1,3-Dithiolium Carbenes from Acetylenes and Carbon Disulfide[1]

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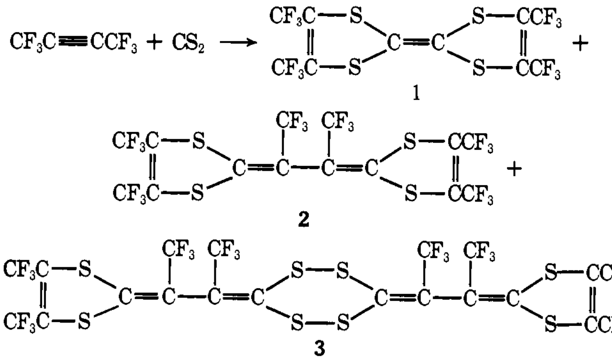
Abstract: Carbon disulfide reacted with electron-deficient acetylenes to generate 1,3-dithiolium carbenes which formed compounds **1**, **2**, and **3** from hexafluoro-2-butyne and **6**, **7**, and **21** from dimethyl acetylenedicarboxylate. The 1,3-dithiolium carbenes were intercepted with alcohols to form 2-alkoxy-1,3-dithioles and with phenols to form hydroxyaryldithioles. Aliphatic aldehydes and ketones produced acylmethylenedithioles. Aromatic aldehydes gave aroyldithioles. Olefins and carboxylic acids were also incorporated into the reactions and the products were identified. The heterocumulenes carbonyl sulfide and diisopropylcarbodiimide reacted differently giving acyclic products and 2 + 2 cycloadducts, respectively. A consistent mechanistic explanation of the results is given.

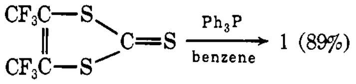
The chemistry of carbon disulfide has been studied extensively. Most reactions of carbon disulfide proceed from an initial nucleophilic attack at carbon.[2,3] Recently, a few cycloadditions to carbon disulfide have been observed.[4] We wish to report a new type of chemistry of carbon disulfide proceeding by way of electrophilic attack at sulfur with an electron-deficient acetylene leading to the aromatic, nucleophilic 1,3-dithiolium carbenes. An extensive chemistry of the 1,3-dithiolium carbenes has been discovered and reactions of the carbenes with alcohols, phenols, aldehydes, ketones, acids, and olefins will be exemplified.

Results

Perfluoro-2-butyne and carbon disulfide reacted slowly at 100° to give the adducts **1**, **2**, and **3**. The predominant product (60%) was **2** when a 3:1 molar ratio of carbon disulfide to acetylene was used. Under these conditions a 20% yield of **3** and a 2% of **1** were obtained. When a 6:1 molar ratio of reactants was used, a 60% yield of **3** and an 8% yield of **2** were obtained. In the presence of trifluoroacetic acid (see below) a quantitative yield of **1** was obtained. The three products are all stable and did not interconvert under the reaction conditions.



Compound **1** was synthesized independently in 89% yield by desulfurization of the trithiocarbonate **4**.



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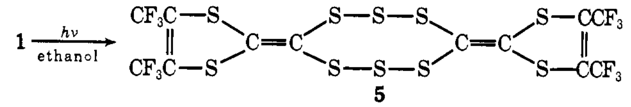
A similar desulfurization of *trans*-1,2-cyclohexene trithiocarbonate with alkyl phosphites to give a bi-1,3-dithiole has been described.[5] Compounds analogous to **1** have also been obtained recently by reactions of carbon disulfide with benzyne[6] and with 3,3,7,7-tetramethylcycloheptyne.[7] The red-orange bi-dithiole **1** is chemically quite inert. It is unreactive toward oxidizing agents such as hydrogen peroxide and potassium permanganate. It undergoes reversible polarographic one-electron oxidation in acetonitrile solution at +1.05 V *vs.* the saturated calomel electrode. The cation radical is further oxidized (irreversibly) at +1.28 V. The cation radical is, therefore, much less readily obtained than is that of the unsubstituted bi-dithiole.[8] Attempted cycloaddition reactions of **1** with tetracyanoethylene, hexafluoro-2-butyne, and dimethyl acetylenedicarboxylate resulted in recovery of **1**. The mass spectrum of **1** exhibited an intense peak at half the molecular weight. Attempts to generate a 1,3-dithiolium carbene by thermolysis or flash photolysis of **1** were unsuccessful. Upon prolonged irradiation at 2537 Å **1** underwent the bizarre transformation to give **5** in 36% yield (assuming a stoichiometry where 4 mol of **1** is required per mol of **5**, or in 27% yield if a 3:1 stoichiometry is assumed). The structure proof of **5** rests primarily upon its symmetry (all fluorines are magnetically equivalent) and upon its mass spectral cracking pattern (see Experimental Section).



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Compound **2** had been characterized previously.[9] Comparison of the two samples by melting point and spectra established identity.

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[1] Preliminary communications: H. D. Hartzler, *J. Amer. Chem. Soc.*, **92**, 1412, 1413 (1970).

[2] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. IV, Chemical Publishing Co., New York, N. Y., 1963, p 422.

[3] W. O. Faye, *J. Chem. Educ.*, 841 (1969).

[4] R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565 (1963); K. B. Sukumaran, C. S. Angadiyavar, and M. V. George, *Tetrahedron*, **28**, 3987 (1972).

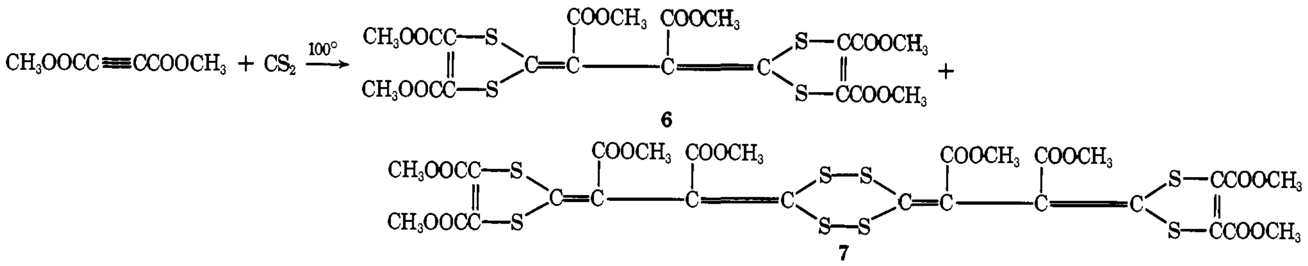
[5] E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Amer. Chem. Soc.*, **87**, 934 (1965).

[6] E. K. Fields and S. Meyerson, *Tetrahedron Lett.*, 629 (1970).

[7] A. Krebs and H. Kimling, *Angew. Chem., Int. Ed. Engl.*, **10**, 509 (1971).

[8] F. Wudl, G. M. Smith, and E. J. Hufnagel, *Chem. Commun.*, 1453 (1970).

[9] C. G. Krespan and D. C. England, *J. Org. Chem.*, **33**, 1850 (1968).

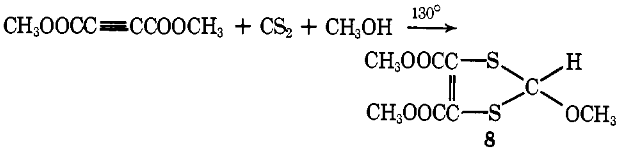


The structure of **3** is based primarily upon the assumed mechanism of its formation (see below). Spectral and analytical data are consistent with this formulation.

Dimethyl acetylenedicarboxylate and carbon disulfide gave a similar reaction. A compound similar to **1** was isolated from this reaction only when an acid catalyst was used. The reaction with the acetylenic ester was not as clean as that with the fluorinated acetylene. A 4.8% yield of **6** and a 5.1% yield of **7** were obtained. No attempt to optimize conditions was made, however.

Compound **6** showed resonances of three methoxyl groups of equal intensity. The mass spectral fragmentation pattern of **6** which shows strong parent and half-parent peaks is consistent with the assigned structure. The assignment of structure **7** as with **3** is discussed below. An independent synthesis of **7** was recently reported.[10]

Simpler chemistry was observed when coreactants were heated with acetylenes and carbon disulfide. A 60% yield of the methoxydithiole **8** was obtained



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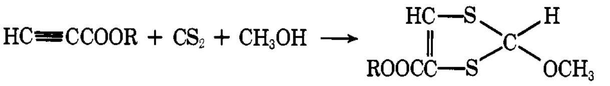
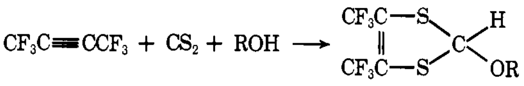
from dimethyl acetylenedicarboxylate, carbon disulfide, and methanol. This is in contrast to the poor yields of **6** and **7** in the reaction without methanol. Dimethyl methoxyfumarate and methoxymaleate were also formed in the reaction. Propiolate esters were also found to undergo this reaction.



