A NOVEL METHOD FOR THE SYNTHESIS OF SUBSTITUTED TETRATHIA, DISELENADITHIA, AND TETRASELENAFULVALENES

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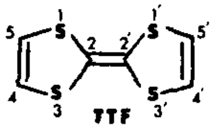
Abstract - A one-step synthesis of tetrathia-, diselenadithia-, and tetraselenafulvalenes at high pressure from CS_2, CSSe, CSe_2, and acetylenes substituted with electron withdrawing groups such as COOH, $COOCH_3$ and $CONH_2$ has been reported. Reactions with CS_2 were found to proceed best at pressures >4000 atm and at 75-100°C. Reaction times in excess of 10 hours were generally employed. CSSe was reacted similarly with these acetylene compounds. Lower temperatures (∿60°C) were needed for reactions involving CSe_2, as this is known to be more reactive than CS_2. Products were obtained in yields >85% and in a high degree of purity. Reactions with propiolic acid gave lower yields, as CO_2 was evolved from the reaction mixture.

INTRODUCTION

In 1973 it was discovered that tetrathiafulvalene (TTF) and tetracyano-p-quinodimethane (TCNQ) form a 1:1 complex which has a conductivity $>10^4 (\text{ohm cm})^{-1}$ at 66°K.[2] This was the highest known conductivity of any organic materials at the time. It was also noted that complexes of TTF derivatives containing selenium in place of some or all of the sulfur were highly conductive, and in some cases had even higher conductivities than TTF:TCNQ.[3] The complex of tetramethyltetraselenafulvalene with PF_6^- was found to be superconducting below 0.9°K at a

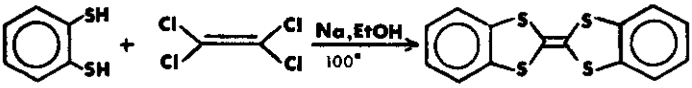


TTF

TCNQ

pressure of about 12,000 atm.[4] As a result of these investigations a considerable research effort was expended on the synthesis of TTF derivatives and their analogs in which some or all of the sulfur has been replaced by the more polarizable selenium.

The first TTF to be synthesized was the 4,5,4',5'-dibenzo derivative (1). This was prepared in 1926 by Hurtley and Smiles[5]. They allowed the disodium salt of o-benzenedithiol to react with tetrachloroethylene, forming (1) in 12% yield. Almost forty years later it was discovered that tetrathiafulvalenes were being formed in good yield upon treating 1,3-dithiolium salts with tertiary amine bases.[6] This was considered the method of choice for preparing tetrathiafulvalenes up until very recently. The one problem associated with this is the synthesis of the 1,3-dithiolium salts. 1,3-Dithiolium hydrogen sulfate was prepared in eight steps from sodium cyanide and carbon disulfide.[7]



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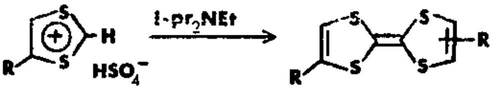
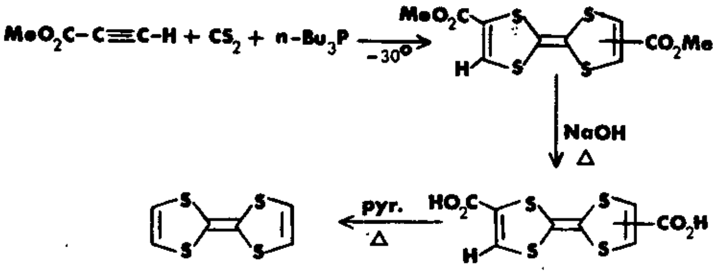


A large amount of effort was expended on improvements to this sequence. Hartzler recently discovered that carbon disulfide reacts directly with acetylenes bearing powerful electron withdrawing substituents such as CF_3 in the presence of a strong acid.[8] A quantitative yield of the substituted TTF was obtained. However, when the acetylene was substituted with CO_2CH_3 groups only 10% of the corresponding TTF was obtained after 4 days at 100°C.

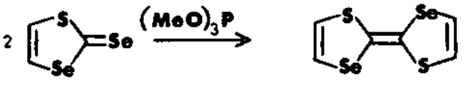
A simple method for the preparation of TTF has been reported, involving the reaction of methyl propiolate with carbon disulfide and tributylphosphine at -30°C.[9]



The product, 4,4'(5')-bis(carbomethoxy)tetrathiafulvalene is then hydrolyzed to the diacid and decarboxylated to give TTF. However, the yield of the first step is only 21%.

