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Bis-(polyfluoroalkyl)-acetylenes. IV. Fluorinated Dithietenes and Related Heterocyclic Compounds From Bis-(polyfluoroalkyl)-acetylenes and Sulfur[1]

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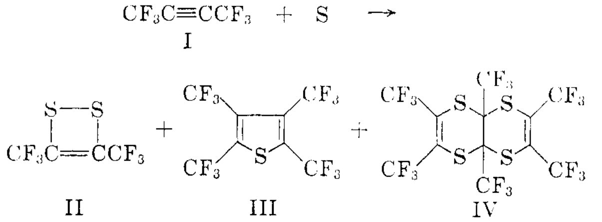
Dithietenes have been prepared for the first time and in good yield by the action of sulfur on bis-(polyfluoroalkyl)-acetylenes. Bis-(trifluoromethyl)-1,2-dithietene has been shown to undergo reaction at the sulfur–sulfur bond, allowing syntheses of trifluoromethylated derivatives of 1,2,5,6-tetrathiocin, *p*-dithiin and thiophene. Tetrakis-(trifluoromethyl)-*p*-diselenin has been prepared in low yield from selenium and hexafluoro-2-butyne.

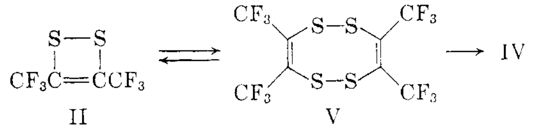
The appearance of synthetic routes to a number of fluorinated acetylenes,[2] particularly hexafluoro-2-butyne, has prompted a study of the reactions that these unusual compounds will undergo. One surprising result of this study was the discovery that hexafluoro-2-butyne (I) reacts with sulfur in the presence of iodine at 200° and under pressure to form 26% of 3,4-bis-(trifluoromethyl)-1,2-dithietene (II) along with 11% of tetrakis-(trifluoromethyl)-thiophene (III) and 29% of 2,3,4a,6,7,8a-hexakis-(trifluoromethyl)-4a,8a-dihydro-*p*-dithiino-[2,3-b]-*p*-dithiin (IV). Iodine facilitates the reaction, but is not essential, since hexafluorobutyne and sulfur alone form the same products at 225° under pressure. The dithietene II can be formed in high yield with no by-products by conducting the reaction at one atmosphere and 445° in a flow system.



3,4-Bis-(trifluoromethyl)-1,2-dithietene is the first known member of a class of compounds containing the unusual dithietene ring. Only one related compound, benzo-1,2-dithietene, has been found in the literature,[3] and the supporting evidence is sparse. Moreover, the high melting point (185–190°) reported for the material seems more compatible with a symmetrical structure of higher molecular weight than it does with a dithietene.

Analysis shows the dithietene II to have the molecular formula $C_4F_6S_2$, and the n.m.r. spectrum for F^{19} exhibits a single peak in the trifluoromethyl region. This peak, located at lower field than that of trifluoroacetic acid, is in a region compatible with attachment of the trifluoromethyl group to a carbon atom doubly bonded to another carbon atom. The most likely alternative to structure II containing only covalent bonds is hexafluoro-2,3-butanedithione, a compound that would be expected to have a nuclear magnetic resonance peak at higher field than that observed and that should also be more highly colored than the yellow product actually obtained. A diepisulfide structure is a formal possibility, but should not give rise to absorption in the double bond regions of the infrared and ultraviolet spectra. The presence of the double bond is confirmed by a band in the infrared spectrum at 6.14 μ, but attempts to detect the disulfide group by Raman spectroscopy have so far failed because of interference due to the color of the compound.

However, indirect evidence for the sulfur–sulfur bond in II is available from its ready conversion to a dimer (V) structurally similar to II. The symmetrical structure of V follows from the double bond absorption in the infrared spectrum (6.40 μ) and a nuclear magnetic resonance spectrum consisting of only one peak at low field. Since a strained disulfide bond is opened readily,[4] it is not surprising to find that the disulfide bond in II is labile. The well-known susceptibility of sulfur–sulfur bonds to attack by base accounts for the accelerated, exothermic conversion of II to V in the presence of a catalyst such as triethylamine.