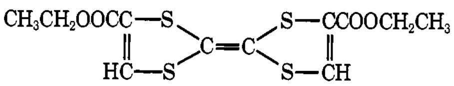
9, R = CH_3
10, R = CH_3CH_2

With hexafluoro-2-butyne the alkoxydithioles were formed to the *complete exclusion* of compounds **1**, **2**, and **3**, whereas the formation of **10** was accompanied



11, R = CH_3
12, R = CH_3CH_2

by a small amount of **13** or **14**. The alkoxydithioles **8–12** were all adequately characterized (see Experimental Section).



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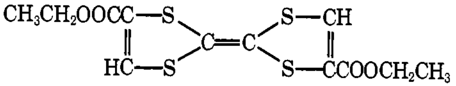

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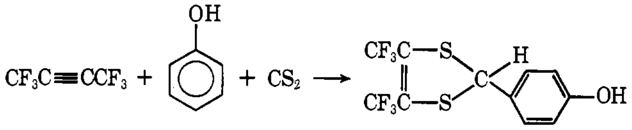
Phenols did not react analogously. Those phenols activated for electrophilic substitution yielded hydroxyaryl-1,3-dithioles.



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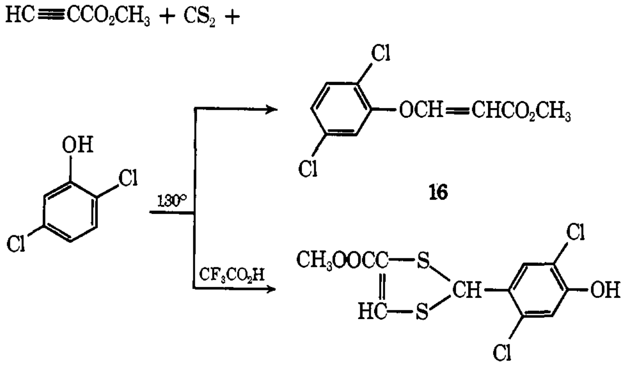
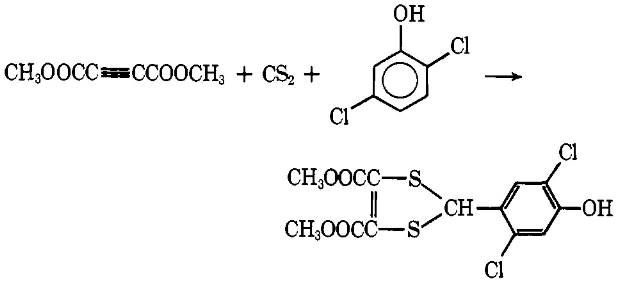
In one case to get the hydroxyaryldithiole, we had to add acid to suppress the Michael addition of phenol to acetylene. Thus, methyl propiolate, 2,5-dichlorophenol, and carbon disulfide gave the acrylate **16**,



but when trifluoroacetic acid was added, the dithiole **17** was obtained in 53% yield. The same phenol with dimethyl acetylenedicarboxylate gave a dithiole in 49% yield without added acid.



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In all cases only products substituted para to the hydroxyl group were isolated.

Carboxylic acids also entered into reaction with acetylenes and carbon disulfide. Acids also catalyzed the formation of the bi-dithioles. While **1** was formed

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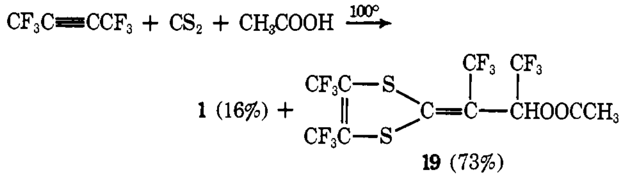
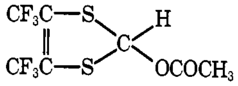
(10) D. L. Coffen, *Tetrahedron Lett.*, 2633 (1970).

in only 2% yield from perfluoro-2-butyne and carbon disulfide, it was formed in 16% yield when acetic acid was present. Along with **1** there was obtained a 73% yield of **19**. No acetoxydithiole **20** was found, although its presence was sought. Compounds analogous to **20** were not found in any of the reactions with carboxylic acids. It was found that stronger acids gave even higher yields of **1**. Formic acid gave a 50% yield of **1**, and the yield was quantitative with trifluoroacetic acid.



19 (73%)



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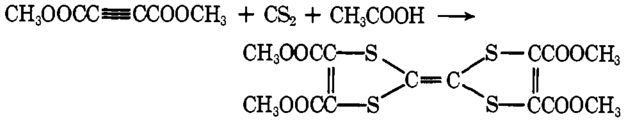
The acid catalysis of bi-dithiole formation was utilized to prepare **21** which had not been isolated in the reaction of the acetylene and carbon disulfide alone.



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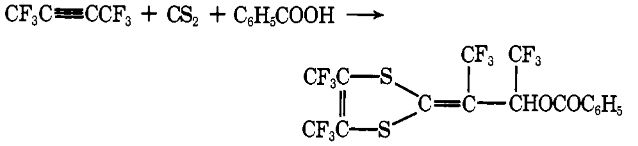
With benzoic acid a 74% yield of **22** was obtained.



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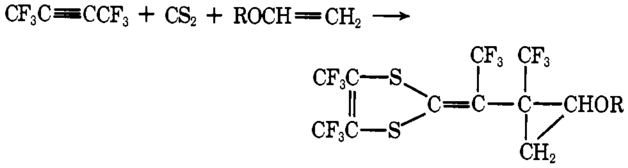
Only trace amounts of bi-dithiole **1** were formed in this reaction.

In certain cases, olefins also entered into reaction with acetylenes and carbon disulfide. Alkyl vinyl ethers gave good yields of cyclopropanes **23** and **24**.

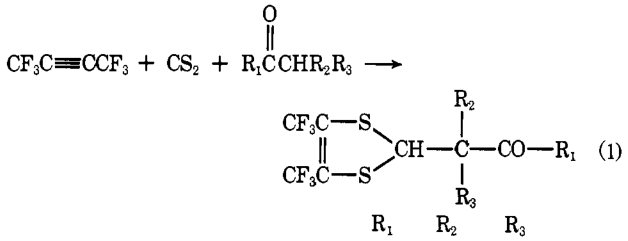


23, R = CH_3
24, R = CH_2CH_3

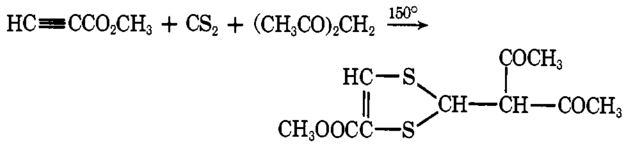
The products were obtained as pairs of isomers which were not completely separated. The isomer mixture made structural elucidation more difficult, but the near infrared absorption characteristic of cyclopropyl methylene[11] at 6060 cm^{-1} was clearly seen. With ethylene a product believed to be analogous to **23** and **24** was obtained, but in a yield too low to permit adequate characterization. The major portion of the reaction product consisted of **1**, **2**, and **3**.

Dimethyl fumarate, perfluoro-2-butyne, and carbon disulfide gave only **1**, **2**, and **3**. With dimethyl maleate, **1**, **2**, and **3** were also formed along with substantial amounts of dimethyl fumarate. Control experiments established that dimethyl maleate was not isomerized by heating with either carbon disulfide or with perfluoro-2-butyne.

Aliphatic aldehydes and ketones gave yet another type of reaction with carbon disulfide and acetylenes. New aldehydes and ketones were obtained in which a dithiole ring had been (formally) inserted into an α hydrogen (eq 1). Yields ranged from 79% with acetophenone and 75% with cyclohexanone to 19% with acetone. Where the yields were poor as with acetone, correspondingly larger amounts of **1**, **2**, and **3** were formed in the reactions. Generally reactions with acetylenic esters and ketones were not clean enough to isolate analogous products, but a 17% yield of **32** was obtained from methyl propiolate, carbon disulfide, and pentane-2,4-dione.



	R_1	R_2	R_3
25	H	H	CH_3
26	CH_3	H	H
27	H	CH_3	CH_3
28	CH_3	H	CH_3
29	CH_3	H	$COCH_3$
30	C_6H_5	H	H
31	-$(CH_2)_4$-		H



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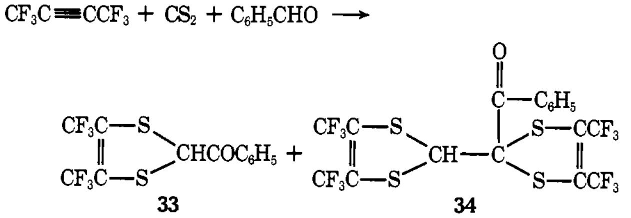
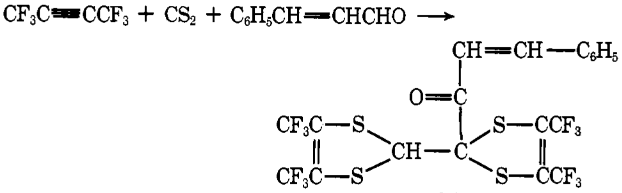
Benzaldehyde formed two products with carbon disulfide and perfluoro-2-butyne. With a 40% excess of benzaldehyde (over acetylene) compounds **33** and **34** were formed in a 3:7 ratio in a total yield of 75%. It was shown that **34** was formed from **33** by a reaction similar to those above with aliphatic aldehydes and ketones. With cinnamaldehyde only **35** was isolated



33 **34**



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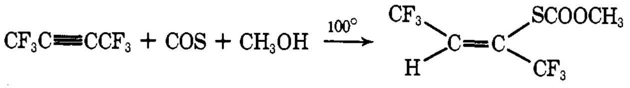
(11) P. G. Gassman and F. V. Zalar, *J. Org. Chem.*, 31, 166 (1966).

although the simpler cinnamoyldithiole was undoubtedly present in the crude reaction mixture.

