Reaction of Sulfide Ion with Fluorinated Olefins

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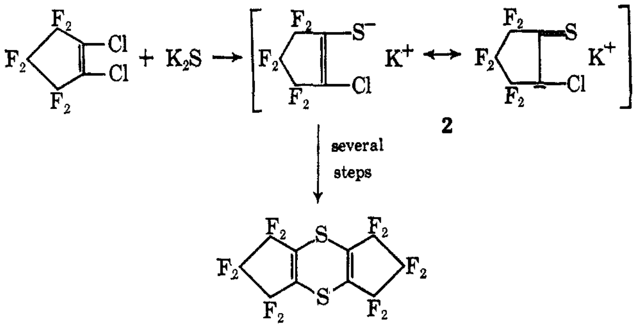
The reaction of sulfide ion with cyclic, acyclic internal, and terminal fluoro olefins, each containing two replaceable halogens, is discussed. Fluorinated cyclic sulfides containing, respectively, six-, five-, and four-membered rings are formed. Convenient syntheses of several compounds containing the dithiole ring system are described, including bis(trifluoromethyl)vinylene trithiocarbonate. Two examples are given in which mass spectrometry was essential to the structure determination.

Displacements of vinylic halogen from fluorinated olefins by mercaptide anion are known for a variety of cases.[1] The very nucleophilic mercaptide ion attacks readily at such double bonds and is postulated to give an intermediate carbanion. In the presence of free mercaptan, proton transfer can occur to give the saturated adduct of mercaptan with the olefin. In aprotic systems, loss of halide ion occurs to give the unsaturated sulfide. This paper describes reactions between sulfide ion and fluorinated olefins in which anions of unsaturated mercaptans are intermediates. Such anions are themselves nucleophiles and react further to give highly fluorinated cyclic sulfides directly.

Cyclic Olefins.—Anhydrous potassium sulfide was treated at room temperature with 1,2-dichlorohexafluorocyclopentene in dimethylformamide to give a 29% yield of *p*-dithiin **1** as essentially the only neutral product. The potassium sulfide is consumed slowly because of its limited solubility in the reaction medium. Four displacements of chloride ion must be involved in the formation of **1**, and some of the water-soluble byproducts are assumed to be mercaptide salts such as **2**. Reaction with excess potassium sulfide followed by treatment with methyl iodide to methylate the presumed potassiomercapto salts again gave a 30% yield of **1** and a viscous mixture of by-products which was not separated. Attempts to make a cyclic trithiocarbonate with potassium sulfide–carbon disulfide or potassium trithiocarbonate gave about the same yield of **1** as the only neutral product.



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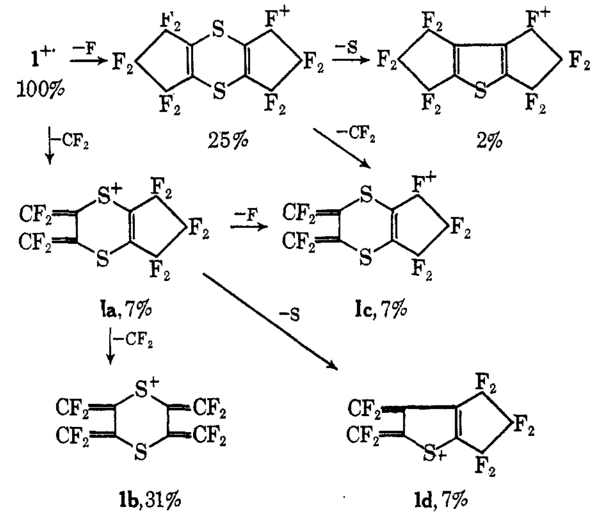
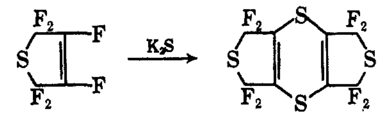
p-Dithiins, with fluorinated as well as unfluorinated substituents, are generally converted into thiophenes by extrusion of sulfur at elevated temperatures.[2,3] Contrary to this behavior, **1** showed no tendency to lose sulfur when heated at 200° for 6 hr in a sealed tube. Since tetrakis(trifluoromethyl)-*p*-dithiin is readily converted into the thiophene at 100–150°,[3] the stability of **1** seems to be due to steric constraints imposed by the two five-membered rings. Nor does loss of sulfur from **1** occur readily in the mass spectrometer. Figure 1 shows the mass spectrum of **1**. The molecule ion is the main species in the mass spectrum, probably because the cation radical is stabilized by more extensive conjugation than is present in the parent. Fragmentation occurs by primary loss of F or CF_2, rather than of S. The pronounced tendency to lose CF_2 is in accord with the presence of ring strain in the tricyclic system, and ring-opened structures **1a–d** are proposed for the resulting fragments.