The dimer V may be thermodynamically stable with respect to the monomer II at low temperatures, but the fact that monomer (and not dimer) is a product of a reaction conducted at 200° over a period of hours indicates that at high temperatures the monomer is the more stable species. Confirmation of a reversible equilibrium between dimer and monomer is obtainable by heating the dimer at 200°, in which case the monomer can be distilled out rapidly. The equilibrium involving the thermally labile disulfide bonds can be disrupted by prolonged exposure of either II or V to weak bases such as triethylamine or ethanol. Side reactions then occur that lead ultimately to IV and sulfur.

Since the formation of the bicyclic compound IV from the dithietene II can be demonstrated, it seems likely that the dithietene is the product first formed from sulfur and hexafluoro-2-butyne, and is the parent from which the thiophene (III) as well as IV is produced. This supposition is supported by reaction of hexafluoro-2-butyne with vapors of

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[1] C. G. Krespan, B. C. McKusick and T. L. Cairns, *J. Am. Chem. Soc.*, **82**, 1515 (1960).

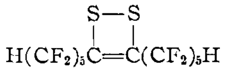
[2] C. G. Krespan, R. J. Harder and J. J. Drysdale, *ibid.*, **83**, 3428 (1961).

[3] P. C. Guha and M. N. Chakladar, *Quart. J. Indian Chem. Soc.*, **2**, 318 (1925); *C. A.*, **20**, 1797 (1926).

[4] M. Calvin and J. A. Barltrop, *J. Am. Chem. Soc.*, **74**, 6153 (1952).

refluxing sulfur and continual withdrawal of product as it is formed, conditions designed to give primary products. When the reaction is carried out under these conditions, only II is formed and in an 80% yield.

This procedure is generally useful for preparing bis-(polyfluoroalkyl)-1,2-dithietenes from fluorinated acetylenes. 3,4-Bis-(5-hydrodecafluoropentyl)-1,2-dithietene (VI) and 3,4-bis-(2-chlorotetrafluoroethyl)-1,2-dithietene (VII) have been synthesized from the corresponding acetylenes by this method in 41 and 82% yields, respectively. The ultraviolet spectra of the three fluorinated dithietenes are so similar as to suggest that ultraviolet absorption can be used as diagnostic test for this system.



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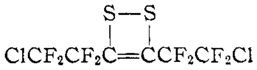
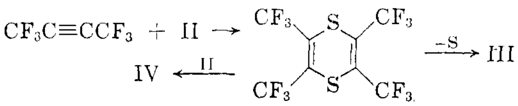


VII

Assuming the dithietene II to be the primary product of the original reaction under consideration, the other products, III and IV, can best be accounted for as arising from the common precursor, tetrakis-(trifluoromethyl)-*p*-dithiin (VIII). The reactive disulfide bond in II results in an addition of II to hexafluoro-2-butyne. Compound VIII, the product of such an addition, is susceptible at 200° to the addition of another molecule of dithietene to one of its double bonds, giving the *p*-dithiino-*p*-dithiin (IV). Alternatively, VIII can eliminate sulfur to form the thiophene III, a reaction previously noted with non-fluorinated *p*-dithiins.[5,6]



VIII

Corroboration for the reaction path outlined above has been obtained by reaction of bis-(trifluoromethyl)-1,2-dithietene with hexafluoro-2-butyne at 100°. At this temperature, the adduct VIII is stable enough to be isolated in 33% yield. When VIII was refluxed with an equivalent of the dithietene, sulfur was eliminated from the *p*-dithiin VIII, and a 79% yield of the thiophene III was obtained. The temperature was apparently too low, however, for the addition of dithietene to the *p*-dithiin to occur, since none of the bicyclic compound IV was found. Advantage can be taken of this fact to prepare tetrakis-(trifluoromethyl)-thiophene (III) in 84% yield directly from sulfur and hexafluoro-2-butyne by a reaction carried out at only 180° in the presence of half an equivalent of iodine.[7] At this temperature, the dithietene is formed slowly enough to be completely consumed in formation of the *p*-dithiin, which does not add another molecule of dithietene readily at 180° and so is converted in high yield to the thiophene by loss of sulfur.

