Electrochemical Synthesis of Unsymmetrical Tetrathiafulvalene Derivatives. Electrocrystallization of their Radical-cation Salts

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A new synthesis of some unsymmetrical tetrathiafulvalene molecules using electrochemical methods is described; ethylenedithio(dimethyl)tetrathiafulvalene and (ethylenedithio)benzotetrathiafulvalene have been obtained and their radical-cation salts prepared by electrocrystallization.

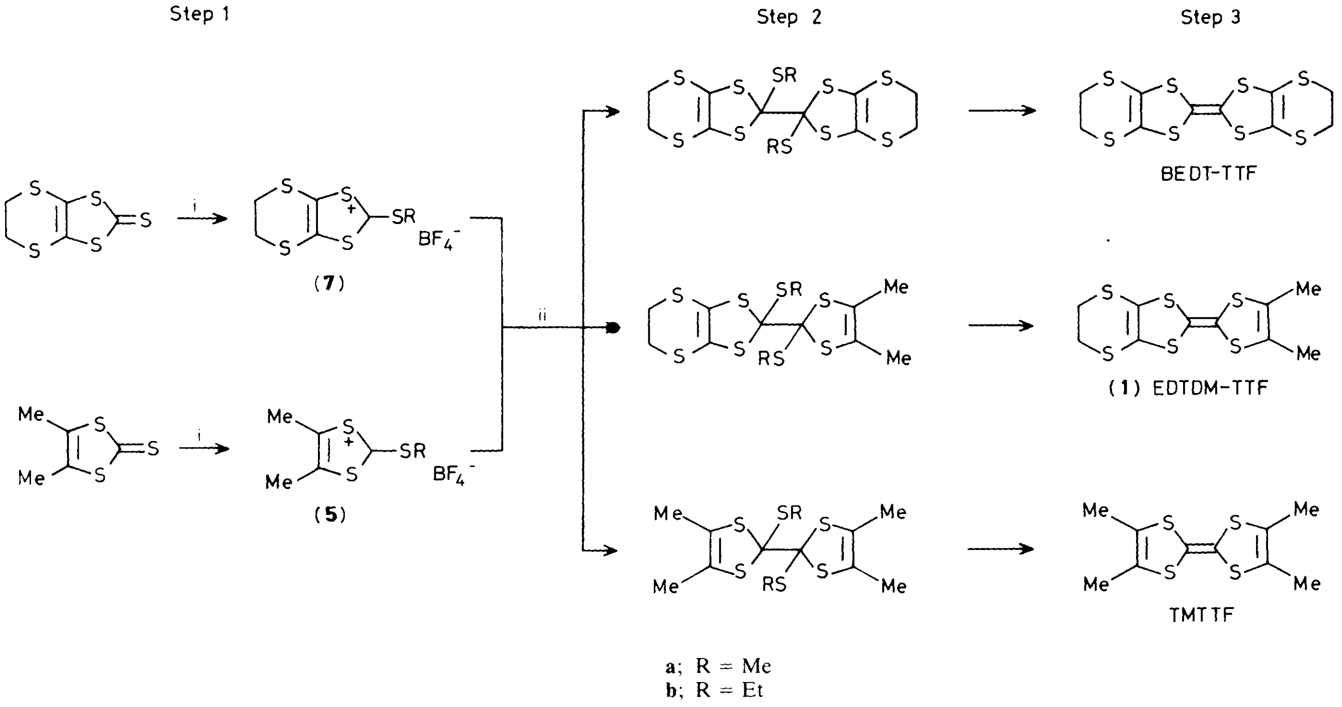
The radical-cation salts of tetrathiafulvalene (TTF) and tetraselenafulvalene (TSF) derivatives constitute the most important series of organic metals known today. Tetramethyltetraselenafulvalene perchlorate, $(TMTSF)_2ClO_4$, is the first sulphur organic superconductor under atmospheric pressure[1] and bis(ethylenedithio)tetrathiafulvalene per-rhenate, $(BEDT\text{-}TTF)_4(ReO_4)_2$, the first sulphur organic superconductor compound.[2] Some salts of BEDT–TTF have the highest superconduction transition temperatures discovered for an organic metal.[3] These results were interpreted in terms of increasing interchain interactions *via* the sulphur atoms. Since some radical-cation salts of unsymmetrical TTF and TSF compounds have a greater metallic character than the corresponding symmetrical compounds,[4] it was considered of interest to test these unsymmetrical TTF compounds containing one ethylenedithio substituent [*e.g.* (**1**) and (**2**)] or thiomethyl substituents [*e.g.* (**3**) and (**4**)].

Compounds (**1**)—(**4**) were synthesized as indicated in Scheme 1. The 2-alkylthio-1,3-dithiolium salts (**5**)—(**8**) (step 1) were prepared[5] by reaction of the corresponding 1,3-dithio-2-thione with triethyloxonium or trimethyloxonium tetrafluoroborate in dichloromethane at 40 °C. Cyclic voltammograms of dithiolium salts exhibit a single irreversible

Table 1. Redox potentials at a rotating platinum disc electrode (2500 rev./min), and conductivities of salts.[a]

Compound	$E_{\frac{1}{2}}/V^b$	Salt, form, conductivity/Ω^{-1} cm^{-1}
(**1**)	0.40, 0.71[c]	Br^-, plates, 80 AsF_6^-, needles, 10 SbF_6^-, rods, 10^{-3}
(**2**)	0.57, 0.87	SbF_6^-, rods, 10^{-3}
(**3**)	0.40, 0.70	No crystals
(**4**)	0.55, 0.83	No crystals

[a] In MeCN, with Et_4NBr (0.2 M). [b] *Vs.* S.C.E. [c] 0.44, 0.83 from ref. 9; 0.369, 0.670 from ref 10.