Under conditions similar with those used to prepare **1**, hexafluoro-2,5-dihydrothiophene was converted into the *p*-dithiin **3** in 20% yield, and 1,2-dichlorotetrafluorocyclobutene was converted into **4** in 6% yield. In each case the yellow *p*-dithiin was obtained as virtually the only organic-soluble product. Both **3** and **4** proved to be stable when heated at 200° for 6 hr, a further indication that the ring structures provide a barrier to extrusion of sulfur.



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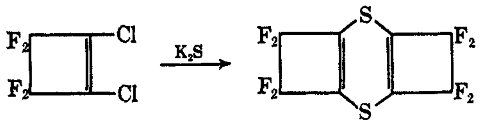

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[1] R. D. Chambers and R. H. Mobbs, *Advan. Fluorine Chem.*, **4**, 61, 62 (1965).

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

[3] C. G. Krespan, *ibid.*, **83**, 3434 (1961).

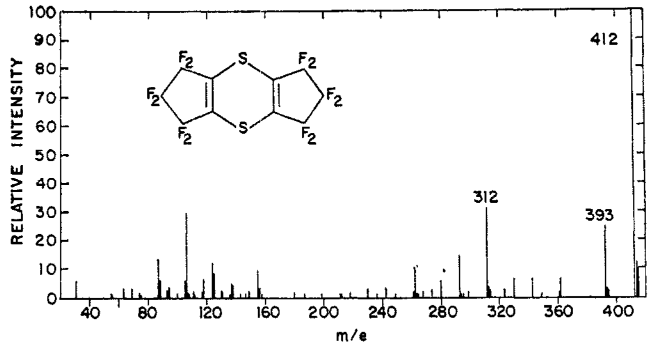


Figure 1.

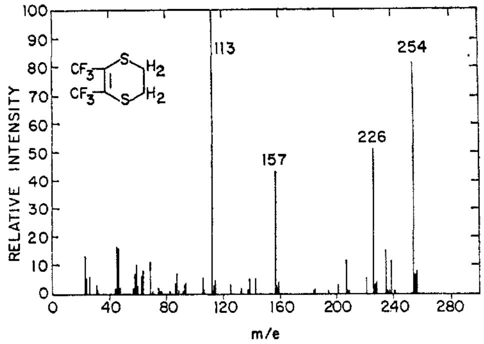


Figure 3.

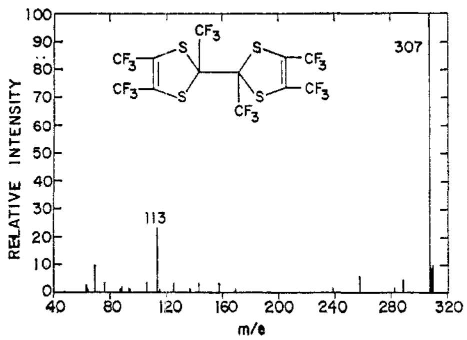


Figure 2.

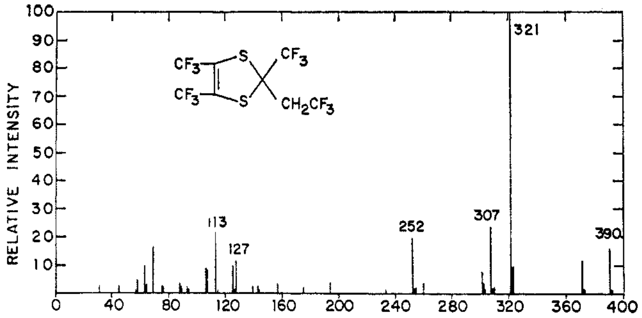
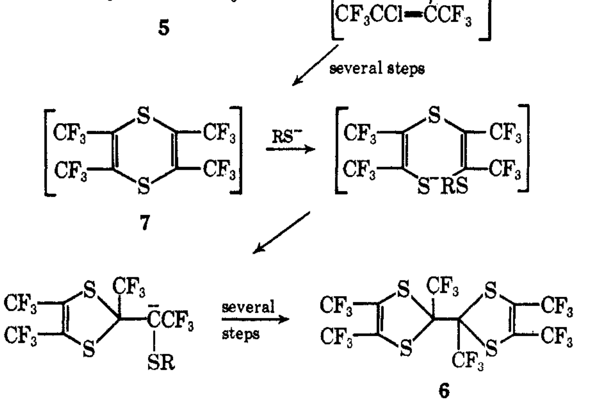


