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Reactions of Dipyridylacetylenes and Carbon Disulfide under High Pressure. Synthesis of Tetra-2-pyridyltetrathiafulvalene

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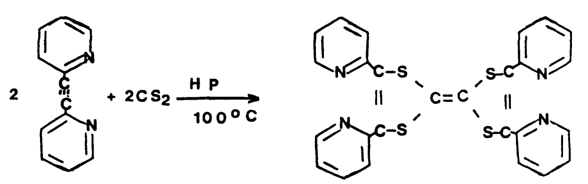
Synopsis The reaction of di-2-pyridylacetylene with CS_2 at 100 °C under 4500 atm for 12 h. gave tetra-2-pyridyltetrathiafulvalene in 80% yield.

Electron-rich tetrathiafulvalene (TTF) reacts with tetra cyanoquinodimethan (TCNQ) to form a charge transfer complex which has unusually high electrical conductivity.[1] Recently certain planar transition metal organic macrocyclic solids were also found to be conductive.[2] Thus, it would be interesting to couple the electron-rich TTF π-systen with a metal complex into a single conjugated and repeating framework. Engler and his coworkers recently synthesized polymers based on TTF and a metal 1,3-dithiolene complex and found they were highly conductive.[3]

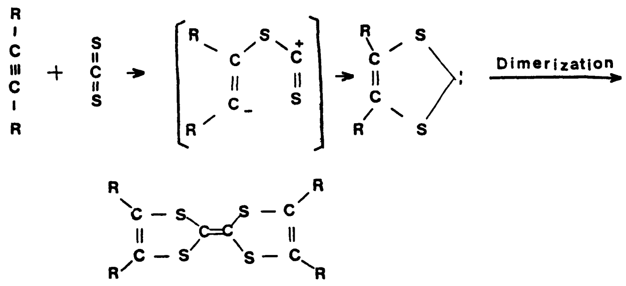
We have shown previously that TTF derivatives can be readily synthesized by the reactions between acetylenic compounds substituted with strong electron-withdrawing groups and CS_2 under high pressure.[4] In exploring a simple synthetic route for the TTF compounds which are capable of forming metal complexes, we have initiated the preparation of pyridyl-substituted TTF compounds from the reaction between a corresponding acetylene compound and CS_2 under high pressure.

Di-2-, 3- and 4-pyridylacetylenes were synthesized according to the reported methods[5—7] and reactions of these pyridyl compounds with CS_2 under pressure were carried out. Di-2-pyridylacetylene was dissolved in CS_2 and the solution was pressurized to 4500 atm and heated at 100 °C for 12 h. Tetra-2-pyridyltetrathiafulvalene was obtained in 80% yield based on the dipyridylacetylene used.



The reactions of di-3- and 4-pyridylacetylene with CS_2 were carried out using similar and more severe conditions (~6000 atm, at 110 °C). However, the corresponding TTF derivatives were not obtained and most of the starting dipyridyl compounds were recovered.

The mechanism for the formation of TTF derivatives under high pressure was proposed to be the dimerization of the 1,3-dithiolium carbene formed from the reaction between an acetylenic compound and CS_2.[4]



Apparently the electronegative nitrogens of di-2-pyridylacetylene make the acetylenic carbon more reactive to CS_2 as compared with those of di-3- and 4-pyridyl compounds. Since pyridinium compounds are highly electron-withdrawing, reactions of di-3- and 4-pyridylacetylenes with CS_2 in the presence of excess CH_3COOH or CF_3COOH were carried out at a pressure of 5000 atm for 12 h at 100 °C. The reactions yielded a brown solid which was found to contain several components, but the corresponding TTF derivatives could not be isolated.

The charge transfer complexes of the tetra-2-pyridyl-TTF synthesized with I_2 and TCNQ were prepared and the electrical conductivities were in the range of 10^{-5}—10^{-4} Ω^{-1} cm^{-1}.

Experimental

Infrared spectra were recorded on a Perkin-Elmer Model 457 grating infrared spectrophotometer. Nuclear Magnetic Resonance spectra were recorded on a Varian A-60 NMR spectrometer or a JEOL JNM-FX 90Q. Ultraviolet spectra were recorded on a Cary 15 UV-VIS spectrophotometer. Mass spectra were obtained at the Rockefeller University Mass Spectrometric Lab. using chemical ionization. Melting points were measured on an electrothermal apparatus and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, New York.

High pressure experiments were performed in Teflon capsules (3 ml capacity) in a stainless steel die and compressed *via* a piston with a Clifton 200 ton hydraulic press.

Materials. Di-2-pyridylacetylene was prepared in a manner identical to that described in the literature[5] in 90% yield, mp 70—73 °C (lit,[5] mp 69—70 °C). Di-3-pyridylacetylene was synthesized in a manner similar to that reported, mp 61—62 °C (lit,[6] mp 60—62 °C). Di-4-pyridylacetylene was also prepared by the method reported, mp 115—116 °C (lit,[7] mp 114 °C).

Synthesis. A typical reaction procedure at high pressure is as follows: Di-2-pyridylacetylene (1.0 g, 5.7 mmol) was dissolved in carbon disulfide (3 ml) and then placed in a Teflon capsule. Pressure was applied at 4500—5000 atm and the capsule was heated at 100 °C for 12 h. Pressure was controlled within 200 atm. After cooling, the capsule was opened and a dark red material was isolated (1.1 g). A brown solid was recrystallized from tetrahydrofuran, mp 287—290 °C. (0.80 g, yield 56%) IR (KBr) 1572, 1442, 1258, 1020, 962, 935 cm^{-1}; λ_{max} 355 nm (ε 8000), 385 (9150), 425 (2000) *m*/*z* 512. Calcd for $C_{26}H_{16}N_4S_4$: C, 60.94; H, 3.10; N, 10.94%. Found: C, 61.10; H, 3.40; N, 11.10%.

TCNQ and I_2 Complexes. To the acetonitrile solution, 20 ml of tetra-2-pyridyl-TTF (1.0 g, 0.02 mol) was added 1 equiv mol of a TCNQ solution (20 ml) in acetonitrile. Upon evaporating the solvent, a dark brown complex was obtained. Tetra-2-pyridyl-TTF powder was exposed to I_2 vapor for 2—4 h and the complex obtained (mol ratio of the TTF to I_2 was 1:0.3, respectively). The electrical conductivities of these compounds were measured on compressed pellets using nickel electrodes with a Keithley electrometer.

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