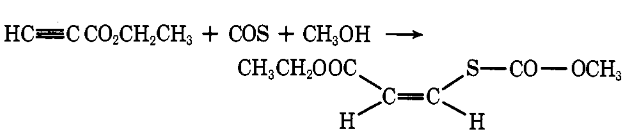
Brief attempts were made to see whether other heterocumulenes could replace carbon disulfide in acetylene addition reactions. No reaction was observed between carbonyl sulfide and perfluoro-2-butyne or ethyl propiolate after 5 days at 100°. Reaction was observed, however, when methanol was present. In a very clean, but slow reaction, **36** was obtained as the



$$\mathrm{CF_3C{\equiv}CCF_3 + COS + CH_3OH \xrightarrow{100^\circ} (CF_3)(H)C{=}C(SCOOCH_3)(CF_3)}$$

36

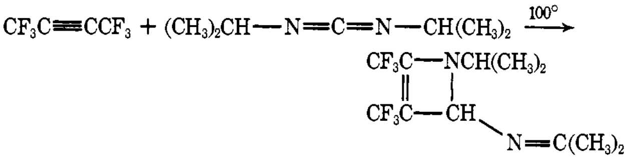
sole product from carbonyl sulfide, methanol, and perfluoro-2-butyne. Only the isomer resulting from trans addition was found. An identical result was obtained with ethyl propiolate, although the reaction was even slower.



$$\mathrm{HC{\equiv}CCO_2CH_2CH_3 + COS + CH_3OH \longrightarrow (CH_3CH_2OOC)(H)C{=}C(S{-}CO{-}OCH_3)(H)}$$

37

A completely different type of cycloaddition was observed with carbodiimides. Diisopropylcarbodiimide and perfluoro-2-butyne gave the azetine **38**.



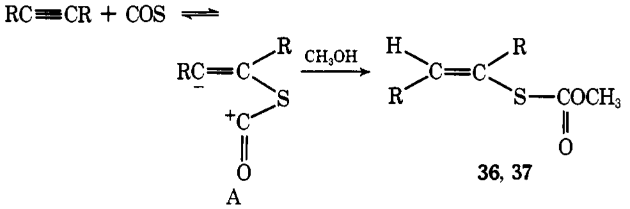
$$\mathrm{CF_3C{\equiv}CCF_3 + (CH_3)_2CH{-}N{=}C{=}N{-}CH(CH_3)_2 \xrightarrow{100^\circ}}$$

38

No evidence for chemistry similar to that of carbon disulfide was found. Phenyl isothiocyanate was totally unreactive toward perfluoro-2-butyne at 100°.

Discussion

The addition of carbon disulfide to acetylenes to produce the wide variety of dithioles outlined above requires an acetylene with at least one electron-withdrawing group. All attempts to find similar chemistry with diphenylacetylene, 2-butyne, vinylacetylene, and acetylene were unsuccessful. This structural requirement suggests an initial nucleophilic attack on the acetylene. The experiments with carbonyl sulfide suggest a reversible nucleophilic attack on the acetylene to produce the zwitterion A. In the absence of

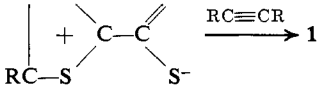


suitable traps, A collapses to starting materials. A does not cyclize as does the analogous intermediate in the carbon disulfide reactions, for this would necessitate nucleophilic attack at the oxygen of the carbonyl (an unprecedented reaction). With alcohols present A goes on to products.[12] Only trans addition to the acetylenes was observed. This appears to be general for sulfur nucleophiles and electron-deficient acetylenes.[13]

With carbon disulfide the formation of B (Scheme I) is the rate-determining step for all the subsequent chemistry. We have no information concerning the reversibility of formation of B, but since B has never been trapped, it must cyclize at a rate faster than a diffusion-controlled protonation. Cyclization produces the 1,3-dithiolium carbene C. The rate of B → C should be high, for C has the aromatic stabilization of a 1,3-dithiolium cation (see below). In the absence of coreactants, C adds readily to the acetylene to form a new carbene D. We find no evidence whatsoever for the alternate adduct the cyclopropene. The addition of C to the acetylene to give D is analogous to reactions of isocyanides with hexafluorobutyne[14] and with dimethyl acetylenedicarboxylate.[15]

In the absence of efficient traps for D, further reaction with carbon disulfide would produce E or F. Dimerization would give the tetrathianes **3** and **7**. Tetrathianes have been obtained previously in reactions of carbon disulfide with diphenyldiazomethane and diazofluorene.[16] It was suggested that the tetrathianes arose by dimerization of α-dithiolactones. Reaction of E or F with the acetylene would produce **2** and **6**. A model for this reaction (the reaction of phosphine carbon disulfide complexes with acetylenes) has been described previously.[17] The partitioning of E or F by reaction with acetylene or by dimerization rationalizes the variation in yield of **2** and **3** with changing acetylene concentration. Reaction of dimethyl acetylenedicarboxylate with a large excess of carbon disulfide gave **7**, but no **6** was isolated.[10]

The formation of **1** in the absence of acid could occur by dimerization of C. Although carbene dimerization in solution is generally improbable, the dithiolium carbene C probably has a much longer lifetime than most carbenes. The yield of **1** was also quite low.



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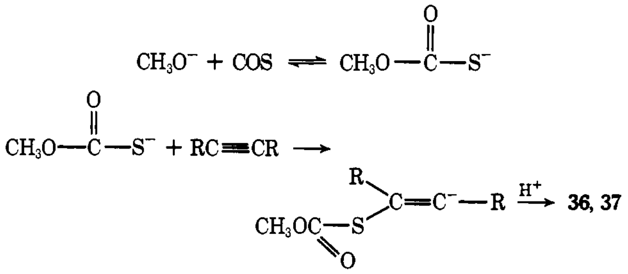
[12] We cannot rigorously exclude the following alternate mechanism



We believe it less likely because the addition can be accomplished with trifluoroacetic acid present.

[13] W. E. Truce and J. A. Simms, *J. Amer. Chem. Soc.*, **78**, 2756 (1956); W. E. Truce and G. J. W. Tichenor, *J. Org. Chem.*, 37, 2391 (1972).

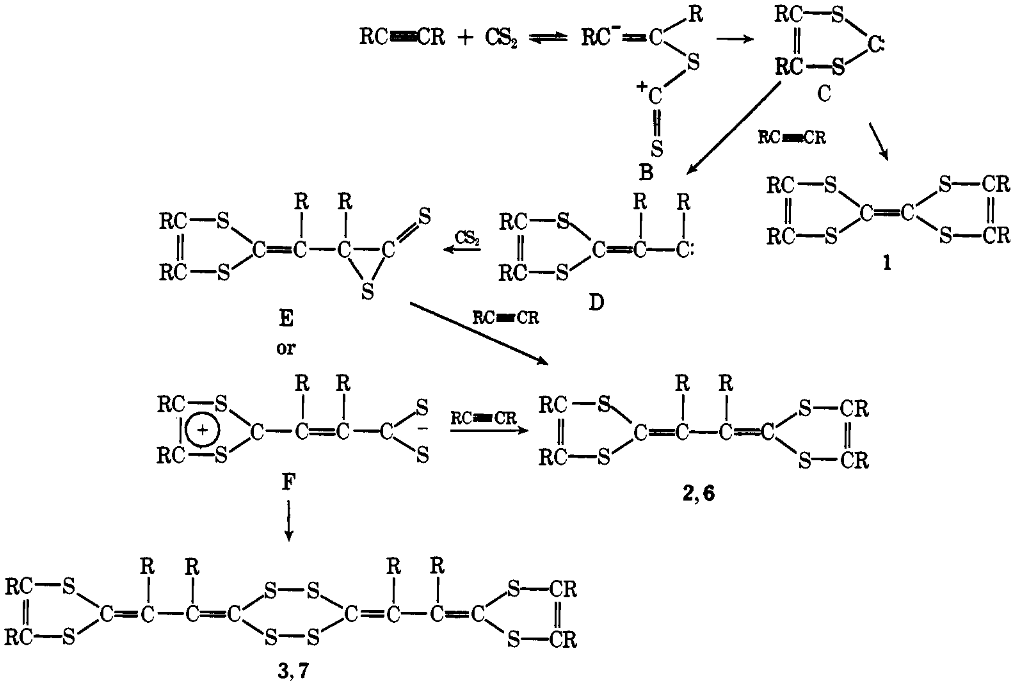
[14] T. R. Oakes, H. G. David, and F. J. Nagel, *J. Amer. Chem. Soc.*, **91**, 4761 (1969).