Analytical and spectral data do not exclude the possibility that the product formulated as the bicyclic compound IV is instead a rearranged product containing coupled 1,3-dithiolene rings. Structure IV is preferred, since its formation is analogous to reactions of other olefins with II.[8] At 200°, however, a normal product such as IV might rearrange to a product containing smaller rings.

The addition of dithietenes to carbon–carbon unsaturated centers is a new reaction, but bears some relation to a known reaction of α-diketones. In special cases, α-diketones have been made to react with olefins to form dihydro-*p*-dioxins.[9]

The easy formation of sulfur heterocycles containing the sulfur as monosulfide is not often possible starting from elemental sulfur. In the present case, a pronounced tendency to first form the dithietene ring which can subsequently react to give monosulfides as products accounts nicely for the absence of polysulfides and polymers as products. This special stability of fluorinated dithietenes must be related not only to the presence of an "aromatic" sextet of electrons in the ring, but also to the presence of fluoroalkyl substituents, for no dithietenes were detected in attempts to prepare them from materials such as acetylene and dimethyl acetylenedicarboxylate.

It is conceivable that polymeric polysulfides rather than the dithietene II form initially in the reaction of sulfur with hexafluoro-2-butyne, and then degrade by loss of sulfur due to a general labilization of sulfur–sulfur bonds by adjacent double bonds. This possibility has been tested by treating tris-(trifluoromethyl)-vinyl iodide (IX) with sulfur in the expectation that an unusual effect due to the double bond would result in a product composed largely of bis-(tris-(trifluoromethyl)-vinyl) sulfide and little or none of the di- and trisulfides. A normal reaction would be one leading mainly to disulfide with smaller amounts of higher polysulfides also formed, as has been observed previously with sulfur and trifluoromethyl iodide.[10] The actual products obtained from IX and sulfur are polysulfides, demonstrating that double bonds are compatible with adjacent polysulfide groups at 225°. Therefore, formation of appreciable amounts of linear polysulfides from hexafluoro-2-butyne should result in the presence of some polymer in the product isolated, whereas no polymer was actually obtained.

$$(CF_3)_2C{=}CICF_3 + S \longrightarrow [(CF_3)_2C{=}C(CF_3){-}]S_{2-3}$$

IX

The foregoing results allow the mechanism of the reaction of sulfur and hexafluoro-2-butyne to be interpreted as a simple process in which the radical end of a sulfur chain adds to the triple bond and the vinyl radical thus formed attacks the sulfur chain to give directly the stable dithietene (II).

A single attempt to extend the reaction to selenium, carried out by heating 2,3-diiodohexafluoro-2-butene with elemental selenium at 180° under pressure, gave tetrakis-(trifluoromethyl)-*p*-diselenin (X) and a mixture of lower boiling products not separable by distillation. The isolation of an appreci-

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[5] W. E. Parham and V. J. Traynelis, *J. Am. Chem. Soc.*, **77**, 68 (1955).

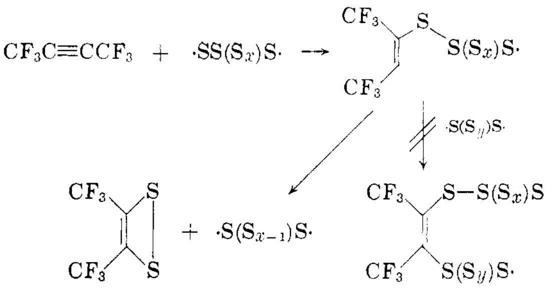
[6] W. E. Parham, G. L. O. Mayo and B. Gadsby, *ibid.*, **81**, 5993 (1959).

