université des Sciences et Techniques du Languedoc (USTL), Place E. Bataillon, 34060 Montpellier Cédex, France*

[c] *Department of General and Organic Chemistry, H. C. Oersted Institute, Universitatparken 5, Copenhagen, DK 2100 Denmark*

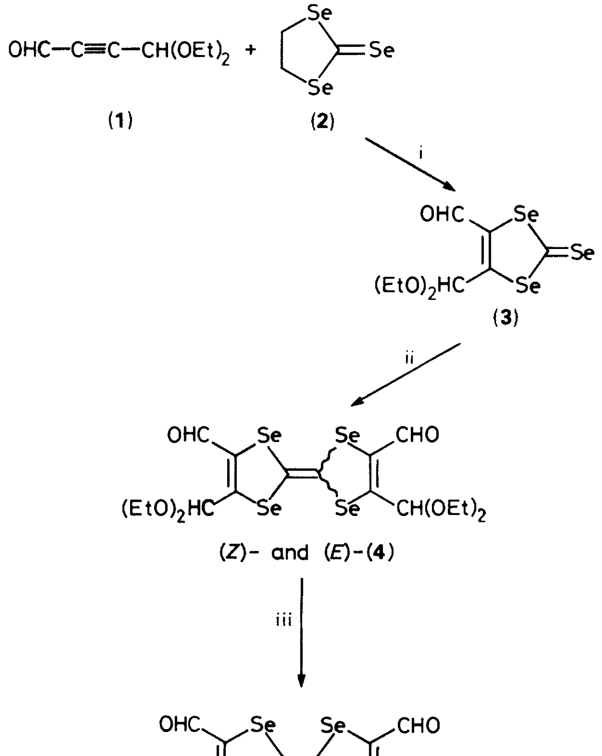
A short synthesis of tetraformyltetraselenafulvalene (TFTSeF) is presented, and a few preliminary results emphasize its use as an efficient precursor of tetrasubstituted TSeFs such as a tetravinylic derivative, *via* a Wittig reaction, and tetrakis(hydroxymethyl)–TSeF by a simple $NaBH_4$ reduction.

Tetraheterofulvalenes[1] (TXF; X = S, Se, or Te), their derivatives and analogues,[2] have been of great interest since the discovery of the conductivity[3] and superconductivity[3,4] of both their electrogenerated cation radical salts and their charge transfer complexes. Many efforts have therefore been devoted to raise T_c in their corresponding organic metals; this can be accomplished, *inter alia*, by subtle modifications of the TXF moiety and significant results have been obtained already with tetrasubstituted TXFs {*e.g.* BEDT–TTF[4] [bis(ethylenedithio)tetrathiafulvalene]}.

A recent report by Cava *et al.*,[5] describing a new synthesis of fully substituted tetraselenafulvalenes (TSeFs) owing to four-fold electrophilic attacks on tetralithio–TSeF, has prompted us to report our findings on such compounds.

Our approach involves the direct tetrafunctionalization of a tetraformyl–TXF through four-fold nucleophilic attack at the highly reactive aldehyde groups, as has been shown previously in the case of tetraformyltetrathiafulvalene TFTTF (X = S).[6] Here we present the first preparation of tetraformyltetraselenafulvalene (TFTSeF) (Scheme 1) and demonstrate the latter to be a convenient precursor for synthesizing a great variety of tetrasubstituted TSeFs.

Thus, when (**1**) (1.35 equiv.)[7] was reacted for 1 h,[8] with (**2**)[9] (1 equiv.) (freshly purified by SiO_2 flash chromatography, toluene) in a refluxing toluene solution [2 ml per mmol of (**1**)], in the dark and under nitrogen, (**3**)† was isolated (80% yield) after evaporation *in vacuo* and recrystallization from pentane–CH_2Cl_2 (9 : 1). The required dimerization with loss of Se was neatly performed using octacarbonyldicobalt[10] [0.71 mmol per mmol of (**3**)], after 45 min in a refluxing toluene solution (33 ml) in darkness and under nitrogen, the reaction being monitored by t.l.c.[11] (SiO_2, pentane–ether, 1 : 1). After filtration of a black insoluble material (washed with CH_2Cl_2–ether, 1 : 1), evaporation to dryness, and chromatography on a short SiO_2 column (pentane–ether, 6 : 4), essentially equal amounts of (*Z*)- and (*E*)-(**4**)[12]† were obtained (30—35% yield) and, if required, separated by SiO_2 thick layer chromatography (pentane–CH_2Cl_2, 1 : 9). Precipitation of dark blue crystals of (**5**)† (80—85% yield) occurred within a few minutes when HCO_2H was added to a dilute CH_2Cl_2 solution of (*Z*)-(**4**), (*E*)-(**4**), or a mixture of the two isomers.



Scheme 1. *Reagents and conditions:* i, reflux, toluene, 1 h, N_2; ii, $Co_2(CO)_8$, toluene, 45 min, N_2; iii, HCO_2H, CH_2Cl_2, 10 min, room temp.

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† Compound (**3**): purple crystals; m.p. 46.5—48.5 °C; i.r. (CCl_4) 1655 cm^{-1}; ^1H n.m.r. (CCl_4) δ 1.27(t), 3.75(q), 5.97(s), 9.92(s); m.s. ($C_9H_{12}O_3{}^{78}Se^{80}Se_2$) 405.8290 (calcd.), 405.8279 (found).