[15] E. Winterfeldt, D. Schumann, and H. J. Dillinger, *Chem. Ber.*, **102**, 1656 (1969).

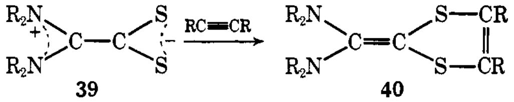
[16] A. Schönberg, E. Frese, and K. Brosowski, *Chem. Ber.*, **95**, 3077 (1962).

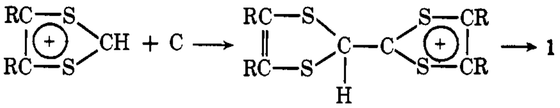
[17] H. D. Hartzler, *J. Amer. Chem. Soc.*, **93**, 4961 (1971).

Scheme I

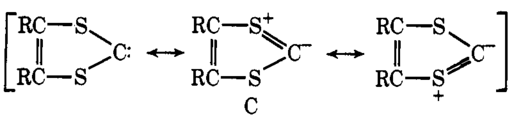


An alternate possibility for the formation of **1** would be reaction of C with carbon disulfide to give G followed by reaction with acetylene. We have no evidence for the formation of G, but the mechanism has good precedent. The formamidinium carbodithioates **39** obtained from peraminoethylenes and carbon disulfide[18] add readily to acetylenes to give the 1,3-dithiole derivatives **40**.[19] In the presence of acid, C would be expected to be protonated. 1,3-Dithiolium cations are well-known[20,21] stable species. Reaction of the cation H with the carbene C would then lead to **1** after deprotonation of the intermediate J.





1,3-Dithiolium carbenes have been previously suggested as intermediates in reactions of 1,3-dithiolium cations with bases.[22,23] They represent a cyclic 6 π-electron system and should possess aromatic stabilization. Most reasonable structures



contributing to the resonance hybrid of C place negative charge at C-2. One expects C to exhibit nucleophilic behavior. It is also apparent that electron-withdrawing substituents R contribute nothing toward stabilization of C. Since they are a prerequisite for the chemistry, direct formation of C by cycloaddition of acetylene and carbon disulfide seems unreasonable.

The dithiolium carbene is always generated in the presence of an electron-deficient acetylene with which it readily reacts. In order to trap the carbene with another reagent, the reaction must be more rapid than that with the acetylene. This is the case with alcohols, selected phenols, acids, aliphatic aldehydes and ketones, and aromatic aldehydes. Alcohols react cleanly to give 2-alkoxy-1,3-dithioles, frequently with total exclusion of the more complex products. The reaction probably proceeds by way of hydrogen abstraction to produce the dithiolium cation analogously to the reaction of diphenyl carbene in methanol.[24] The addition of methanol to dimethyl acetylenedicarboxylate is competitive with the addition of carbon disulfide and ultimate formation of **8**.

The reactions with phenols also proceed by way of 1,3-dithiolium cations. The dithiolium cations undergo a normal electrophilic substitution onto the phenols. Phenols with electron-withdrawing substituents were not incorporated into the reaction.

The formation of **19** and **22** from perfluoro-2-butyne, carbon disulfide, and carboxylic acids was at first surprising. A reaction analogous to those with alcohols would have given 2-acyloxy-1,3-dithioles, but these were completely absent. Their absence may be attributed to their solvolytic reactivity during the reaction conditions (Scheme II). If the acetate **20** were formed, it would ionize rapidly under the reaction conditions (100°, acetic acid solution). The cation and carbene would be in equilibrium, and the irreversible step which funnels the material to **19** is the reaction of the 1,3-dithiolium carbene with the acetylene to give the second carbene.

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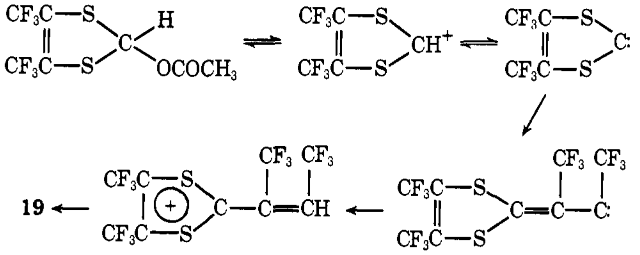
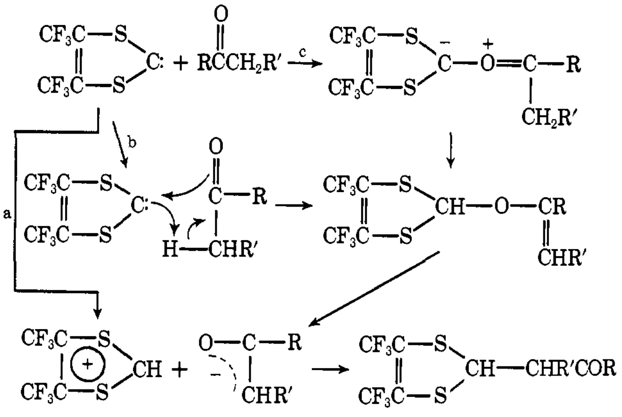
Scheme II



The reactions which incorporate aliphatic aldehydes and ketones are interesting in that they represent formal insertion reactions of the 1,3-dithiolium carbenes into the acidic hydrogens α to the carbonyl group. It seems unlikely that the reaction occurs by this path (Scheme III, path a), for many compounds with acidic hydrogens were inert to the reaction conditions. Malononitrile, diethyl malonate, and phenylacetylene were all recovered unchanged from attempted reaction with perfluoro-2-butyne and carbon disulfide. In these reactions compounds **1**, **2**, and **3** were formed. Yields of **1** were not increased by "acid" catalysis as they were with carboxylic acids.

Scheme III



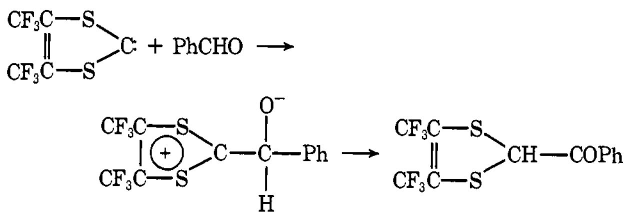
It is also unlikely that the reactions are those between 1,3-dithiolium carbenes and enols. The enol concentrations in acetophenone and cyclohexanone are minimal, yet yields of 79 and 75% of "insertion" products were obtained. No insertion was observed with diethyl malonate, which has a higher enol content than does acetone. Enol ethers have already been shown to enter into the reaction at a later stage.

The mechanisms indicated in Scheme III, paths b and c, seem unlikely, but are consistent with the experimental facts. Although most of the reactions of 1,3-dithiolium carbenes appear to be those of nucleophiles, there is still a vacant orbital at C-2. Coordination with the oxygen of the carbonyl would lead to the ylide (path c). The negative charge would be stabilized by the vacant d orbitals of the adjacent sulfur atoms. There would thus be no need for the dithiole ring to be planar which would represent an antiaromatic 8 π-electron system. The ylide should readily collapse to the enol ether. Alternatively, and perhaps more probably, an "ene" reaction of the carbene and carbonyl compound could go directly to the enol ether (path b). In either case the thermodynamically more stable enol ether should be formed, and this is the orientation observed with methyl ethyl ketone. Under the reaction conditions, ionization of the enol ether to dithiolium cation and enolate anion should be facile. These would recombine to the observed product.

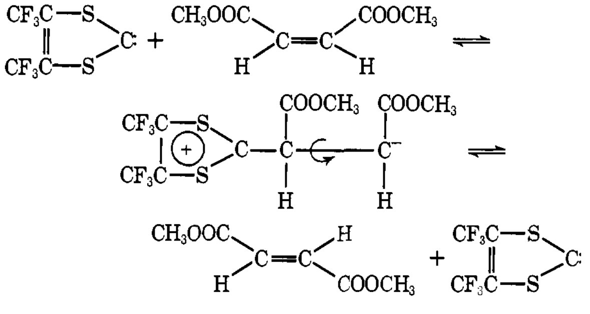
In the reactions with aldehydes and ketones the carbonyl compound competes with the acetylene for the carbene. When there are low yields of "insertion" product, the yields of **1**, **2**, and **3** are higher. Yields with aliphatic aldehydes are generally lower than with aliphatic ketones. This is consistent with the lower basicity of the carbonyl oxygen of the aldehydes.

The suggested reaction paths for α alkylation of aldehydes and ketones are consistent with all experimental data. They are certainly not satisfying in that in all other reactions the carbenes behaved as nucleophiles. Additional work will be required to resolve this problem.

With no α-hydrogen atoms, aromatic aldehydes appear to react with the dithiolium carbenes by nucleophilic attack at the carbon of the carbonyl. The dipolar intermediate could give product directly by a 1,2-hydride shift. Alternatively, if a proton source were available, the dipolar intermediate could be protonated and give product through the enol. The benzaldehyde used showed no benzoic acid by nmr analysis, but small amounts of acid could have been present. The product which now does have an α hydrogen readily undergoes the characteristic "insertion" reaction of aliphatic aldehydes and ketones.