[7] This experiment was carried out by Dr. W. A. Sheppard of these laboratories.

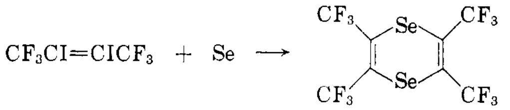
[8] C. G. Krespan and B. C. McKusick, *J. Am. Chem. Soc.*, **83**, 3438 (1961).

[9] J. P. Simons, *Quart. Revs.*, **13**, 19 (1959).

[10] G. A. R. Brandt, H. J. Emeleus and R. N. Haszeldine, *J. Chem. Soc.*, 2198 (1952).



able amount of X after exposure to a temperature at which the *p*-dithiin ring contracts shows the *p*-diselenin ring to be relatively stable toward loss of selenium to form a selenophene. If a bridged transition state is required for expulsion of selenium as has been suggested for expulsion of sulfur,[4] difficulty in forming the new carbon–carbon bond because of the greater distance involved with selenium in place of sulfur could explain the stability of X. Details of the mechanism by which *p*-dithiins can collapse are still somewhat uncertain,[4,5,11] and apparently no compounds containing the isolated *p*-diselenin ring have previously been prepared, so that no definite conclusions can yet be drawn.



X

Acknowledgment.—The author is indebted to Drs. V. A. Engelhardt and B. C. McKusick for encouragement and helpful discussions during the course of this work.

Experimental[12]

Sulfur and Hexafluoro-2-butyne under Pressure.—Reaction of 6.4 g. (0.20 gram-atom) of sulfur, 12.7 g. (0.05 mole) of iodine and 30 g. (0.19 mole) of hexafluoro-2-butyne at 200° for 6 hours under autogenous pressure gave 42 g. of product, mainly liquid. Distillation of this liquid gave four crude products contaminated with free iodine and having b.p. 90–92° (A), 130–132° (B), 68–71° (44 mm.) (C) and 125–126° (44 mm.) (D). The iodine in these fractions was removed by shaking them with mercury and decanting the liquid.

Redistillation of A gave 5.8 g. (26% yield based on sulfur) of yellow, malodorous 3,4-bis-(trifluoromethyl)-1,2-dithietene (II). An analytical sample, b.p. 93–94°, m.p. *ca.* −79° (determined by differential thermal analysis), was prepared.

Anal. Calcd. for $C_4F_6S_2$: C, 21.24; F, 50.40; S, 28.36; mol. wt., 226. Found: C, 21.41; F, 51.01; S, 28.65; mol. wt., 226 (mass spec.).

The infrared spectrum contained double bond absorption at 6.14 μ. Absorption in the ultraviolet occurred at $\lambda_{\max}^{\text{isooctane}}$ 238 mμ (ϵ 7,440), 340 mμ (ϵ 80). The nuclear magnetic resonance spectrum was a band for CF_3 at −811 c.p.s. Electron paramagnetic resonance revealed no free radical character at 25°. The dipole moment in benzene was 2.4 D. using a calculated molar refraction based on either a dithietene or a dithione structure.

Product B was redistilled to give 3.8 g. (11% yield based on butyne) of colorless tetrakis-(trifluoromethyl)-thiophene (III). An analytical sample, b.p. 134–135°, m.p. 5°, $n^{25}\text{D}$ 1.3540, was prepared.

Anal. Calcd. for $C_8F_{12}S$: C, 26.98; F, 64.02; S, 9.01. Found: C, 27.51; F, 64.02; S, 9.05.

Bands for aromatic unsaturation occurred at 6.38 and 6.69 μ in the infrared. Absorption in the ultraviolet was at $\lambda_{\max}^{\text{ethanol}}$ 231 mμ (ϵ 4,450), 242 mμ (ϵ 4,200), shoulder at 250 mμ. Nuclear magnetic resonance revealed two CF_3 peaks of equal intensity at −1227 and −1124 c.p.s.