The most convenient method reported for the preparation of tetraselenafulvalene (TSeF) involves the reaction of ethylene triselenocarbonate with dimethyl acetylenedicarboxylate forming the substituted 1,3-diselenole-2-selone which is coupled with a tertiary phosphine and decarbomethoxylated with LiBr in HMPA yielding TSeF.[10]

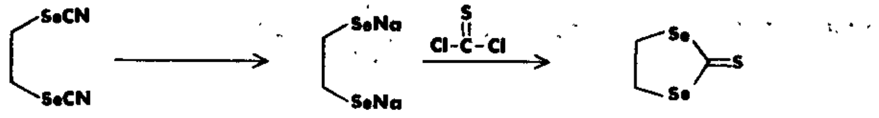
The synthesis of diselenadithiafulvalene derivatives (DSeDTF) is more difficult. Engler and Patel reported that the reaction of sodium acetylide with sulfur, followed by carbon diselenide and a proton source gave 1,3-thioselenole-2-selone which was coupled with trimethylphosphite to give sym(E/Z)-diselenadithiafulvalene (DSeDTF).[11] Although the phosphite coupling step proceeds in good yield

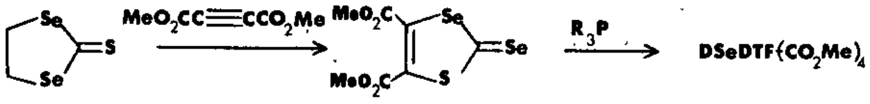


DSeDTF

(∿ 80%), the selone was obtained in only 0.82% yield.

An improved preparation of DSeDTF was developed by Lakshmikantham and Cava.[12] 1,3-Diselenole-2-thione is prepared from ethylene diselenocyanate and thiophosgene in two steps. Upon reaction of the thione with dimethyl acetylenedicarboxylate, 4,5-dicarbomethoxy-1,3-selenothiole-2-selone is formed. This is coupled





as previously mentioned giving DSeDTF after treatment with LiBr in HMPA.

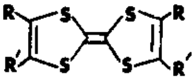
It is a well known fact that liquid-phase reactions characterized by multiple bond formation are greatly facilitated by the application of hydrostatic pressure.[13] Our interest in this field stems from an ongoing investigation on applications of high pressure to organic synthesis.

Recently we disclosed a one-step synthesis of alkoxylcarbonyl substituted tetrathia- and tetraselenafulvalenes from CS_2 or CSe_2 and acetylenes.[14,15] We now report the full details of these reactions as well as the reaction of CSSe with acetylenes.

RESULTS AND DISCUSSION

Recently we have shown that certain TTF derivatives can be readily synthesized by reaction of the corresponding acetylenic compound with CS_2 at high pressure in the absence of a catalyst.[14]

$2R\text{-}C\equiv C\text{-}R' + 2CS_2 \xrightarrow[\text{heat}]{\text{high pressure}}$



and trans isomer

(2), $R=CO_2CH_3$; $R'=H$
(3), $R=R'=CO_2CH_3$
(4), $R=CO_2H$; $R'=H$
(5), $R=R'=CONH_2$

The reaction of dimethyl acetylenedicarboxylate with carbon disulfide at 4900 atm and 75°C for 20 h yielded the desired tetrathiafulvalene(3)in 92% yield. This was identical to the known compound in all respects.[8] Temperature was found to be an important variable. When the reaction was attempted at 4500 atm and room temperature for 70 h no product was obtained.

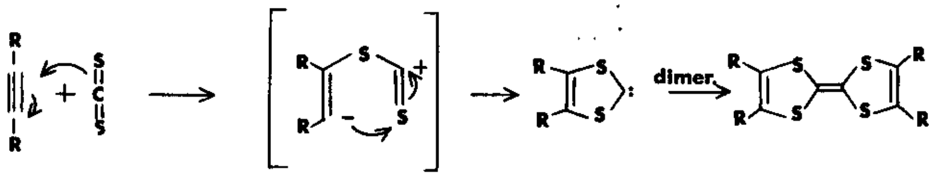
Methyl propiolate reacted in an analogous manner at 5800 atm and 100°C for 26 h.