Olefins appear to be less reactive toward 1,3-dithiolium carbenes than the electron-deficient acetylenes. Possible exceptions are electron-deficient olefins such as dimethyl maleate which undergo cis → trans isomerization under the reaction conditions. The most likely species for effecting the isomerization is the 1,3-dithiolium carbene. Michael addition to the maleate, followed by bond rotation, and Michael reversal account most simply for the facts (eq 2). The addition of the carbene to the maleate is completely analogous to what was already suggested for addition of the carbene to the acetylene to give the second carbene **D**. This type of addition to olefins is in contrast to the reported stereospecific addition of the nucleophilic carbene cycloheptatrienylidene to fumaronitrile and maleonitrile.[25] We have found no


(2)

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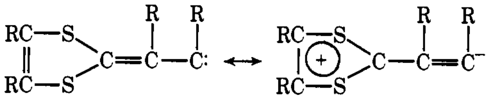
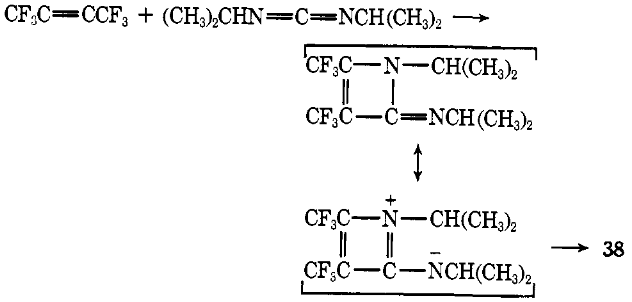
evidence for cyclopropane formation from 1,3-dithiolium carbenes.

Cyclopropanes were formed from olefins and the vinyl carbene D. The vinyl carbene might be expected to exhibit both electrophilic and nucleophilic properties. The variation of yield of cyclopropanes with olefin structure where good yields of cyclopropanes were only obtained with electron-rich olefins suggests that D functions as an electrophile in the olefin addition reaction. Reactions of D with acetic and benzoic acid suggest that D is reacting as a nucleophile and is being protonated.



D

Crude bond-energy calculations indicate that reaction of a carbodiimide with an acetylene to produce a 1,3-imidazolium carbene would be less endothermic than the reaction of carbon disulfide with an acetylene to give a 1,3-dithiolium carbene. We were unable to observe any imidazolium carbene formation, apparently because of an energetically more favorable 2 + 2 cycloaddition. The azetine **41** which was probably initially formed was not isolated, but rather its tautomer **38**. The normal resonance stabilization enjoyed by an amidine should be absent in **41** because of the unfavorable azacyclobutadiene structure in the dipolar form.



41

Experimental Section

Melting points were taken on a Thomas-Hoover apparatus and are uncorrected. Boiling points are uncorrected. Spectral measurements were determined with the following instruments: ir, Perkin-Elmer Model 21; uv and near-ir, Cary Model 14; nmr, Varian A-60 and A-56/60; mass spectra, CEC 21-103C and CEC 21-110B. ^{1}H nmr chemical shifts are given in parts per million from tetramethylsilane. ^{19}F nmr chemical shifts are given in parts per million from fluorotrichloromethane. Most preparative reactions were not repeated so that yields have not been optimized.

Except where noted (compounds **12**, **23**, **24**, and **27**), all new compounds had elemental analyses in agreement with calculated values to within 0.3% for carbon and hydrogen analyses and to within 0.5% for chlorine, fluorine, and sulfur analyses. Analytical data were made available to the Editor.

4,4′,5,5′-Tetrakis(trifluoromethyl)-$\Delta^{2,2'}$-bi-1,3-dithiole (1). A Carius tube containing 19 g of carbon disulfide, 15.6 g of perfluoro-2-butyne, and 23 g of trifluoroacetic acid was heated at 100° for 4 days. Filtration of the reaction mixture gave 23.2 g (100%) of the red-orange bi-dithiole: mp 90–91°; ir (KBr) 1610 (C=C) and 1270, 1160 cm^{-1} (CF); uv (isooctane) λ_{max} 412 nm (ϵ 1520), 310 (13,600), and 222 (12,600); ^{19}F nmr (acetone) δ -57.6 (s); mass spectrum (70 eV) *m/e* 238 base peak, 476 (parent).

Polarographic oxidation of **1** in acetonitrile with 0.1 *M* tetrabutylammonium perchlorate gave one-electron waves at +1.05 (reversible) and +1.28 V (irreversible) *vs.* saturated calomel electrode.

Heating the acetylene and carbon disulfide in the absence of acid gave a low (2%) yield of **1**. With acetic acid the yield of **1** was 16% and with formic acid, 50%.

Preparation of 1 from 1,2-Bis(trifluoromethyl)vinylene Trithiocarbonate and Triphenylphosphine. A solution of 25 g of the trithiocarbonate[9] and 39 g of triphenylphosphine in 120 ml of benzene was heated at reflux under nitrogen for 18 hr. The solvent was removed. The residue was stirred with pentane and filtered. The solid was rinsed with pentane until colorless. There remained 26.7 g of triphenylphosphine sulfide, mp 150.5–151.5°. The filtrate was evaporated and the residue was sublimed at 60° (0.25 Torr) to give 19.6 g (89%) of **1**, mp 90–91°.

***s*-Tetrathianediylidenebis[bis(trifluoromethyl)ethanediylidene]-2,2′-bis[4,5-bis(trifluoromethyl)-1,3-dithiole] (3).** A mixture of 16.8 g of perfluoro-2-butyne and 50.4 g of carbon disulfide was heated at 100° for 2.5 days. The addition of hexane precipitated 12.8 g (60%) of the crude product. Recrystallization from acetone gave material which decomposed at 195° when immersed in a preheated bath: ir (KBr) 1575 (C=C) and 1250 and 1150 cm^{-1} (CF); uv (isooctane) λ_{max} 288 nm (ϵ 16,500); ^{19}F nmr (acetone) δ -61.2 (s) and -55.8 (m); mol wt (ebullioscopic in acetone) 921 (calcd 932).

1,2,3,5,6,7-Hexathiocanediylidenebis[4,5-bis(trifluoromethyl)-1,3-dithiole] (5). A solution of 2.5 g of **1** in 250 ml of ethanol was irradiated (2537 Å) at 20° for 3 days. The mixture was filtered to give 0.33 g of yellow solid, mp 171–173°. Recrystallization from methanol gave material which melted at 181–182°: ^{19}F nmr (DCCl$_3$) δ -56.9 (s); uv (isooctane) λ_{max} 405 nm (ϵ 20,900), 322 (9,750), and 213 (34,600); mass spectrum (70 eV) *m/e* (assignment) 691.67 (P$^+$), 673 (P − F), 660 (P − S), 628 (P − S$_2$), 595.7852 (P − S$_3$), 564 (P − S$_4$), 442 (P − $C_6F_6S_2$), 410 (P − $C_6F_6S_3$), 378 (P − $C_6F_6S_4$), 314 (P − $C_6F_6S_6$), and 282 (P − $C_6F_6S_7$).

An isomeric 1,2,3,4,5,7-hexathiocane structure cannot be rigorously excluded, but the apparent chemical shift identity of all fluorine atoms would be unexpected for the alternative structure.

The yield of **5** was not increased by addition of sulfur to the photolysis.

Tetramethyl *s*-Tetrathianediylidenebis[bis(methoxycarbonyl)ethanediylidene]-2,2′-bis(1,3-dithiole-4,5-dicarboxylate) (7). A mixture of 14.2 g of dimethyl acetylenedicarboxylate and 50.4 g of carbon disulfide was heated at 100° for 18 hr. The mixture was filtered to give 1.11 g of solid which melted at 237–239° with decomposition. Recrystallization from diethylene glycol dimethyl ether raised the melting point to 247–250° dec; ir (KBr) 1750, 1740 (C=O), 1550 (C=C), and 1220 cm^{-1} (C—O).

Tetramethyl Bis(methoxycarbonyl)ethanediylidene-2,2′-bis(1,3-dithiole-4,5-dicarboxylate) (6). From the initial filtrate of the above reaction there remained a dark oil. Alcohol was added and the mixture was refiltered to give 0.92 g of yellow solid, mp 200–205°. Two recrystallizations from ethanol gave material which melted at 212.5–213.5°: ir (KBr) 1740 and 1720 (C=O) and 1580 cm^{-1} (C=C); ^{1}H nmr (DCCl$_3$) δ 3.75, 3.87, 3.92 (equal intensity singlets); mass spectrum (70 eV) *m/e* (rel intensity) 578 (100), 547 (7.2), 519 (5.9), 460 (6.1), 372 (0.4), 360 (0.3), and 289 (8.1).