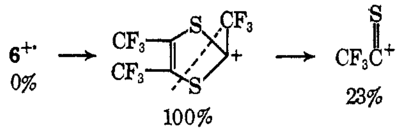
Figure 4.

Acyclic Olefin.—Although *p*-dithiins were obtained from cyclic olefins, the acyclic olefin, 2,3-dichlorohexafluoro-2-butene (**5**), yielded none. Instead, 1,3-dithioles were obtained from a variety of reagents.

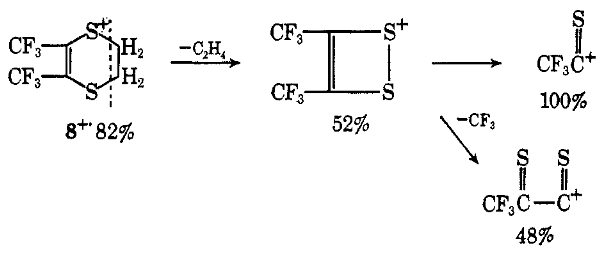
Potassium sulfide was treated with **5** in either dimethylformamide or dimethylformamide-water to give a 35% yield of the bidithiole **6**. The reaction must involve mercaptide intermediates and also an oxidation at some point. If the *p*-dithiin **7** is an intermediate, it is apparently attacked by sulfur anion to give ring opening and preferential reclosure to a five-membered ring. This conversion is similar to the previously observed formation of **6** from tetrakis(trifluoromethyl)-1,2,5,6-tetrathiocin in alcohol.[3]



When **6** was first obtained as one of the main products from sulfur and hexafluoro-2-butyne at 200°, the isomeric *p*-dithiinodihydro-*p*-dithiin structure was suggested for it.[3] Although the latter compound may well be present as a minor product of the reaction, the mass spectrum of **6** (Figure 2) is clearly different from that of a known dihydro-*p*-dithiin[2] (**8**) and points instead to the bi(1,3-dithiole) structure for **6**. Cleavage of **6** to give a stable dithiolium cation occurred so easily that the M/2 fragment was essentially the highest mass seen, and the predominant ring cleavage produced a thioacylium fragment.



Dihydro-*p*-dithiin **8**, on the other hand, had a substantial parent, and cleaved mainly to ethylene and bis(trifluoromethyl)-1,2-dithiete cation radical in a reversal of the reaction by which **8** was formed. Further fragmentation to thioacylium ions derived from the dithiete is also observed. Figure 3 shows the mass spectrum of **8**.



Another 1,3-dithiole (**9**) was formed in 48% yield from sodium thiosulfate and olefin **5** in dimethylformamide. Comparison of the mass spectrum of **9** (Figure 4) with that of **6** confirmed the 1,3-dithiole structure for **6** in that a strong tendency to form stable dithiolium cations **9a-c** and cation radical **9d** and cleavage to the corresponding thioacylium ions and thioketene cation radical were apparent in **9**, similar to the fragmentation observed for **6**.