Product C was judged to be a mixture of the *cis*- and *trans*-diiodides of hexafluoro-2-butyne, since it boiled at the correct place for these diiodides and was destroyed in an exothermic reaction with magnesium in ether.

Product D gave on redistillation 8.9 g. (29% yield based on sulfur) of pale yellow 2,3,4a,6,7,8a-hexakis-(trifluoromethyl) - 4a,8a - dihydro - *p* - dithiino[2,3 - b] - *p* - dithiin (IV), b.p. 97–99° (14 mm.).

Anal. Calcd. for $C_{12}F_{18}S_4$: C, 23.46; F, 55.67; S, 20.88; mol. wt., 614. Found: C, 23.93; F, 55.92; S, 20.58; mol. wt., 612.

The infrared spectrum showed C=C absorption at 6.14 μ. Ultraviolet absorption occurred at $\lambda_{\max}^{\text{isooctane}}$ 287 mμ (ϵ 4,280), shoulder at 250 mμ. Nuclear magnetic resonance bands for CF_3 occurred at −1188 and at −596 c.p.s. with intensities of 2:1, respectively.

A similar result could be obtained from sulfur and hexafluoro-2-butyne under pressure with no iodine present, but a temperature of 220° was required for a rapid reaction. This temperature could be reduced to 180° when benzene was added as a solvent for the reaction with no iodine present.

Sulfur and Hexafluoro-2-butyne at One Atmosphere.[13]—A 2-necked flask containing 250 g. of sulfur was purged with nitrogen while the sulfur was heated to reflux. The nitrogen was shut off, and 36 g. (0.22 mole) of hexafluoro-2-butyne was passed in one neck at one atmosphere over a period of 20 minutes while the product was continually withdrawn from the other neck. The system was then flushed with nitrogen while it cooled. Distillation of the liquid product gave 39.6 g. (80% yield) of 3,4-bis-(trifluoromethyl)-1,2-dithietene (II), b.p. 93–96°, identified by comparison of the nuclear magnetic resonance spectrum with that of an authentic sample.

Sulfur and Hexafluoro-2-butyne Diiodide.—A mixture of 166 g. (0.40 mole) of 2,3-diiodohexafluoro-2-butene[14] and 48.0 g. (1.50 gram-atoms) of sulfur was heated to reflux for 10 hours under atmospheric pressure. During this time a liquid, b.p. 92–95°, was removed slowly through a Vigreux column attached to the reaction flask. The distillate was cooled, decanted from precipitated iodine, shaken briefly with mercury, filtered, and distilled to give 57.0 g. (63% yield) of 3,4-bis-(trifluoromethyl)-1,2-dithietene (II), b.p. 95–96° (760 mm.), 39–40° (100 mm.), identified by comparison of the nuclear magnetic resonance spectrum with that of an authentic sample.

3,4,7,8-Tetrakis-(trifluoromethyl)-1,2,5,6-tetrathiocin (V).—A sample of 3,4-bis-(trifluoromethyl)-1,2-dithietene (5.2 g.) crystallized on standing 2 months at 25°. The yellow 3,4,7,8-tetrakis-(trifluoromethyl)-1,2,5,6-tetrathiocin, 4.5 g. (87% yield), m.p. 110–111° (subl.), was obtained analytically pure by slow sublimation at 80° (1 atm.).

Anal. Calcd. for $C_8F_{12}S_4$: C, 21.24; F, 50.40; S, 28.36; mol. wt., 452. Found: C, 21.57; F, 50.31; S, 27.96; mol. wt., 459 (f.p. benzene).

An infrared band for C=C was found at 6.40 μ (KBr wafer). Ultraviolet absorption occurred at $\lambda_{\max}^{\text{isooctane}}$ 253 mμ (ϵ 7,730), 292 mμ (ϵ 5,330), 341 mμ (ϵ 2,860). Nuclear magnetic resonance revealed a single peak for CF_3 at −1150 c.p.s. (in benzene).

