(m, 6, CH_2), 1.73 (d, 6, J = 7 Hz, CH_3). Anal. Calcd for $C_7H_{14}N_2$: C, 66.62; H, 11.18; N, 22.20. Found: C, 66.54; H, 11.16; N, 22.27.

Synthesis of *cis*-3,7-Dimethyl-1,2-diaza-(*Z*)-1-cycloheptene (2). The procedure used was similar to that described above except that the reaction time was only 18 h. Isolation of the product, lyophilization, and a pot-to-pot distillation produced analytically pure *cis*-3,7-dimethyl-1,2-diaza-(*Z*)-1-cycloheptene (2) in 95.5% yield. Compound 2 is a pale yellow liquid: $n^{25.4}_{\mathrm{D}}$ 1.4669; IR (neat) 6.38 (N=N), 7.25 μm (CCH_3); UV (isooctane) λ_{max} 401 nm (ε 85.5); NMR ($CDCl_3$) δ 4.47 (m, 2, CH_3CH), 1.58 (m, 6, CH_2), 1.50 (d, 6, J = 7 Hz, CH_3). Anal. Calcd for $C_7H_{14}N_2$: C, 66.62; H, 11.18; N, 22.20. Found: C, 66.67; H, 11.30; N, 22.14.

Dipole Moment Measurements. A DM01 dipole meter[13] operating at a fixed frequency of approximately 2.0 MHz and a cylindrical, gold-plated, thermostated cell were used for all dielectric determinations. On the average, five solutions of the compound of varying concentrations in dry cyclohexane (molecular sieves) were used.

Indices of refraction were measured by using a Zeiss dipping refractometer. The same solutions were used for both the dielectric and refractometric measurements. The dipole moments were calculated by using the method of Guggenheim.[14,15]

Europium Shift Experiments. Approximately 25% solutions of the europium shift reagent [Eu(fod)$_3$] in either CCl_4 or $CDCl_3$ were prepared and stored in 5-mL standard septum bottles equipped with Teflon Mininert valves (Thompson Packard, Little Falls, NJ). When not in use, the shift reagent solution was stored in the refrigerator in a jar containing Drierite as desiccant.

In a typical experiment, after 25–50 mg of the substrate was weighed into an NMR tube, 0.3 mL of the solvent was added by syringe, and the NMR spectrum was obtained. Successive 50- to 100-μL portions of the shift reagent were added; the NMR spectrum was recorded after each addition of shift reagent. An average of five points was obtained for each experiment. The ΔEu values were obtained by calculating the slope of the line from a plot of the observed downfield chemical shifts (δ) against the Eu(fod)$_3$/substrate molar ratios.

The chemical shifts of the methyl protons of the shift reagent were obtained in a similar manner. However, the chemical-shift values reported for these methyl protons in the presence of various azo compounds represent the values where the molar ratio Eu(fod)$_3$/substrate is equal to 0.10.

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Registry No. 1, 15391-75-0; 2, 75767-79-2; 3, 75767-80-5; 4, 56485-35-9; 5, 75767-81-6; 6, 5700-00-5; 6-monooxalic acid salt, 75767-82-7; 6-monotartaric acid salt, 75780-67-5; 7, 75767-83-8; 8 (cis), 75767-84-9; 8 (trans), 75767-85-0; 9, 75767-86-1; 10, 75767-87-2; 1,2-dicarbethoxyhydrazine, 4114-28-7; 1,5-dibromopentane, 111-24-0; 2,6-heptanediol, 5969-12-0; 2,6-heptanedione, 13505-34-5.

