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SYNTHESIS OF THE HIGHLY CONDUCTING ORGANIC SALT TETRAMETHYLTETRATHIOFULVALENIUM - TETRACYANO-p-QUINODIMETHANIDE[1]

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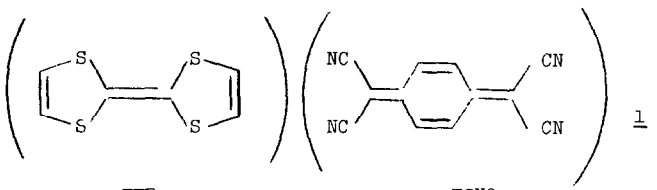
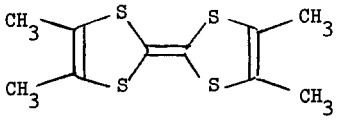
As part of a systematic program underway in our laboratories to develop and study new, highly conducting organic materials,[5] we previously reported the synthesis and d c electrical conductivity of the salt of tetrathiofulvalene and tetracyano-p-quinodimethane, (TTF-TCNQ) 1.[6] This compound behaves like a metal over a large temperature range and displays the highest conductivity of any known organic solid [σ_{max} ca $10^4(\Omega - cm)^{-1}$] [7,8]

In order to lower the ionization potential of the donor (TTF) and thus alter the electronic band structure of the organic solid we have synthesized the related compound, tetramethyltetrathiofulvalene (TMTTF), 2, and its TCNQ salt

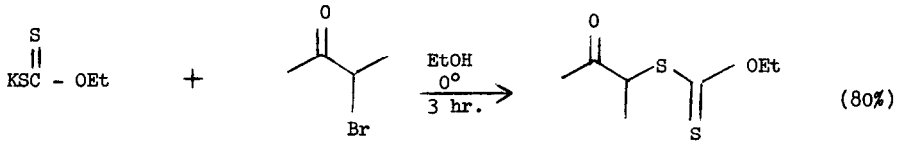


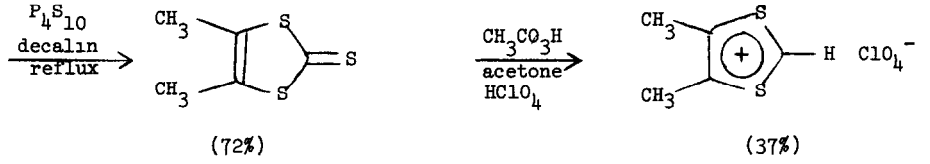
TTF TCNQ 1



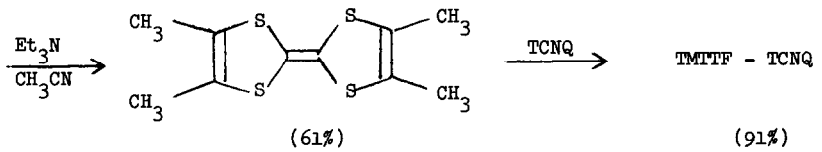
2

The synthesis of TMTTF follows from those used previously to prepare compounds of this class [9,10]





(72%) (37%)



(61%) (91%)

Potassium O-ethyldithiocarbonate was stirred with 3-bromo-2-butanone in ethanol at 0° for three hours and then the mixture was poured into water. The oil that separated was collected, dried in ether ($CaCl_2$), and the solvent removed in vacuo to give O-ethyl-S-1-methyl-2-propanonyldithiocarbonate as a yellow oil (80% yield) which was used directly in the next step Cyclization of this ester was accomplished with P_2S_5 (3 mole/mole of ester) in refluxing decaling (20 ml/gm of ester) for 30 min. The cooled solution was poured into twice its volume of anhydrous ether, the organic layer was washed with water, 10% NaOH, water, and dried over $CaCl_2$. This mixture was poured into a saturated methanolic mercuric chloride solution to obtain the mercuric chloride - thione complex as a bright yellow solid. The complex was decomposed by shaking it with a saturated aqueous sodium sulfide solution. The resulting solid was separated by filtration and extracted with boiling acetone. The acetone

solution was dried over $MgSO_4$, treated with decolorizing carbon, and the solvent removed in vacuo to give the yellow 4,5-dimethyl-1,3-dithiole-2-thione in a 72% yield, m.p 86-91° C This product could be used without further purification Oxidation to the perchlorate salt was done with 40% peracetic acid (4 moles/mole of thione) in acetone at 0° C for 30 min with the subsequent addition of abs MeOH (5 ml/gm of thione), 70% perchloric acid (1-2 ml/gm of thione), and dilution with anhydrous ether Upon cooling the solution, 4,5-dimethyl-1,3-dithiolium perchlorate separated as pale pink crystals in 35-37% yield This salt was suspended in acetonitrile and treated with excess triethylamine at room temperature to obtain TMTTF Recrystallization from acetonitrile gave orange-pink needles in 61 3% yield, m p 244 5-245° C IR (KBr) 2910 cm^{-1} (m), 1625 (w), 1435 (m), 1386 (m), 1180 (s), 1090 (s), 778 (s), 442 (s) NMR (CS_2) 1 88 δ relative to TMS Anal Calcd for $C_{10}H_{12}S_4$ C, 46 11, H, 4 65 Found C, 46 19, H, 4 57

When equimolar amounts of TMTTF and TCNQ were mixed in hot acetonitrile, the black 1 1 salt separated as very fine, needle-like crystals (91%)[11] which recrystallized from acetonitri

Preliminary microwave electrical conductivity measurements on TMTTF-TCNQ indicate a very high room temperature electrical conductivity [ca $10^3(\Omega - cm)^{-1}$] In contrast with that of TTF-TCNQ in the metallic region, the conductivity of TMTTF-TCNQ depends but weakly on the temperature over a wide range At low temperatures the material is an insulator Detailed studies of the temperature-dependent microwave electrical conductivity and dielectric constant for TMTTF-TCNQ and other derivatives will appear elsewhere [12,13]

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11. Anal. Calcd for $C_{22}H_{16}N_4S_4$ C, 56.87, H, 3 47 Found C, 56 73, H, 3 38.

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13 For comparison the room temperature electrical conductivities of several elements are as follows Cu, 5 9 x 10^5, Li, 1.1 x 10^5, C (graphite), 7 1 x 10^2, S (yellow) 10^{-22} $(\Omega - cm)^{-1}$.