Dimethyl 2-Methoxy-1,3-dithiole-4,5-dicarboxylate (8). A mixture of 15 ml of carbon disulfide, 15 ml of methanol, and 14.2 g of dimethyl acetylenedicarboxylate was heated in a sealed tube at 130° for 8 hr. The addition of ether to the contents of the tube precipitated 15.2 g (60%) of the crude product, mp 39–44°. Recrystallization from methanol gave the pure ether: mp 60.5–61.5; uv (ethanol) λ_{max} 314 nm (ϵ 5120), 238 (3780), and 218 (3190); nmr (DCCl$_3$) 3.30 (s, 3, methoxyl), 3.82 (s, 6, ester methoxyl), and 6.83 (s, 1, methine). Distillation of the ethereal filtrate gave 4.4 g of a mixture of dimethyl methoxyfumarate and methoxymaleate, bp 82–88° (0.7 Torr). The distillation residue was stirred with methanol and filtered to give 1.01 g of tetramethyl $\Delta^{2,2'}$-bi-1,3-dithiole-4,4′-5,5′-tetracarboxylate (**21**), mp 160–163°.

Methyl 2-Methoxy-1,3-dithiole-4-carboxylate (9). A mixture of 9 g of methyl propiolate, 15 ml of carbon disulfide, and 15 ml of methanol was heated at 100° for 4 days. Distillation gave 2.7 g of the dithiole: bp 99° (0.9 Torr); n^{25}D 1.5696; ir (film) 3000 (CH), 1710 (>C=O), and 1550 cm^{-1} (C=C); nmr (DCCl$_3$) δ 3.07 (s, 3, methoxyl), 3.67 (s, 3, ester methoxyl), 6.89 (s, 1, methine at C-2), and 7.32 (s, 1, methine at C-4); uv (ethanol) λ_{max} 304 nm (ϵ 6600) and sh 230 (4050).

Ethyl 2-Methoxy-1,3-dithiole-4-carboxylate (10). A Carius tube containing 20 g of ethyl propiolate, 20 ml of carbon disulfide, and 20 ml of methanol was heated at 100° for 4 days. Unreacted starting materials were removed under reduced pressure and the residue was distilled through a micro column to give 3.0 g of the dithiole: bp 92–95° (0.5 Torr), n^{25}D 1.5656; ir (film) 3000 (CH), 1700 (C=O), and 1550 (C=C); uv (ethanol) λ_{max} 304 nm (ϵ 6080) and sh 230 (4260); nmr ($\mathrm{DCCl_3}$) δ 1.23 (t, 3, methyl, J = 7 Hz), 3.12 (s, 3, methoxyl), 4.18 (q, 2, methylene, J = 7 Hz), 6.98 (s, 1, methine at C-2), and 7.40 (s, 1, methine at C-5).

Diethyl (*Z*)- and (*E*)-[$\Delta^{2,2'}$-Bi-1,3-dithiole]-4,4′-dicarboxylate (13). The addition of ether to the distillation residue of the above reaction gave a red-brown precipitate. Recrystallization from methanol gave 0.57 g of product: mp 169–172°; ^{1}H nmr ($\mathrm{DCCl_3}$) δ 1.35 (t, 3, methyl, J = 7 Hz), 4.31 (q, 2, methylene), and 7.40 (s, 1, methine).

4,5-Bis(trifluoromethyl)-2-methoxy-1,3-dithiole (11). A mixture of 15 ml of carbon disulfide, 15 ml of methanol, and 16 g of perfluoro-2-butyne was heated in a sealed tube at 100° for 2 days. Distillation of the reaction mixture gave 5.6 g (21%) of the product: bp 80° (24 Torr); $n^{25}\mathrm{D}$ 1.4255; ir (film) 1595 (C=C) and 1100–1200 cm^{-1} (CF); uv (isooctane) λ_{max} sh 287 nm (ϵ 3210), 269 (3910) and 212 (3670); ^{1}H nmr ($\mathrm{DCCl_3}$) δ 3.09 (s, 3) and 6.43 (s, 1); ^{19}F nmr ($\mathrm{DCCl_3}$) δ −55.6 (s); mass spectrum (70 eV) m/e (rel intensity) 270 (1.9), 251 (0.76), 239 (100), 201 (0.17), 194 (0.31), 157 (0.66), 143 (0.50), 125 (0.46), 69 (1).

4,5-Bis(trifluoromethyl)-2-ethoxy-1,3-dithiole (12). A mixture of 15 ml of ethanol, 15 ml of carbon disulfide, and 16 g of perfluoro-2-butyne was heated in a sealed tube at 100° for 3 days. The reaction mixture was distilled to give 17.1 g (60%) of the dithiole: bp 70–73° (10 Torr), $n^{25}\mathrm{D}$ 1.4264; ir (film) 1590 (C=C) and 1100–1200 cm^{-1} (CF); uv (isooctane) λ_{max} sh 287 nm (ϵ 3240) and 272 (3890); ^{1}H nmr ($\mathrm{DCCl_3}$) δ 1.03 (t, 3, methyl, J = 7 Hz), 3.38 (q, 2, methylene, J = 7 Hz), and 6.42 (s, 1, methine); ^{19}F nmr ($\mathrm{DCCl_3}$) δ −54.8 (s).

The fluorine analysis was within 1.0% of theory.

4,5-Bis(trifluoromethyl)-2-(4-hydroxyphenyl)-1,3-dithiole (15). A mixture of 20 g of phenol, 20 ml of carbon disulfide, and 16 g of hexafluoro-2-butyne was heated in a sealed tube at 100° for 3 days. The reaction mixture was distilled through a short still head to give 17.7 g (53%) of the substituted phenol, bp 125–136° (0.5 Torr), mp 51–56°. Recrystallization from hexane gave material which melted at 68–69.5°: ir (KBr) 3300 (OH), 1605 (C=C), and 1270, 1180 cm^{-1} (CF); uv (isooctane) λ_{max} 325 nm (ϵ 2590) and 282 (3980); ^{1}H nmr ($\mathrm{DCCl_3}$) δ 6.22 (s, 1) and 6.7–7.2 (m, 5, aromatic plus hydroxyl); ^{19}F nmr ($\mathrm{DCCl_3}$) δ −56.2 (s).

Methyl 3-(2,5-Dichlorophenoxy)acrylate (16). A sealed tube containing 21 g of methyl propiolate, 45 g of 2,5-dichlorophenol, and 100 ml of carbon disulfide was heated at 130° for 8 hr. The reaction product was dissolved in ether and extracted with aqueous base. The neutral product was isolated by crystallization at −70° and filtration to give 29.73 g of solid, mp 43–48°. This was a mixture of cis and trans isomers in a ratio of 1:3 as judged by nmr spectroscopy. Recrystallization from hexane gave material which melted at 69°. Neutralization of the basic extracts of above led to partial recovery of unreacted phenol.

Methyl 2-(2,5-Dichloro-4-hydroxyphenyl)-1,3-dithiole-4-carboxylate (17). A mixture of 21 g of methyl propiolate, 45 g of 2,5-dichlorophenol, 100 ml of carbon disulfide, and 3 ml of trifluoroacetic acid was heated at 130° for 8 hr. The product was dissolved in ether and the acid product was isolated by standard techniques. Crystallization and recrystallization from methanol gave 21.33 g (26%) of product: mp 161–162°; ^{1}H nmr [$\mathrm{(CD_3)_2CO}$] 3.4 (broad, 1, hydroxyl) 3.78 (s, 3, methyl), and 6.41, 7.13, 7.37, 7.75 (each s, 1).

Dimethyl 2-(2,5-Dichloro-4-hydroxyphenyl)-1,3-dithiole-4,5-dicarboxylate (18). A mixture of 36 g of dimethyl acetylenedicarboxylate, 50 g of 2,5-dichlorophenol, and 100 ml of carbon disulfide was heated in a sealed vessel at 130° for 8 hr. Filtration of the reaction mixture gave 49.7 g (49%) of crude product. Recrystallization from ethanol gave material which melted at 177–178°: ir (KBr) 3300 (OH), 2970 (CH), 1740, 1700 (C=O), and 1600, 1580 cm^{-1} (C=C); uv (ethanol) λ_{max} 350 nm (ϵ 4080) and 286 (6400); nmr [$\mathrm{(CD_3)_2CO}$] δ 2.55 (s, 1, broad, hydroxyl), 3.23 (s, 6, methyl), 5.80 (s, 1, dithiole), and 6.60, 7.24 [s, s, 1,1, aromatic uncoupled (para)].

2-(4,5-Bis(trifluoromethyl)-1,3-dithiol-2-ylidene)-1-(trifluoromethyl)-3,3,3-trifluoropropyl Acetate (19). A mixture of 15 ml of acetic acid, 15 ml of carbon disulfide, and 17.6 g of perfluoro-2-butyne was heated at 100° for 3 days in a sealed tube. The tube was cooled and opened and the contents were poured into water. The organic products were separated and there was obtained orange bi-dithiole **1** (3.8 g, 16%, mp 86–89°) and the acetate **19** 16.9 g (73%): bp 40–48° (0.3 Torr); $n^{25}\mathrm{D}$ 1.4200; ^{1}H nmr ($\mathrm{DCCl_3}$) δ 1.98 (s, 3, methyl) and 5.73 (q, 1, methine, J = 7 Hz); ^{19}F nmr ($\mathrm{DCCl_3}$) δ −56.9 (s, 6, trifluoromethyl on dithiole), −62.8 (q, 3, 1-trifluoromethyl), and −75.8 (m, 3, 2-trifluoromethyl).