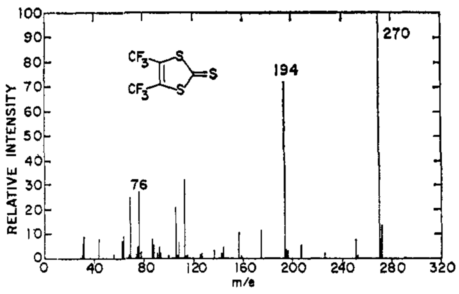
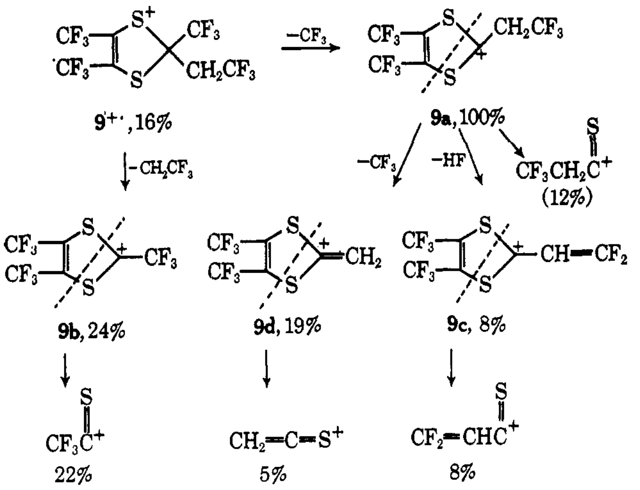
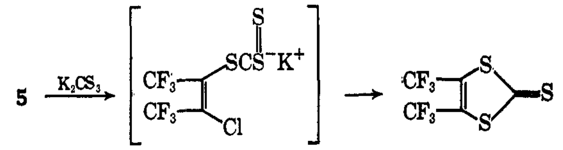


Figure 5.

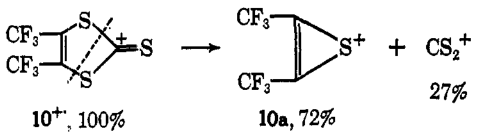


With potassium trithiocarbonate prepared from potassium sulfide and carbon disulfide in dimethylformamide, olefin **5** was converted into the new cyclic trithiocarbonate **10** in one convenient step. In this instance, the intermediate anion could close directly to a five-membered ring.



10

The mass spectrum of **10** (Figure 5) had a large molecular ion, presumably due to the presence of the stable 1,3-dithiolium ring with (4*n* + 2) electrons. Cleavage of the ring occurred mainly by elimination of carbon disulfide. The fragment corresponding to C_4F_6S, observed in several of the other mass spectra in minor amount, is major in the spectrum of **10**. The stabilization energy of the cation radical of carbon disulfide is apparently much less than that of a thioacylium ion, so that only for $10^{+\cdot}$ does cleavage of the dithiole ring give preferentially a C_4F_6S cation radical. We suggest that this fragment is a cation–radical derived from an acetylene episulfide (**10a**), and that this system has achieved some measure of stabilization from the loss of one electron.



An alternative synthesis of **10** is the reaction of hexafluoro-2-butyne, sulfur, and carbon disulfide at 200°.

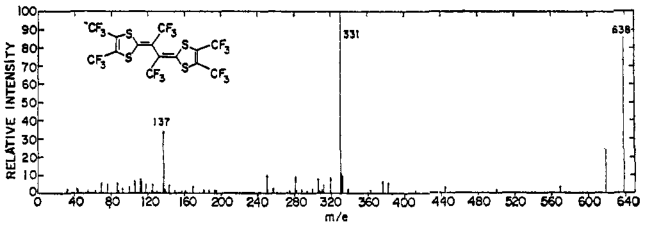
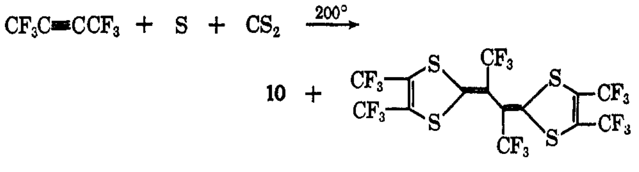


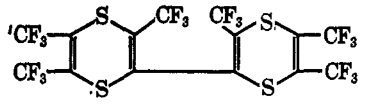
Figure 6.

The interesting by-product of this synthesis was a yellow solid (33% yield) which contained three molecules of the butyne plus two of carbon disulfide. Although other spectral methods did not help distinguish among the three isomeric structures (**11**, **12**, and **13**), mass spectrometry allowed a clear choice to be made in favor of **11**.