Compound (*E*)-(**4**): purple crystals; m.p. 173—176 °C; i.r. ($CHCl_3$) 1645 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ 1.25(t), 3.69(q), 5.80(s), 9.90(s); u.v.–vis., λ_{max} [CH_2Cl_2, ε(nm)] 286(30100), 472(3670); m.s. ($C_{18}H_{24}O_6{}^{78}Se^{80}Se_3$) 653.82417 (calcd.), 653.8247 (found).

Compound (*Z*)-(**4**): orange coloured crystals; m.p. 153—157 °C; i.r. ($CHCl_3$) 1650 cm^{-1}; ^1H n.m.r. ($CDCl_3$) δ (*E*)-(**4**); u.v.–vis., λ_{max} [CH_2Cl_2, ε(nm)] 286(22500), 466(3100); m.s. 653.8232 (found).

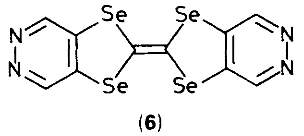
Compound (**5**): dark blue crystals; m.p. 315 °C (decomp.); i.r. (hexachlorobuta-1,3-diene) 1640 cm^{-1}; ^1H n.m.r. [$^2H_6$](Me_2SO) δ 10.28(s); m.s. ($C_{10}H_4O_4{}^{78}Se^{80}Se_3$) 505.67785 (calcd.), 505.6766 (found).

Compound (**6**): orange coloured spangles; m.p. 296 °C (decomp.); ^1H n.m.r. ([$^2H_6$]DMSO (DMSO = dimethyl sulphoxide)] δ 9.32(s); m.s. ($C_{10}H_4N_4{}^{78}Se^{80}Se_3$) 497.71049 (calcd.), 497.7131 (found).

Compound (**7**): dark ochre red needles; m.p. 124.5—126 °C; ^1H n.m.r. (CCl_4) δ 1.83(d), 5.72(m); m.s. ($C_{22}H_{28}{}^{78}Se^{80}Se_3$) 609.88598, (calcd.), 609.8859 (found).

Compound (**8a**): yellow powder; m.p. 220 °C (decomp.); i.r. (Nujol) 3200 cm^{-1}; ^1H n.m.r. ([$^2H_6$]DMSO) δ 4.04(d); 5.28(t); m.s. ($C_{10}H_{12}O_4S_4$) 323.96184 (calcd.), 323.9622 (found).

Compound (**8b**): pink powder; m.p. 247 ° C (decomp.); i.r. (Nujol) 3200 cm^{-1}; ^1H n.m.r. ([$^2H_6$]DMSO) δ 4.21(d), 5.69(t); m.s. ($C_{10}H_{12}O_4{}^{80}Se_4$) 515.73967, (calcd.), 515.7417 (found).



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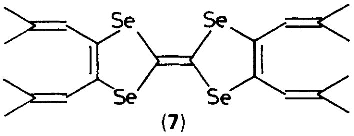

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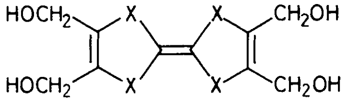

(8)a ; X = S
b ; X = Se

We took advantage of the bis-vicinal position of two CHO groups in (**5**) to readily build the bis-pyridazino derivative (**6**)† (71% yield) in a one-step treatment with N_2H_4, H_2O in *N,N*-dimethylformamide (DMF). Then we focused on the synthesis of (**7**)† in order to obtain a good π-donor with a large space extension. This compound was obtained (66% yield) through a four-fold Wittig reaction with the unstabilized ylide Ph_3PCMe_2 [from (**5**) and a 25% excess of ylide from Ph_3PCHMe_2I, Bu^tLi as the base, −5 °C, tetrahydrofuran (THF)]. The π-donor ability of (**7**) was provided by cyclic voltammetry, with two reversible peaks at E^1p = +0.71 and E^2p = +0.89 V/S.C.E. (S.C.E. = standard calomel electrode) at 20 °C [THF, $Bu^n_4NClO_4$ (0.1 M), (**7**) (10^{-3} M)], and by its black charge transfer complex with I_2 (CH_2Cl_2) [no complex was observed with tetracyanoquinodimethane (TCNQ)].

Since the potential hydrogen bonding ability of the tetrakis(hydroxymethyl)–TXF (**8a**)† and (**8b**)† is expected to result in stronger inter- and intra-chain contacts in their corresponding organic metals, we have prepared them by simple $NaBH_4$ reduction (THF–MeOH solvent) of TFTTF (80% yield) and of TFTSeF (**5**) (53% yield), respectively. It is worth noting that this 'simplistic' preparation will avoid the puzzling reduction problems encountered with the ester– or carboxylic acid–TXF derivatives[13] and will improve the recent preparation of (**8a**).[14] Good π-donor properties of these tetra-alcoholic–TXFs was shown by cyclic voltammetry with two reversible peaks, and their chemical oxidation with TCNQ and/or I_2: for (**8a**), E^1p = +0.39, E^2p = + 0.65 V/S.C.E. [dimethyl formamide (DMF), $Bu^n_4NClO_4$ (0.1 M), (**8a**) (10^{-3} M)], and for (**8b**), E^1p = + 0.48, E^2p = + 0.70 V/S.C.E. (same conditions).

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