4,4'(5')-Bis(carbomethoxy)tetrathiafulvalene(2) was formed in 96% yield. The reaction was found to work best at high pressures. Reaction at 8 atm and 100°C for 24 h yielded only 3% of product(2). Increased yields were also observed when reactions were allowed to proceed overnight. When the reaction was run at 4900 atm and 110°C for only 4h, a 38% yield of (2) was obtained.

Acetylene dicarboxamide reacts with carbon disulfide at 6200 atm and 95°C to form 4,4',5,5'-tetrakis(carboxamido)tetrathiafulvalene.

The reaction of propiolic acid with carbon disulfide was found to be particularly sensitive to temperature. When the reaction was run at >80°C, a relatively large volume of CO_2 was evolved and the TTF dicarboxylic acid was obtained in about 70% yield. At 60°C very little gas evolution was observed, but the yield of diacid (4) was low, 8%. Upon heating propiolic acid to 100°C at 5000 atm in the absence of carbon disulfide, no CO_2 was evolved. It is believed that decarboxylation of TTF diacid at elevated temperatures occurs, giving rise to CO_2.

A mechanism for the formation of TTF derivatives under high pressure is believed to be that proposed by Hartzler[8]; dimerization of the 1,3-dithiolium carbene.



The reaction of carbon disulfide with acetylenes substituted with non-electron withdrawing groups under similar conditions to those described above yields only traces of products except for those cases in which the acetylene can polymerize. 1-Pentyne reacted with CS_2 at high pressure to give only a trace amount of red oil which was not found to have a TTF structure. Phenylacetylene yielded a reasonable amount of product which was identified as a polyphenylacetylene. Diphenylacetylene gave back starting material quantitatively upon attempted reaction with carbon disulfide at high pressure. Selenium is known to be more polarizable and reactive than sulfur. Thus, we have investigated the reactions of CSe_2 with acetylenic compounds.

Dimethyl acetylenedicarboxylate, methyl propiolate, propiolic acid, and acetylene dicarboxamide were reacted with CSe_2 in methylene chloride solution at 60-65°C and 4500-5000 atm for 10 h resulting in corresponding tetraselenafulvalenes (TSeF) in good yield (85-90%). Carbon diselenide was more reactive toward the acetylenic compounds than carbon disulfide. However, acetylenes disubstituted with methyl, phenyl, and chloromethyl groups did not react with CSe_2 under conditions similar to those mentioned above. At higher temperatures ∿100°C, CSe_2 tended to polymerize.

Carbon sulfoselenide (CSSe) reacted with acetylenes, such as dimethyl acetylenedicarboxylate, methyl propiolate, propiolic acid, and acetylene dicarboxamide at high pressure, giving the corresponding sym-diselenadithiafulvalenes. These results along with those of CS_2 and CSe_2 are summarized in Table .

Sym (E and Z)

DSeDTF

where

R = CO_2Me R' = CO_2Me
= CO_2Me = H
= CO_2H = H
= $CONH_2$ = $CONH_2$

Table Results from the Reaction of CS_2, CSe_2 and CSSe with Acetylenes Bearing Electron Withdrawing Groups

Compounds

(R_1-C≡C-R_2)

	R_1	R_2	P(atm)	Temp. (°C)	Time(hr)	Crude Yield(%)
CS_2	$-CO_2Me$	$-CO_2Me$	5100	100	24	87
			4900	75	20	92
			4500	20	70	0
"	$-CO_2Me$	-H	5800	100	26	96
			4700	100	23	84
			4100	80	23	88
			8	100	24	3
			90	100	23	12
			4900	110	4	38
"	$-CO_2H$	-H	5800	85	19	69
			5400	95	26	20
			4700	60	24	8
			9	100	22	5
			86	100	23	12
"	$-CONH_2$	$-CONH_2$	6200	95	24	85

Table (cont)

CSe_2	$-CO_2Me$	$-CO_2Me$	5000	60	13	90
			sealed tube	70-80	72	10
"	$-CO_2Me$	-H	5000	60	13	85
			sealed tube	70-80	72	0
"	$-CO_2H$	-H	5000	60	15	62
"	$-CONH_2$	$-CONH_2$	5000	65	15	87
CSSe	$-CO_2Me$	$-CO_2Me$	5000	100	15	89
"	$-CO_2Me$	-H	5000	100	15	85
"	-COOH	-H	5000	85	12	70
"	$-CONH_2$	$-CONH_2$	5000	90	12	80

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-FX90Q. Ultraviolet spectra were recorded on a Cary 15 UV-VIS spectrophotometer. Melting points were measured on an Electrothermal apparatus and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

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. Autoclave experiments were done in a Parr Pressure reactor and compressed with nitrogen.