Equilibrium of 3,4-Bis-(trifluoromethyl)-1,2-dithietene with Its Dimer. A.—To 5.4 g. (0.024 mole) of 3,4-bis-(trifluoromethyl)-1,2-dithietene was added 1 drop of triethylamine. An immediate exothermic reaction occurred

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(11) W. E. Parham, B. Gadsby and R. A. Mikulec, *J. Org. Chem.*, **24**, 1819 (1959).

(12) Boiling points and melting points are uncorrected. The nuclear magnetic resonance spectra were obtained by means of a high resolution nuclear magnetic resonance spectrometer and associated electromagnet, both manufactured by Varian Associates, operating at 56.4 mc./sec. and approximately 14,000 gauss. Spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the F^{19} resonance of trifluoroacetic acid and H^1 resonance of water. Negative frequency displacements indicate resonances occurring at lower field than the references.

(13) The author is indebted to Dr. E. G. Howard of these laboratories for devising and carrying out this synthesis.

(14) Prepared as described by C. G. Krespan, *J. Am. Chem. Soc.*, **83**, 3434 (1961).

with simultaneous deposition of solid. The reaction mixture was cooled to room temperature and allowed to stand for 10 minutes. Then 2 drops of acetic acid were added, and the product was recrystallized from hexane to give 3.0 g. (56% yield) of pale yellow crystals, m.p. 110° (subl.) alone or mixed with an authentic sample of 3,4,7,8-tetrakis-(trifluoromethyl)-1,2,5,6-tetrathiocin. Similarly, an attempted reaction of the dithietene with inhibited acrylonitrile resulted in an exothermic formation of the dimer in 84% yield.

B.—When 20.0 g. (0.044 mole) of 3,4,7,8-tetrakis-(trifluoromethyl)-1,2,5,6-tetrathiocin was heated at 180–220°, a liquid, b.p. 90–95°, distilled out. The liquid, identified as 3,4-bis-(trifluoromethyl)-1,2-dithietene by comparison of the nuclear magnetic resonance spectrum with that of a known sample, weighed 12.7 g. (64% yield).

Instability of 3,4,7,8-Tetrakis-(trifluoromethyl)-1,2,5,6-tetrathiocin in Alcohol.—A solution of 7.6 g. (0.017 mole) of 3,4,7,8-tetrakis-(trifluoromethyl)-1,2,5,6-tetrathiocin in 35 ml. of warm absolute alcohol deposited crystals of the tetrathiocin when cooled. When the mixture was allowed to stand 3 days at room temperature, the crystals redissolved. After one month, a second liquid phase and some yellow solid were present. The mixture then was diluted with 75 ml. of water and extracted with three portions of methylene chloride. The combined extracts were dried, filtered and distilled to give 2.3 g. (35% yield) of 2,3,4a,6,7,-8a-hexakis-(trifluoromethyl)- 4a,8a- dihydro- *p*- dithiino[2,3-b]-*p*-dithiin (IV), b.p. 83–84° (5 mm.), identified by comparison of the infrared and nuclear magnetic resonance spectra with those of a known sample.

3,4-Bis-(5-hydrodecafluoropentyl)-1,2-dithietene (VI).—A large excess of sulfur (100 g.) was heated to reflux under one atmosphere of nitrogen in a two-necked flask. Then 15.2 g. (0.029 mole) of 1,12-dihydroeicosafluoro-6-dodecyne[2] was passed through the hot vapors by dropwise addition into one neck over a 10-minute period. The crude product, which was continually removed from the reaction flask, was collected and fractionated to give 4.2 g. (27%) of recovered dodecyne, b.p. 51–53° (5 mm.), and 5.1 g. (30% conversion, 41% yield) of 3,4-bis-(5-hydrodecafluoropentyl)-1,2-dithietene, b.p. 103–104° (5 mm.).