Scheme 1. *Reagents and conditions:* i, $R_3O^+BF_4^-$, CH_2Cl_2; ii, −1.0 V *vs.* standard calomel electrode (S.C.E.), Pt electrode, MeCN, Et_4N^+ BF_4^- (0.2 M).

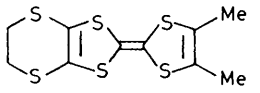
Table 2. Half-wave potentials at a rotating platinum disc electrode (2500 rev./min).

Compound[a]	$E_{\frac{1}{2}}$/V[b]	
	a; R = Me	**b**; R = Et
(**5**)	−0.630	−0.600
(**6**)	−0.410	−0.400
(**7**)	−0.425	−0.380
(**8**)	−0.420	−0.400

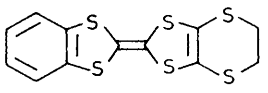
[a] 1 mM in MeCN, with Et_4NBr (0.2 M). [b] *Vs.* S.C.E.

reduction wave[5,6] and it was shown that the electrolysis of dithiolium salts gave orthothio-oxalates.[7] The half-wave potentials determined on a rotating platinum disc electrode are listed in Table 2. They are about −0.4 V *vs.* S.C.E., except for compounds (**5a**) and (**5b**), which are about −0.6 V *vs.* S.C.E.

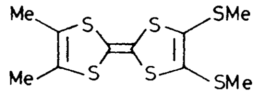
During step 2 (Scheme 1), the two dithiolium salts were reduced simultaneously to give two symmetrical and one unsymmetrical orthothio-oxalate. The electrolyses were carried out by adjusting the potentiostat to −1.0 V *vs.* S.C.E. Because of the uncompensated resistance of the solution it was necessary to maintain a low current in the cell by introducing slowly an equimolar solution of the two salts. Current and concentrations of electroactive species remained constant during the experiment. The voltammograms observed at the same time indicated that at +1.0 V *vs.* S.C.E. orthothio-oxalate formation increases linearly with time. 1 Faraday per mole was necessary to obtain orthothio-oxalates (yield 90%). With the salt (**5b**), TMTTF was obtained directly as well as a low yield of orthothio-oxalates.



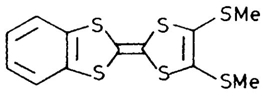
(**1**)



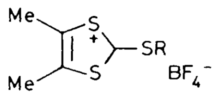
(**2**)



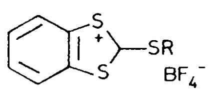
(**3**)



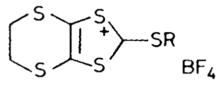
(**4**)



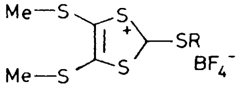
(**5**)



(**6**)



(**7**)



(**8**)

The orthothio-oxalates were decomposed to give the corresponding TTF compounds (step 3) by heating in refluxing 1,2-dichloroethane with a small quantity of toluene-4-sulphonic acid[8] (yield 80%). Capillary gas chromatographic analysis, possible for (**3**) and (**4**), indicated a proportion close to 50% for the unsymmetrical TTF and 25% for each symmetrical compound. Flash chromatography gave the pure TTF derivatives (benzene–hexane, 1 : 1, as eluant).

Voltammograms of the unsymmetrical TTF compounds (**1**)—(**4**) show two reversible waves; the associated redox potentials are listed in Table 1. They are between the redox potentials of the two corresponding symmetrical TTF compounds.

Electrocrystallizations were carried out at 0 °C in 1,1,2-trichloroethane solutions of Bu_4NBr, Bu_4NAsF_6, or Bu_4NSbF_6 using a constant current (10 μA) and a platinum anode. Under those conditions, crystals were obtained with compounds (**1**) and (**2**) but not with compounds (**3**) and (**4**), probably because the bulk of the thiomethyl group hinders the electrocrystallization. Compound (**1**) gave with the AsF_6^- ion black semi-conducting needles and with the bromide ion black weakly metallic plates as described before.[9,11] Compound (**1**) with the SbF_6^- ion give black semiconducting rods with an antiferromagnetic phase transition at 11 K.[12,13] Similarly salts have been obtained with compound (**2**) and physical characterization is currently under investigation.

To conclude, electrochemical techniques can be used to obtain new unsymmetrical TTF compounds. Ethylenedithio(dimethyl)tetrathiafulvalene and (ethylenedithio)benzotetrathiafulvalene gave Bechgaard salts. The new salt ethylenedithio(dimethyl)tetrathiafulvalenium hexafluoroantimonate exhibits an antiferromagnetic phase transition at 11 K.

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