$CF_3C{\equiv}CCF_3 + S + CS_2 \xrightarrow{200°} 10 +$

11



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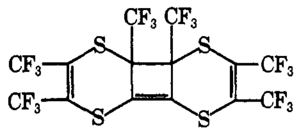

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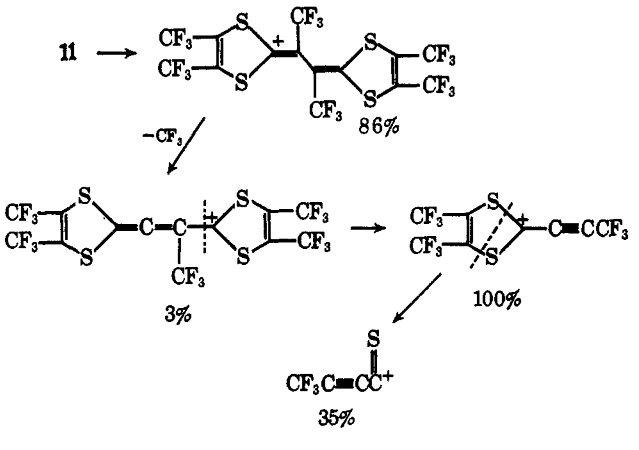
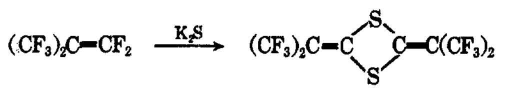
All three structures have appropriate possibilities for conjugation (indicated by the infrared and ultraviolet spectra) and contain two identical CF_3 groups and two pairs of slightly dissimilar CF_3 groups (indicated by nmr). The mass spectrum (Figure 6) contained a relatively large parent ion (reasonable for all three structures), a small M − CF_3 fragment (likely for **11** or **13**, not **12**), and a large fragment at M/2 + C (indicative of **11** only). A fragment characteristic of cleavage of the dithiole ring provided confirmation of structure **11**.



Terminal Olefins.—Treatment of octafluoroisobutylene with potassium sulfide in dimethylformamide at 0° for 0.5 hr gave a 62% yield of 2,4-bis[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-dithietane (**14**). This compound has been reported to result from dimerization of bis(trifluoromethyl)thioketene,[4] so that in the present case either the thioketene or various anions are possible intermediates. In the reaction mixture, **14** proved to be susceptible to attack by sulfide, and increases in time and temperature gave reduced yields of **14**.



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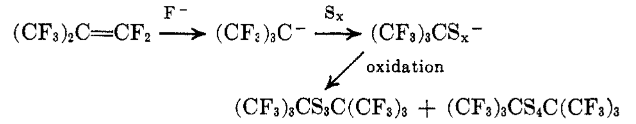
As the reaction proceeds, the concentration of fluoride ion increases to the point where it competes with sulfide ion for olefin. A minor product, bis(perfluoro-1,1-dimethylethyl) trisulfide (**15**) is produced from bis(perfluoro-1,1-dimethylethyl) carbanion and some form of sulfur. Increased yields of trisulfide **15** and tetrasulfide **16** resulted from reaction of cesium fluoride and sulfur with octafluoroisobutylene. As with the internal olefin plus sulfide ion, an oxidation step is involved in formation of the product.



$$(CF_3)_2C{=}CF_2 \xrightarrow{F^-} (CF_3)_3C^- \xrightarrow{S_x} (CF_3)_3CS_x^- \xrightarrow{\text{oxidation}} (CF_3)_3CS_3C(CF_3)_3 + (CF_3)_3CS_4C(CF_3)_3$$

15 **16**

Experimental Section[5]

Dodecafluoro-2,3,6,7-tetrahydro-1H,5H-dicyclopenta[*b*,*e*]-*p*-dithiin (1).[6]—A mixture of 61.2 g (0.25 mol) of 1,2-dichlorohexafluorocyclopentene, 27.5 g (0.25 mol) of granulated sulfurated potash (principal component of which is anhydrous potassium sulfide), and 100 ml of dimethylformamide was stirred for 2 weeks at 25°. The reaction mixture was then shaken with 1 l. of cold water, the organic layer which separated was removed, and the aqueous layer was extracted with two 50-ml portions of petroleum ether (30–60°). The combined organic layers were washed with dilute HCl, then with water, and dried. Evaporation of most of the solvent gave a yellow solid. Recrystallization of this solid from petroleum ether yielded 14.8 g (29%) of the yellow *p*-dithiin **1**, mp 60–63°. An analytical sample was obtained by recrystallization from methanol: mp 63–64°.

Anal. Calcd for $C_{10}F_{12}S_2$: C, 29.13; F, 55.31; S, 15.55; mol wt, 412. Found: C, 29.39; F, 55.72; S, 15.40; mol wt, 412 (mass spectrometry).

