

[CONTRIBUTION NO. 650 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

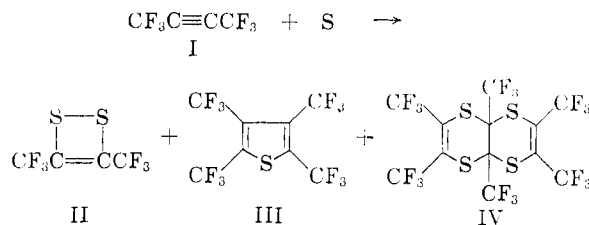
Bis-(polyfluoroalkyl)-acetylenes. IV. Fluorinated Dithietenes and Related Heterocyclic Compounds From Bis-(polyfluoroalkyl)-acetylenes and Sulfur¹

BY C. G. KRESPAN

RECEIVED JANUARY 31, 1961

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 tetrakis-(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 C₄F₈S₂, and the n.m.r. spectrum for F¹⁹ 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

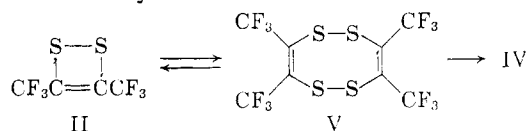
(1) C. G. Krespan, B. C. McKusick and T. L. Cairns, *J. Am. Chem. Soc.*, **82**, 1515 (1960).

(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).

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.



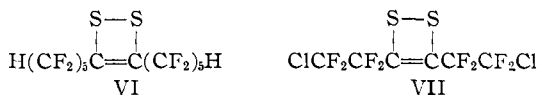
The dimer V may be thermodynamically stable with respect to the monomer II at low temperatures, but the fact that monomer (and not dimer) is a product of a reaction conducted at 200° over a period of hours indicates that at high temperatures the monomer is the more stable species. Confirmation of a reversible 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

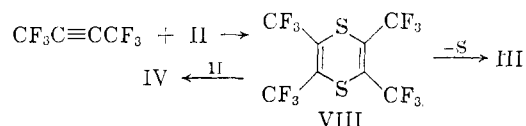
(4) M. Calvin and J. A. Barltrop, *J. Am. Chem. Soc.*, **74**, 6153 (1952).

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.



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}



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.

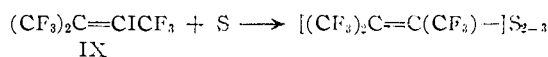
Analytical and spectral data do not exclude the possibility that the product formulated as the bi-

cyclic 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.



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*-diselenium (X) and a mixture of lower boiling products not separable by distillation. The isolation of an appreci-

(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).

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-dihydroicosafuoro-6-dodecyne² 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 C₁₂H₂F₂₀S₂: 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 λ_{max}^{isoctane} 243 mμ (ε 10,000), 334 mμ (ε 60). The nuclear magnetic resonance spectrum contained CF₂ peaks at +1678 c.p.s. for CF₂ adjacent to dithietene ring, at +2454, +2580 and +2973 c.p.s. for internal CF₂ groups, and a doublet at +3384 and +3438 c.p.s. for terminal CF₂ 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-dichlorooctafluoro-3-hexyne² 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 C₈Cl₂F₈S₂: 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 λ_{max}^{isoctane} 242 mμ (ε 9,540), 335 mμ (ε 65). The nuclear magnetic resonance spectrum consisted of peaks for CF₂ adjacent to dithietene ring at +1585 c.p.s. and CF₂Cl 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 C₈F₁₂S₂: 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 λ_{max}^{isoctane} 275 mμ (ε 4,530), 285 mμ (ε 4,530), shoulders at 256, 266 mμ. Nuclear magnetic resonance showed one CF₃ 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 CF₃ 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 C₁₀F₁₈S₂: 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 λ_{max}^{isoctane} 216 mμ (ε 10,700), 318 mμ (ε 1,460). The nuclear magnetic resonance spectrum contained two groups of peaks for CF₃ in a 2:1 ratio centered at –1121 and –973 c.p.s. Considerable splitting of the CF₃ 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 C₁₀F₁₈S₃: 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 λ_{max}^{isoctane} 246 mμ (ε 5,270), 320 mμ (ε 3,340). The nuclear magnetic resonance spectrum contained three CF₃ 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 C₈F₁₂Se₂: 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 λ_{max}^{ethanol} 288 mμ (ε 5,780). A nuclear magnetic resonance peak for CF₃ was at –1252 c.p.s. (benzene solution).