Anal. Calcd. for $C_{12}H_2F_{20}S_2$: C, 24.42; H, 0.34; F, 64.38; S, 10.86. Found: C, 24.55; H, 0.53; F, 64.60; S, 10.57.

Infrared analysis showed $C{=}C$ at 6.25 μ. The ultraviolet spectrum was $\lambda_{\max}^{\text{isooctane}}$ 243 mμ (ε 10,000), 334 mμ (ε 60). The nuclear magnetic resonance spectrum contained CF_2 peaks at +1678 c.p.s. for CF_2 adjacent to dithietene ring, at +2454, +2580 and +2973 c.p.s. for internal CF_2 groups, and a doublet at +3384 and +3438 c.p.s. for terminal CF_2 split by proton; proton resonance was a triplet centered at −56 c.p.s. with satellites at −108 and −4 c.p.s.

3,4-Bis-(2-chlorotetrafluoroethyl)-1,2-dithietene (VII).—Passage of 29.5 g. (0.10 mole) of 1,6-dichloroöctafluoro-3-hexyne[2] through vapors of sulfur refluxing at one atmosphere was carried out over a 20-minute period, during which time the product was continually withdrawn. Distillation gave 11.8 g. (40%) of recovered hexyne, b.p. 46–50° (220 mm.), and 17.7 g. (49% conversion, 82% yield) of 3,4-bis-(2-chlorotetrafluoroethyl)-1,2-dithietene, b.p. 98° (40 mm.).

Anal. Calcd. for $C_6Cl_2F_8S_2$: Cl, 19.75; F, 42.33; S, 17.86. Found: Cl, 19.58; F, 42.34; S, 18.08.

A band in the infrared for $C{=}C$ fell at 6.24 μ. Ultraviolet absorption occurred at $\lambda_{\max}^{\text{isooctane}}$ 242 mμ (ε 9,540), 335 mμ (ε 65). The nuclear magnetic resonance spectrum consisted of peaks for CF_2 adjacent to dithietene ring at +1585 c.p.s. and CF_2Cl at −465 c.p.s.

2,3,5,6-Tetrakis-(trifluoromethyl)-*p*-dithiin (VIII).—A mixture of 20.0 g. (0.09 mole) of 3,4-bis-(trifluoromethyl)-1,2-dithietene and 30 g. (0.18 mole) of hexafluoro-2-butyne was heated at 100° for 4 hours under autogenous pressure. Distillation of the liquid product gave 13.4 g. of a mixture of the desired 1,4-dithiin and tetrakis-(trifluoromethyl)-thiophene, b.p. 70° (90 mm.) −54° (25 mm.), and 11.4 g. (33% yield) of 2,3,5,6-tetrakis-(trifluoromethyl)-*p*-dithiin, b.p. 54–55° (25 mm.), m.p. 24–25°.

Anal. Calcd. for $C_8F_{12}S_2$: C, 24.75; F, 58.73; S, 16.52. Found: C, 25.02; F, 59.16; S, 16.01.

Double bond absorption in the infrared was at 6.31 μ. Ultraviolet absorption occurred at $\lambda_{\max}^{\text{isooctane}}$ 275 mμ (ε 4,530), 285 mμ (ε 4,530), shoulders at 256, 266 mμ. Nuclear magnetic resonance showed one CF_3 peak at −1094 c.p.s.

Pyrolysis of 2,3,5,6-Tetrakis-(trifluoromethyl)-*p*-dithiin.—A mixture of 15.7 g. (0.04 mole) of 2,3,5,6-tetrakis-(trifluoromethyl)-*p*-dithiin and 9.0 g. (0.04 mole) of 3,4-bis-(trifluoromethyl)-1,2-dithietene was refluxed for 7 hours in an attempted addition of the dithietene to a double bond of the dithiin. At the pot temperature of about 130°, however, elimination of sulfur from the dithiin occurred. Distillation of the reaction mixture gave 5.6 g. (62%) of recovered dithietene, b.p. 93–97°, and 11.4 g. (79% yield) of tetrakis-(trifluoromethyl)-thiophene, b.p. 130–133°, identified by comparison of its nuclear magnetic resonance spectrum with that of an authentic sample. The residue was washed with petroleum ether to give 1.0 g. (77% yield) of insoluble sulfur.