Materials

Dimethyl acetylenedicarboxylate, methyl propiolate, propiolic acid, dimethylacetylene, phenyl and diphenylacetylenes were purchased from Aldrich and purified by distillation or recrystallization. CSe_2 was synthesized according to the literature[16] and was also obtained from Alfa Products. CSSe was prepared by the modified method described in the U.S. patent[17] from phenyl isothiocyanate and hydrogen selenide.

Synthesis

A typical reaction procedure at high pressure is as follows: Methyl propiolate (5 mL, 56 mmol) was dissolved in carbon disulfide (15 mL, 250 mmol) and a portion (3 mL) of this mixture was placed in a Teflon capsule. Pressure was applied at 5000-5500 atm and the capsule was heated at 100°C for 26 h. Pressure was controlled within ±200 atm. After cooling, the capsule was opened and a dark red solid and a small amount of a red solution were obtained. The solid was isolated, washed repeatedly with CS_2, and dried in vacuum. The dark brown solid obtained was 1.28 g (96% yield, bases on the acetylene compound used) and the melting point was 236-240°C. Recrystallization from 1,2-dimethoxyethane gave red crystals: mp 242-244°C (lit.[9] mp 244-245°C). IR(KBr) 3060,3040,1700,1580,1250,820 cm^{-1}. UV(CH_2Cl_2) $\lambda_{max}(\varepsilon)$450(2000) 312 (9154) 301 (8846) 290 (8000) 235 nm (10,500). For the reactions with CSe_2 and CSSe, methylene chloride was used as a solvent and typical examples are as follows: a mixture of dimethyl acetylenedicarboxylate (0.28 g, 2.0 mmol) and CSe_2 (0.38 g, 2.2 mmol) in CH_2Cl_2 (3 mL) was heated while being compressed in a Teflon capsule in a hydraulic press. A dark, brownish solid and red solution were obtained. The odor of CSe_2 (rotten radish) disappeared after completion of the reaction. The solid was filtered and washed with hexane. The dried solid (0.58 g) had m.p. 136-142°C, yield 93% based upon dimethyl acetylenedicarboxylate used. The crude product was recrystallized from methanol-benzene m.p. 144-145°C (Lit.[10] 144-145°C) IR (KBr) 1720, 1565, 1435, 1250 and 1275 cm^{-1}; λmax (cyclohexane)(log ε) 260 (4.40), 285 (4.43), 328 sh (3.70) and 422 nm (3.56); m/e 628 (based on ^{80}Se).

A mixture of methyl propriolate (0.5 g, 5.8 mmol) and CSSe (0.8 g, 6.4 mmol) in 5 ml methylene chloride was prepared. The three ml capacity Teflon reaction capsule was filled with a portion of this starting mixture and heated at 100°C under 5000 atm for 15 h. A brown solid and a red solution were obtained. The solid was filtered and washed with hexane and then dried under reduced pressure. A brown solid obtained was 0.53 g, 82% yield based upon methylene propiolate used. Column chromatography of the solid obtained, on silica, eluting with cyclohexane-benzene, afforded a red solid which was crystallized from benzene-methanol to yield a red crystal mp 254-255°C. IR(KBr) 1710, 1545, 1430, 1250, 1040, 940, 830 and 730 cm^{-1}; m/e 416 (based on ^{80}Se)

Typical experimental conditions for the synthesis under low pressure are as follows. Propiolic acid (10 mL, 163 mmol), CS_2(15 mL, 250 mmol), and methylene chloride (15 mL) were mixed in a stainless-steel autoclave. The autoclave was repeatedly evacuated and filled with nitrogen and then nitrogen was admitted up to 70 atm. The contents were heated at 100°C for 23 h (pressure increased to 100 atm). After cooling, the autoclave was opened and the CO_2 gas evolved was detected with $Ba(OH)_2$solution. The compound was isolated as described above. The yield was 2.90 g, 12% based on the starting acetylene.

References:

1a. The authors wish to dedicate this work to Professor H. C. Brown on the occasion of his 70th birthday.

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