The infrared spectrum (KBr wafer) contained bands at 6.27 (C=C) and 7.5–10 μ (C—F). Ultraviolet absorption occurred at $\lambda_{\max}^{\text{isooctane}}$ 214 (ε 6200), 242 (3800), 261 (4000), and a broad band appeared at 350 mμ (ε 66). Nmr resonances for F^{19} were a triplet (J_{FF} = 3.5 cps) at +114 ppm (area 2) and a quintet (J_{FF} = 3.5 cps) at +121 ppm (area 1).

Octafluoro-1,3,5,7-tetrahydrodithieno[3,4-*b*:3′,4′-*e*]-*p*-dithiin (3).[6]—Hexafluoro-2,5-dihydrothiophene was prepared from sulfur and hexafluorocyclobutene at 300°.[7]

Dithiin **3** was prepared similarly to **1** by reaction of 38.8 g (0.20 mol) of hexafluoro-2,5-dihydrothiophene, 22.0 g (0.20 mol) of potassium sulfide, and 100 ml of dimethylformamide at 25° for 12 hr. Isolation of the water-insoluble product and recrystallization from aqueous methanol gave 7.4 g (20%) of **3**, mp 98–100°.

Anal. Calcd for $C_8F_8S_4$: C, 25.53; F, 40.39; S, 34.08; mol wt, 376. Found: C, 25.84; F, 40.43; S, 34.48; mol wt, 375, 364.

Infrared absorption occurred at 6.20 (C=C) and 8–10 μ (C—F). Ultraviolet absorption occurred at $\lambda_{\max}^{\text{isooctane}}$ 218 mμ (ε 6200) and 292 (2600) with a shoulder at 237 (8000) and a very broad shoulder at about 350 (86). The nmr spectrum for F^{19} consisted of a singlet at +72.2 ppm.

Octafluoro-2,7-dithiatricyclo[6.2.0.0^{3,6}]deca-1(8),3(6)-diene (4).[6]—Reaction of 48.8 g (0.25 mol) of 1,2-dichlorotetrafluorocyclobutene, 27.5 g (0.25 mol) of potassium sulfide, and 100 ml of dimethylformamide was carried out at 25° for 12 hr and worked up similarly to that for **1**. The final purification gave 2.5 g (6%) of **4**, mp 132–133° (sublimed).

Anal. Calcd for $C_8F_8S_2$: C, 30.78; F, 48.69; S, 20.54; mol wt, 312. Found: C, 31.15; F, 48.56; S, 19.98, 21.36; mol wt, 286, 282.

The infrared spectrum contained bands at 6.38 (C=C) and 7.5–9 μ (C—F). Ultraviolet absorption occurred at $\lambda_{\max}^{\text{isooctane}}$ 230 mμ (ε 7400) and a very broad band at 370 (65) with shoulders at 221 (6500) and 245 (3300). The nmr spectrum for F^{19} consisted of a singlet at +117 ppm.

2,2′-Bi[2,4,5-tris[trifluoromethyl]-1,3-dithiole] (6).—A reaction mixture of 27.5 g (0.25 mol) of potassium sulfide, 58.2 g (0.25 mol) of 2,3-dichlorohexafluoro-2-butene, and 150 ml of purified dimethylformamide was stirred at 25° for 6 days. The lower layer of product was then removed, and the upper layer was extracted with two 50-ml portions of petroleum ether. The layers containing product were combined, washed with dilute hydrochloric acid, dried, and distilled. The product was 18.0 g (35% based on olefin) of **6**, bp 82–84° (3 mm). Similar results were obtained using aqueous dimethylformamide, showing that these sulfide reactions tolerate the presence of water. This compound was identified by comparison of the infrared and nmr spectra with those of a sample prepared by reaction of sulfur with hexafluoro-2-butyne.[3] Nmr resonances for F^{19} were a singlet at +56.7 ppm (area 2) and a singlet at +72.2 ppm (area 1). Infrared absorption occurred at 6.14 μ (C=C).

2-(2,2,2-Trifluoroethyl)-2,4,5-tris(trifluoromethyl)1,3-dithiole (9).—A mixture of 124.1 g (0.50 mol) of sodium thiosulfate pentahydrate, 58.2 g (0.25 mol) of 2,3-dichlorohexafluoro-2-butene, and 300 ml of purified dimethylformamide was stirred for 3 weeks at 25°. Volatiles were then removed at 25–80° (1 mm). The volatiles were mixed with 500 ml of water and extracted with two 100-ml portions of petroleum ether. Distillation of the organic extracts afforded 23.2 g (48%) of **9** as a pale yellow oil: bp 80–81° (60 mm); n^{25}D 1.3707. Gas chromatography indicated the product to be a single compound.