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One-Step Synthesis of Substituted Tetrathiofulvalenes under High Pressure

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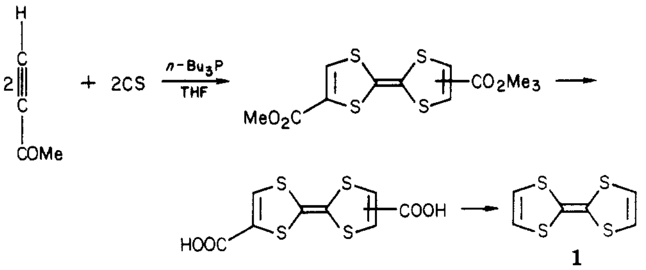
Since the discovery that tetrathiofulvalene (TTF) (1) can form a complex with tetracyanoquinodimethane (TCNQ), which has one of the highest known conductivities of any organic material,[1,2] there has been an enormous amount of research on the synthesis and properties of TTF and its derivatives.[3-6] One of the simplest routes reported for the synthesis of TTF involved the reaction of methyl propiolate with CS_2 in the presence of tributylphosphine.[4]

Table I. Reactions of Carboxyl- and Methoxycarbonyl-Substituted Acetylenes with CS_2 under Pressure

reactant	temp, °C	time, h	pressure, atm	% yield
$MeO_2CC{\equiv}CCO_2Me$	100	24	5000	87
$MeO_2CC{\equiv}CCO_2Me$	20	70	4500	0
$MeO_2CC{\equiv}CH$	100	26	5500	96
$MeO_2CC{\equiv}CH$	80	24	4000	88
$MeO_2CC{\equiv}CH$	100	24	100	12
$MeO_2CC{\equiv}CH$	100	24	10	3
$HO_2CC{\equiv}CH$	85	19	5500	69
$HO_2CC{\equiv}CH$	95	25	5500	20
$HO_2CC{\equiv}CH$	100	23	100	12
$HO_2CC{\equiv}CH$	100	22	10	5



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THF was employed as the solvent and the reaction was carried out at –30 °C. The yield of the first step was only 21%.

It is a well-known fact that liquid-phase reactions characterized by multiple bond formation are greatly facilitated by the application of hydrostatic pressure.[7] Our interest in this field stems from an ongoing investigation on the application of high pressure to organic synthesis. Thus, we initiated an investigation of the reactions of carboxyl and alkoxylcarbonyl-substituted acetylenes with CS_2 under high pressure in the absence of catalyst.

Results are summarized in Table I. In general, these reactions under high pressure gave rather pure products in good yield. During the reaction of propiolic acid with CS_2, CO_2 was evolved. This was found to be more pronounced at higher reaction temperatures. CO_2 may be formed by the decomposition of the product to TTF.[8] Thus, the yield of the TTF dicarboxylic acid was found to be lower than that of the ester derivatives.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 457

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[7] K. E. Weale, "Chemical Reactions at High Pressure", E. and F. N. Spon, Ltd., London, 1967, pp 175–200.

[8] TTF was obtained by decarboxylation of the dicarboxylic acid derivative in a sealed tube.[4]

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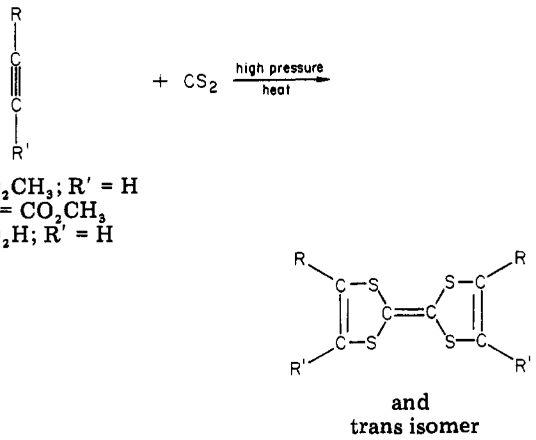
J. Org. Chem. **1981**, *46*, 447–450



2, R = CO_2CH_3; R' = H
3, R = R' = CO_2CH_3
4, R = CO_2H; R' = H

grating infrared spectrophotometer as KBr pellets. Melting points were measured with an electrothermal melting-point apparatus and are uncorrected. Dimethyl acetylenedicarboxylate, methyl propiolate, propiolic acid, and carbon disulfide were purchased from Aldrich and were used as received. Reactions at high pressure (4000–6000 atm) were run in Teflon capsules (3-mL capacity) placed in a steel die equipped with a heating band and pressed with a hydraulic press (Clifton 200 ton press). Reactions at low pressure (10–100 atm) were run in a Parr pressure reactor and were compressed with nitrogen.