Tetramethyl [$\Delta^{2,2'}$-Bi-1,3-dithiole]-4,4′-5,5′-tetracarboxylate (21). A mixture of 14.2 g of dimethyl acetylenedicarboxylate, 25.2 g of carbon disulfide, and 22 g of acetic acid was heated at 100° for 4 days in a Carius tube. The mixture was filtered to give 2.1 g of the bi-dithiole, mp 165–168°. Recrystallization from benzene–hexane gave red-purple crystals: mp 169–170°; ir (KBr) 1740 (C=O), 1710 (C=O), 1570 cm^{-1} (C=C); nmr ($\mathrm{CDCl_3}$) δ 3.85 (s); uv (ethanol) λ_{max} 445 nm (ϵ 1930), 315 (13,100), 284 (14,300), and 245 (15,500).

2-(4,5-Bis(trifluoromethyl)-1,3-dithiol-2-ylidene)-1-(trifluoromethyl)-3,3,3-trifluoropropyl Benzoate (22). A mixture containing 15 g of benzoic acid, 17 g of perfluoro-2-butyne, 25 ml of carbon disulfide, and 100 ml of ether was heated at 130° for 8 hr. Acid materials were removed by extraction with aqueous base. The product crystallized after evaporation of the ether. Recrystallization from methanol gave 19.4 g (74%) of white solid: mp 63°; ir (KBr) 1650 (C=O), 1600, 1540 (C=C), and 1260, 1180 cm^{-1} (CF); ^{1}H nmr ($\mathrm{DCCl_3}$) δ 6.14 (q, 1, methine, J = 7 Hz) and 7.3–8.2 (m, 5, aromatic); ^{19}F nmr ($\mathrm{DCCl_3}$) δ −56.0 (m, 6, groups on dithiole ring), −61.7 (q, 3, group at C-1, J = 10 Hz), −74.2 (q split into d, 3, group at C-2, J_1 = 10 Hz, J_2 = 7 Hz).

2-[1-(2-Methoxy-1-trifluoromethylcyclopropyl)-2,2,2-trifluoroethylidene]-4,5-bis(trifluoromethyl)-1,3-dithiole (23). A mixture containing 18 g of perfluoro-2-butyne, 25.2 g of carbon disulfide, and 19 g of methyl vinyl ether was heated at 100° for 3.5 days in a sealed tube. The product was distilled under reduced pressure through a spinning-band column. There was obtained a mixture of stereoisomers: bp 85–88° (3.0 Torr); 17.6 g (69%); $n^{25}\mathrm{D}$ 1.4291; ir (film) 6060 (cyclopropyl methylene), 1610, 1540 (C=C), and 1270, 1160 cm^{-1} (CF); uv (isooctane) λ_{max} 280 nm (ϵ 11,400) and 208 (8420); ^{1}H nmr ($\mathrm{DCCl_3}$) δ 1.0–1.6 (m, 2, cyclopropyl methylene) 3.4 (two peaks, 3, methoxyl), and 3.85 (m, 1, cyclopropyl methine).

The carbon analysis was within 0.5% of theory.

2-[1-(2-Ethoxy-1-trifluoromethylcyclopropyl)-2,2,2-trifluoroethylidene]-4,5-bis(trifluoromethyl)-1,3-dithiole (24). A sealed tube containing 16.5 g of perfluoro-2-butyne, 25.2 g of carbon disulfide, and 14 g of ethyl vinyl ether was heated at 70° for 6 days. Volatile liquids were removed under reduced pressure at room temperature. The residue was filtered to give 0.69 g of solid which melted at 52–54°. Distillation of the filtrate gave 6.12 g of product, bp 53–62° (0.40 Torr). The liquid and solid had nearly identical ir and nmr spectra. Recrystallization of the solid from hexane gave material which melted at 64–65.5°: ir (KBr) 1600, 1540 (C=C) and 1270, 1160 cm^{-1} (CF); ^{1}H nmr ($\mathrm{DCCl_3}$) δ 1.0–1.6 (m, 5, methyl plus cyclopropyl methylene) 3.83 (m, 1, cyclopropyl methine), and 3.3–3.5 (m, 2, methylene); mass spectrum (70 eV) m/e 472 (parent).

The carbon analysis was within 0.5% of theory.

Isomerization of Dimethyl Maleate in the Presence of Perfluoro-2-butyne and Carbon Disulfide. A mixture of 39 g of carbon disulfide, 28.8 g of dimethyl maleate, and 16 g of perfluoro-2-butyne was heated in a sealed tube at 100° for 4 days. The tube contents were filtered and the solid was rinsed with methylene chloride to obtain 13.7 g of dimethyl fumarate, mp 98–102°. A similar reaction with dimethyl fumarate in place of dimethyl maleate gave only products derived from perfluoro-2-butyne and carbon disulfide.

Separate experiments showed that dimethyl maleate was recovered unchanged by heating at 100° with carbon disulfide or perfluoro-2-butyne.

α-Methyl-4,5-bis(trifluoromethyl)-1,3-dithiole-2-acetaldehyde (25). A mixture of 15 g of propionaldehyde, 15 ml of carbon disulfide, and 16.5 g of perfluoro-2-butyne was heated in a sealed tube at 100° for 4 days. Distillation of the reaction mixture yielded the aldehyde as a pale-yellow liquid: bp 54–55° (0.25 Torr); $n^{25}\mathrm{D}$ 1.4428; ir (film) 1730 (C=O), 1600 (C=C), and 1270, 1160 cm^{-1} (CF); ^{1}H nmr ($\mathrm{CDCl_3}$) δ 1.24 (d, 3, methyl, J = 7 Hz); 2.81 (m, 1, methine α to carbonyl); 5.03 (d, 1, dithiole methine, J = 6 Hz); and 9.40 (broad, 1, formyl); uv (isooctane) λ_{max} 310 nm (ϵ 2340), sh 290 (2180) and sh 232 (2260).

1-(4,5-Bis(trifluoromethyl)-1,3-dithiol-2-yl)-2-propanone (26). A Carius tube with 15 ml of acetone, 15 ml of carbon disulfide, and 17.3 g of perfluoro-2-butyne was heated at 100° for 4 days. There still remained considerable unreacted acetylene. Distillation of the reaction mixture through a small column gave the ketodithiole: bp 64–65° (2.5 Torr); $n^{25}\mathrm{D}$ 1.4441; ^{1}H nmr ($\mathrm{DCCl_3}$) δ 1.93 (s, 3, methyl); 3.03 (d, 2, methylene, J = 7 Hz); 4.90 [t, 1, methine, J = 7 Hz); ir (film) 1720 (C=O), 1600 (C=C), and 1270, 1160 cm^{-1} (CF); uv (isooctane) λ_{max} 311 nm (ϵ 2480), sh 285 (2210), and 233 (2300).

A small amount of **2** was isolated from the distillation residue.

α,α-Dimethyl-4,5-bis(trifluoromethyl)-1,3-dithiole-2-acetaldehyde (27). A mixture of 15 ml of carbon disulfide, 15 ml of isobutyraldehyde, and 16.5 g of perfluoro-2-butyne was heated in a sealed tube at 100° for 3 days. The reaction mixture was distilled through a short still head to give 9.0 g of the dithiole: bp 45–50° (0.6 Torr); $n^{25}\text{D}$ 1.4400; ^{1}H nmr ($DCCl_3$) δ 1.17 (s, 6, methyl), 5.08 (s, 1, methine), and 9,37 (s, 1, formyl).

The sulfur analysis was within 0.8% of theory.

3-(4,5-Bis(trifluoromethyl)-1,3-dithiol-2-yl)-2-butanone (28). A Carius tube with 15 ml of carbon disulfide, 15 ml of 2-butanone, and 16.5 g of perfluoro-2-butyne was heated at 100° for 4 days. Distillation gave 9.2 g of the dithiole: bp 52–56° (0.15 Torr); $n^{25}\text{D}$ 1.4443; ir (film) 1710 (C=O), 1600 (C=C), and 1270, 1150 cm^{-1} (CF); uv (isooctane) λ_{max} 314 nm (ϵ 2700), sh 285 (1780), and sh 235 (ϵ 2120); ^{1}H nmr ($DCCl_3$) δ 1.14 (d, 3, methyl, J = 7 Hz), 1.95 (s, 3, acetyl methyl), 2.91 (m, 1, methine α to carbonyl), 4.90 (d, 1, dithiole methine, J = 8 Hz); ^{19}F nmr ($DCCl_3$) δ −57.1 (m). The slight difference in chemical shifts of the trifluoromethyl groups may be attributed to the presence in the molecule of the asymmetric center.

3-(4,5-Bis(trifluoromethyl)-1,3-dithiol-2-yl)-2,4-pentanedione (29). A sealed tube containing 15 ml of carbon disulfide, 15 g of 2,4-pentanedione, and 16 g of perfluoro-2-butyne was heated at 100° for 4 days. From the reaction mixture there was obtained 18.4 g of solid, mp 68–69°. Recrystallization from hexane gave pure dithiole: mp 70–71°; ir (KBr) 1725, 1700 (C=O), 1590 (C=C), and 1260, 1180 cm^{-1} (CF); uv (isooctane) λ_{max} 315 nm (ϵ 2560) and sh 235 (2550); ^{1}H nmr ($DCCl_3$) δ 2.33 (s, 6, methyl); 5.0 (m, 2, methines, J = 11 Hz); ^{19}F nmr ($DCCl_3$) δ −55.8 (s).