Bis-(tris-(trifluoromethyl)-vinyl) Disulfide and Trisulfide.—Reaction of 98 g. (0.50 mole) of trifluoromethyl iodide and 81 g. (0.50 mole) of hexafluoro-2-butyne at 240° under autogenous pressure for 15 hours gave 125 g. of crude tris-(trifluoromethyl)-vinyl iodide. The product was purified by shaking with mercury, filtration, and distillation. The yellow distillate, b.p. 56° (180 mm.), weighed 106 g. (59% yield) and was shown to contain iodine. It was characterized by its nuclear magnetic resonance spectrum, which had the expected three peaks for CF_3 in 1:1:1 ratio with considerable splitting of all three peaks.

Tris-(trifluoromethyl)-vinyl iodide (53.7 g., 0.15 mole) and 9.6 g. (0.30 gram-atom) of sulfur were heated together at 225° for 6 hours under autogenous pressure. Distillation of the reaction mixture gave two major products. Bis-(tris-(trifluoromethyl)-vinyl) disulfide was obtained as 7.8 g. (20% yield) of light yellow oil, b.p. 82° (25 mm.).

Anal. Calcd. for $C_{10}F_{18}S_2$: C, 22.82; F, 64.99; S, 12.18. Found: C, 23.07; F, 64.82; S, 11.96.

A band for $C{=}C$ in the infrared spectrum fell at 6.19 μ. Ultraviolet absorption was at $\lambda_{\max}^{\text{isooctane}}$ 216 mμ (ε 10.700), 318 mμ (ε 1,460). The nuclear magnetic resonance spectrum contained two groups of peaks for CF_3 in a 2:1 ratio centered at −1121 and −973 c.p.s. Considerable splitting of the CF_3 peaks by each other was evident.

The other product was 5.5 g. (13% yield) of yellow bis-(tris-(trifluoromethyl)-vinyl) trisulfide, b.p. 88–89° (8 mm.)

Anal. Calcd. for $C_{10}F_{18}S_3$: C, 21.51; F, 61.26; S, 17.23. Found: C, 21.89; F, 61.10; S, 17.07.

The infrared spectrum contained a band for $C{=}C$ at 6.21 μ. Ultraviolet absorption occurred at $\lambda_{\max}^{\text{isooctane}}$ 246 mμ (ε 5,270), 320 mμ (ε 3,340). The nuclear magnetic resonance spectrum contained three CF_3 peaks at −1191, −1125 and −1009 c.p.s. with considerable splitting of each.

2,3,5,6-Tetrakis-(trifluoromethyl)-*p*-diselenin (X).—A reaction of 83.2 g. (0.20 mole) of 2,3-diiodohexafluoro-2-butene and 31.6 g. (0.40 gram-atom) of selenium carried out at 180° for 8 hours under autogenous pressure gave a mixture of liquid and solid. The liquid product was decanted and distilled to give a large forerun followed by 4.0 g. (8% yield based on diiodide) of pale yellow 2,3,5,6-tetrakis-(trifluoromethyl)-*p*-diselenin, b.p. 106–107° (110 mm.). Recrystallization of the solidified product from 95% ethanol gave an analytical sample, m.p. 55°.

Anal. Calcd. for $C_8F_{12}Se_2$: C, 19.93; F, 47.30; Se, 32.8. Found: C, 20.17; F, 46.85; Se, 33.4 (X-ray emission).

An infrared band for $C{=}C$ occurred at 6.30 μ (KBr wafer). Ultraviolet absorption was at $\lambda_{\max}^{\text{ethanol}}$ 288 mμ (ε 5,780). A nuclear magnetic resonance peak for CF_3 was at −1252 c.p.s. (benzene solution).