Representative High-Pressure Reactions. Synthesis of 4,4'(or 5')-Bis(carbomethoxy)tetrathiafulvalene. 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, based 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.[4] mp 244–245 °C); IR 3060, 3040, 1700, 1580, 1250, 820 cm^{-1}.

Synthesis of 4,4',5,5'-Tetrakis(carbomethoxy)tetrathiafulvalene. The reaction of dimethyl acetylenedicarboxylate and CS_2 was carried out and the solid **3** was isolated as described in the synthesis of **2**. Recrystallization from ether–hexane gave red crystals: mp 163–167 °C (lit.[6] mp 168–169 °C); IR 1740, 1720, 1575, 1225 cm^{-1}.

Synthesis of Tetrathiafulvalene-4,4'(or 5')-dicarboxylic Acid. The reaction of propiolic acid and CS_2 yielded the crude compound **4** under high pressure as described above. It was found that CO_2 gas was evolved from the reaction mixture when the capsule was opened. The solid was washed with CS_2, dissolved in 1 N NaOH, filtered, and acidified with 2 N HCl. The product was filtered and dried overnight under reduced pressure at 60 °C: mp 360 °C (lit.[4] mp 360 °C); IR 3500–2500, 1660, 1550 cm^{-1}.

Typical experimental conditions for the synthesis of **2**–**4** 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.

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Registry No. (*E*)-**2**, 75444-58-5; (*Z*)-**2**, 75444-59-6; **3**, 26314-39-6; (*E*)-**4**, 74857-63-9; (*Z*)-**4**, 74857-62-8; methyl propiolate, 922-67-8; propiolic acid, 471-25-0; dimethyl acetylenedicarboxylate, 762-42-5; CS_2, 75-15-0.

Effect of Metal Ions in Organic Synthesis. 6. Reactivity of the Azo Ene System of Phenylazostilbene in the Presence of Copper and Iron Ions

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Our previous papers discussed some effects of metal ions in organic synthesis.[1-4] Preliminary results were reported on the stereospecific 1,4-additions of certain alcohols to the azo ene system of phenylazostilbene (PAS) in the presence of copper and iron ions.[2] This paper reports further findings about the role of metal ions in these reactions.

A rapid decomposition of PAS in the presence of copper(II) chloride dihydrate (CCD) was previously mentioned.[2b] However, by reduction of the amount of CCD to a catalytic one, a very fast and quantitative conversion of PAS into the corresponding alkyl ethers of benzoin phenylhydrazone (AEBP) was observed. Under such conditions these reactions will occur either at room temperature or at lower temperatures. An activity lower than that of CCD, but considerably higher than that of the other inorganic salts, was revealed by anhydrous iron(III) chloride. Scheme I shows a general representation of this reactivity. The relative ratio between the syn-anti AEBP derivatives, the reaction times, and conditions are listed in Table I.

The stereospecificity of the 1,4-addition of the alcohols to the azo ene system of PAS appears to be considerably dependent upon the type of inorganic salt used. On the basis of the results reported in Table I, we can formulate the following reactivity order: copper(II) chloride dihydrate > anhydrous iron(III) chloride > iron(III) sulfate *n*-hydrate > copper(II) sulfate pentahydrate > iron(II) sulfate heptahydrate > anhydrous copper(I) chloride. The oxidized forms of the inorganic ions are much more effective than the reduced form and, for the same oxidation state of metal ions, chloride derivatives seem to be much more effective than the corresponding sulfate derivatives.

At this stage, we can hypothesize the formation of organometallic complexes which activate the azo ene system in these 1,4-addition reactions. Indeed, several metal ion–nitrogen derivative complexes are known.[1-4,6,7] Our

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