2-(4,5-Bis(trifluoromethyl)-1,3-dithiol-2-yl)acetophenone (30). A sealed tube containing 12 g of acetophenone, 15 ml of carbon disulfide, and 16.7 g of perfluoro-2-butyne was heated at 100° for 6 days. Filtration of the reaction mixture gave 28.3 g (79%) of the dithiole, mp 85–87°. Recrystallization from hexane gave pure product: mp 87–88°; ir (film) 1690 (C=O), 1590 (C=C), 1270, 1180 cm^{-1} (CF); uv (isooctane) λ_{max} 315 nm (ϵ 2950), 292 (2920), 283 (2910), and 243 (12,200); ^{1}H nmr ($DCCl_3$) δ 3.65 (d, 2, methylene), 5.20 (t, 1, methine), and 7.1–7.6 (m, 5, aromatic); ^{19}F nmr ($DCCl_3$) δ −55.9 (s).

2-(4,5-Bis(trifluoromethyl)-1,3-dithiol-2-yl)cyclohexanone (31). A Carius tube with 15 ml of cyclohexanone, 15 ml of carbon disulfide, and 17.2 g of perfluoro-2-butyne was heated at 100° for 5 days. The product was distilled through a short still head to give 25.2 g (75%) of the dithiole: bp 108° (1.5 Torr); $n^{25}\text{D}$ 1.4739; ir (film) 1710 (C=O), 1600 (C=C), 1270, 1150 cm^{-1} (CF); uv (isooctane) λ_{max} 318 nm (ϵ 2680) and sh 285 (1780); ^{1}H nmr ($DCCl_3$) δ 1.0–3.0 (broad, 9, cyclohexyl) and 5.12 (d, 1, dithiole, J = 6 Hz); ^{19}F nmr ($DCCl_3$) multiplet at δ −56.0. The slight difference in chemical shift of the trifluoromethyl groups may be attributed to the presence of the asymmetric center in the molecule.

Methyl 2-Diacetylmethyl-1,3-dithiole-4-carboxylate (32). A steel bomb containing 21 g of methyl propiolate, 40 g of pentane-2,4-dione, and 100 ml of carbon disulfide was heated at 150° for 6 hr. Volatile materials were removed under vacuum (0.5 Torr). Methanol was added to the residue and solid was obtained after cooling to −70°. Recrystallization from methanol gave 11.31 g (17%) of product: mp 119–120°; ir (KBr) 3050 (OH), 1720 (C=O), 1550 (C=C), and 1260 cm^{-1} (C–O); uv (ethanol) λ_{max} 335 nm (ϵ 4450) and 230 (5500); ^{1}H nmr ($DCCl_3$) δ 2.28 (s, 6, C-methyl), 3.78 (s, 3, O-methyl), 4.60 (d, 1, exocyclic methine, J = 11 Hz), 5.48 (d, 1, dithiole, J = 11 Hz), and 7.12 (1, s, dithiole H).

4,5-Bis(trifluoromethyl)-1,3-dithiol-2-yl Phenyl Ketone (33) and 2-[4,5-Bis(trifluoromethyl)-1,3-dithiol-2-yl]-4,5-bis(trifluoromethyl)-1,3-dithiol-2-yl Phenyl Ketone (34). A Carius tube containing 20 ml of carbon disulfide, 15 g of benzaldehyde, and 16.5 g of perfluoro-2-butyne was heated at 100° for 6 days. Volatile materials were removed under reduced pressure. Addition of hexane to the oily residue and filtration gave 1.8 g of pale yellow solid, mp 82–86°. Recrystallization from hexane gave the pure dithiole: mp 87–88°; ir (KBr) 1690 (C=O), 1610, 1590 (C=C), and 1160 cm^{-1} (CF); uv (isooctane) λ_{max} sh 357 nm (ϵ 743), sh 310 (2000), and 249 (12,800); ^{1}H nmr ($DCCl_3$) δ 6.19 (s, 1, methine) 7.1–7.7 (m, 5, aromatic); ^{19}F nmr ($DCCl_3$) δ −57.3 (s).

Part of the filtrate residue from above was chromatographed on Florisil using hexane as eluent. This gave crystalline bi-dithiole: mp 43–45°; ir (KBr) 1660 (C=O), 1610, 1590 (C=C), and 1170 cm^{-1} (CF); uv (isooctane) λ_{max} sh 380 nm (ϵ 245), sh 325 (2690), and 267 (13,400); ^{1}H nmr ($DCCl_3$) δ 5.52 (s, 1, methine) and 7.2–7.8 (m, 5, aromatic); ^{19}F nmr ($DCCl_3$) δ −56.1 (s, 6) and −56.7 (s, 6); mass spectrum (70 eV) *m/e* 582 (parent).

Analysis of the original uncrystallized reaction mixture by nmr (the lines at δ 6.19 and 5.52) indicated the two compounds were formed in a 30:70 ratio, respectively, and in a total conversion of 75%.

3-[2-(4,5-Bis(trifluoromethyl)-1,3-dithiol-2-yl]-4,5-bis(trifluoromethyl)-1,3-dithiol-2-yl]acrylophenone (35). A tube containing 15 g of cinnamaldehyde, 16.5 g of perfluoro-2-butyne, and 20 ml of carbon disulfide was heated at 100° for 3.5 days. The product was crystallized by adding methanol to the reaction mixture and cooling to −70°. Recrystallization from hexane gave 10.25 g of solid: mp 88°; ^{1}H nmr ($DCCl_3$) δ 5.50 (s, 1, dithiole methine), 7.3–7.8 (m, 7, aromatic and vinyl); ^{19}F nmr ($DCCl_3$) δ −56.3 (s, 6) and −56.7 (s, 6).

Methyl *S-trans*-(1-Trifluoromethyl)-3,3,3-trifluoro-1-propenyl) Thiocarbonate (36). A mixture of 12 g of carbonyl sulfide, 16 g of perfluoro-2-butyne, and 20 ml of methanol was heated in a sealed tube at 100° for 3 days. There was a considerable amount of unreacted starting materials. Distillation gave 12.8 g of product: bp 90° (123 Torr); $n^{25}\text{D}$ 1.3730; ir (film) 1745 (C=O) 1660 (C=C), 1260, 1190, and 1140 cm^{-1} (CF and C–O); uv (isooctane) λ_{max} 260 nm (ϵ 810) and sh 215 (2160); ^{1}H nmr ($DCCl_3$) δ 3.88 (s, 3, methoxyl) and 7.12 (q into q, 1, J_1 = 6.8 Hz, J_2 = 1.3 Hz); ^{19}F nmr ($DCCl_3$) δ −60.9, −61.1 (q, q, 3, J_{HF} = 6.8 Hz, J_{FF} = 1.5 Hz), and −69.1 (m, 3). The low F–F coupling constant is only consistent with the trans isomer.

Heating carbonyl sulfide and the acetylene alone at 100° for 5 days gave no reaction.

Methyl *S-cis*-(2-Ethoxycarbonylvinyl) Thiocarbonate (37). A sealed tube containing 9 g of ethyl propiolate, 15 ml of methanol, and 6.2 g of carbonyl sulfide was heated at 100° for 6 days. The product distilled at 80–90° (0.9 Torr) and crystallized to give 3.78 g of solid. Recrystallization from pentane gave material which melted at 44–45°: ir (KBr) 1730, 1700 (C=O) and 1590 cm^{-1} (C=C); ^{1}H nmr ($DCCl_3$) δ 1.33 (t, 3, C-methyl), 3.96 (s, 3, O-methyl), 4.23 (q, 2, methylene), 6.08 (d, 1, J = 10 Hz), and 7.73 (d, 1, J = 10 Hz). The coupling constant of 10 Hz indicates cis stereochemistry and, therefore, a trans addition.

2,3-Bis(trifluoromethyl)-1-isopropyl-4-isopropylidenamino-2-azetine (38). A mixture of 14.5 g of diisopropylcarbodiimide, 16 g of hexafluoro-2-butyne, and 15 ml of ethyl acetate was heated in a sealed tube at 100° for 6 days. The mixture was filtered to remove some polymeric material. The filtrate was taken up into ether and the basic product was extracted with dilute acid. Basification gave 8.5 g of solid, mp 40–41°. Recrystallization from hexane gave material which melted at 41–45°; ir (KBr) 1660 (C=C), 1540 (C=N), and 1260, 1150 cm^{-1} (CF); ^{1}H nmr ($DCCl_3$) δ 1.32 (d, 6, isopropyl methyl, J = 11 Hz), 1.55 (s, 6, isopropylidene methyl), 3.71 (septet, 1), and δ 7.23 (s, 1, cyclobutyl methine); ^{19}F nmr ($DCCl_3$) δ −57.0 (q, 3, J = 11.8 Hz) and −69.5 (q, 3); mass spectrum (70 eV) *m/e* 288.1065 (calcd 288.1060), 245, 232, 231.

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