Vinyltetrathiafulvalene

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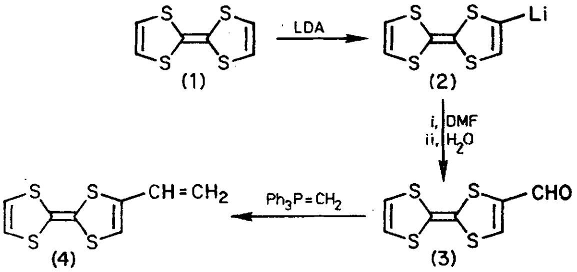
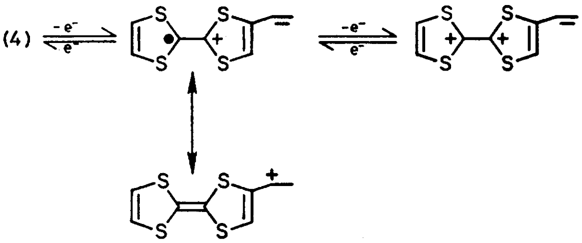
Summary Vinyltetrathiafulvalene was obtained from the Wittig reaction of 2-formyltetrathiafulvalene with methylenetriphenylphosphorane, and was polymerized to form low molecular weight polymers.

INTEREST in donor molecules, such as tetrathiafulvalene (TTF) (**1**), that form electrically conducting, 'metallic-like,' organic charge-transfer salts[1,2] has expanded recently with attempts to incorporate such donor molecules into polymeric frameworks.[3–5] The resulting polymers might be expected to exhibit novel electronic properties. However, all the systems developed thus far have been condensation polymers based on difunctionalized TTF monomers such as the dicarboxamide and di-isocyanate derivatives. Systems with TTF in the polymer backbone were considered too constrained[5] to allow for the stacked structure found in conducting charge-transfer salts. In addition the presence of electron-withdrawing substituents reduce the electron donating ability of TTF,[6] and the resulting polymers have not exhibited high conductivities. In an attempt to overcome these difficulties and provide a low ionization potential TTF system for addition polymerization, with TTF as a unit pendant to the polymer backbone, vinyltetrathiafulvalene (**4**) was prepared, *via* a Wittig reaction of methylenetriphenylphosphorane with 2-formyltetrathiafulvalene (**3**), which was obtained by reaction of tetrathiafulvalenyllithium (**2**) with dimethylformamide (DMF).



Compound (**2**) was prepared by the addition of 1 equiv. of lithium di-isopropylamide (LDA) in ether to an ether solution of (**1**) at −70 °C. The resulting slurry was then added to a five-fold excess of DMF in ether at −70 °C, and the mixture was slowly warmed to 25 °C. Deaerated water was added, and the mixture was extracted with ether. Purification was effected by column chromatography on silica gel, eluting first with hexane to remove (**1**) and then with benzene to isolate the 2-formyltetrathiafulvalene (**3**), which was obtained as red crystals (m.p. 98—99 °C) in 44% yield. An ether solution of (**3**) was then added to an equimolar amount of methylenetriphenylphosphorane[7] in ether at 25 °C and stirred for 1 h. The salts were removed by filtration, and after evaporation the residue was chromatographed on silica gel using hexane to give (**4**) in 30% yield. Recrystallization from hexane gave yellow needles (m.p. 32 °C).

The reaction of (**2**) with a vinyl halide might be considered a more direct route to (**4**); however this would present a difficult separation problem since some TTF and disubstituted derivatives are usually formed in the reaction.[8] Although the monovinyl derivative is chromatographically similar to TTF and the divinyl derivative, (**3**) is easily separated from TTF and the TTF dialdehyde derivative by chromatography because of the polar functional group.



One potential problem with the radical cation of (**4**) is formation of other radicals with the vinyl group and rearrangement products. However the cyclic voltammogram of (**4**) shown in the Figure exhibits two reversible oxidation waves at 0·41 and 0·77 V.† There is no evidence in the cyclic voltammogram to indicate any oxidation of the vinyl group or rearrangements that would interfere with vinyl polymerization.

Compound (**4**) slowly polymerized upon standing (over a period of weeks) at room temperature in an argon atmosphere. Initiation with azobisisobutyronitrile, u.v. irradiation, or addition of tetracyanoquinodimethane (TCNQ) also produced low molecular weight polymers. These polymers formed dark, charge transfer complexes with bromine or TCNQ. Efforts are currently underway to obtain high molecular weight polymers of this and other vinylic TTF systems.

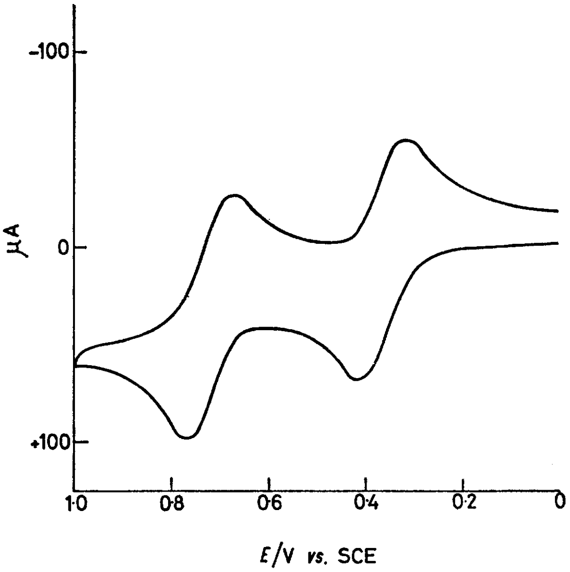


FIGURE. Cyclic voltammogram of vinyltetrathiafulvalene (**4**).

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† Peak potentials *vs.* SCE; MeCN, 0·1M tetraethylammonium perchlorate, Pt electrode, 0·2 V/s.

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