Anal. Calcd for $C_8H_2F_{12}S_2$: C, 24.62; H, 0.52; F, 58.43; S, 16.43; mol wt, 390. Found: C, 25.37; H, 0.83; F, 58.78; S, 16.66; mol wt, 390 (mass spectrometry).

The infrared spectrum contained bands at 3.32 and 3.43 (saturated C-H), 5.90 (C=C), and 7.5–10 μ (C—F and C—H). The nmr spectrum for F^{19} consisted of a singlet at +57.2 ppm for CF_3—C=C (area 2), an octet centered at +61.3 ppm composed of a triplet (J_{HF} = 9 cps) split into overlapping quartets (J_{FF} = 4.5 cps) for CF_3CH_2 (area 1), and a quartet (J_{FF} = 4.5 cps) at +81 ppm for the other CF_3 (area 1). The H^1 spectrum is a quartet (J_{HF} = 9 cps) centered at +2.8 ppm.

1,2-Bis(trifluoromethyl)vinylene Trithiocarbonate (10). **A.**—A mixture of 6.4 g (0.20 g-atom) of sulfur, 32 g (0.20 mol) of hexafluoro-2-butyne, and 20 ml of carbon disulfide was heated at 200° for 6 hr under autogenous pressure. Distillation of the liquid part of the reaction mixture gave 0.4 g (2% yield base on sulfur) of 3,4-bis(trifluoromethyl)-1,2-dithiete, bp 36° (90 mm), identified by its nmr spectrum for F^{19},[3] and 6.1 g (11% yield based on the butyne) of 1,2-bis(trifluoromethyl)vinylene trithiocarbonate, bp 96–98° (50 mm). Redistillation gave an analytical sample: bp 77–78° (20 mm); n^{25}D 1.5124.

Anal. Calcd for $C_5F_6S_3$: C, 22.22; F, 42.19; S, 35.59; mol wt, 270. Found: C, 22.56; F, 42.30; S, 35.37, mol wt, 270 (mass spectrometry).

The infrared spectrum contained bands at 6.30 (C=C) and 7.5–9.5 μ (C—F, C=S). Ultraviolet absorptions were at $\lambda_{\max}^{\text{isooctane}}$ 225 mμ (ε 7020), 345 (10,800), and 440 mμ (35), with shoulders at 286 and 360 mμ. The F^{19} nmr resonance occurred at +56.3 ppm.

Extraction of the solid reaction product with petroleum ether and concentration of the extracts gave a pale yellow solid. Recrystallization of the solid from petroleum ether gave 14.0 g (33% yield based on the butyne) of pale yellow **11**, mp 125–127°.

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(4) M. S. Raasch, *Chem. Commun.*, 577 (1966).

(5) Fluorine nmr spectra were obtained with a Varian Associates high-resolution spectrometer operating at 56.4 Mc/sec. Spectra were calibrated in terms of higher field displacement in parts per million (ppm) from the F^{19} resonance of the solvent, trichlorofluoromethane. Proton spectra were obtained on a Varian A-60 spectrometer with tetramethylsilane as internal reference. Mass spectra were run at 70 eV on a CEC 21-103C instrument.

(6) C. G. Krespan, U. S. Patent 3,096,342 (1963).

(7) C. G. Krespan, U. S. Patent 3,069,431 (1962).

Anal. Calcd for $C_{14}F_{18}S_4$: C, 26.34; F, 53.57; S, 20.09; mol wt, 638. Found: C, 26.49; F, 53.83; S, 20.09; mol wt, 638 (mass spectrometry).

Infrared absorptions (KBr wafer) were at 6.18 and 6.54 (C═C) and 7.5–9 μ (C—F). Ultraviolet absorption occurred at $\lambda_{max}^{isooctane}$ 296 mμ (ϵ 21,100). F^{19} nmr resonances are an A_3B_3 group centered at +56.2 ppm for CF_3—C═C (area 2) and a singlet at +61.6 ppm for CF_3 (area 1).

B.—A mixture of 27.5 g (0.25 mol) of potassium sulfide, 30 ml (38 g, 0.50 mol) of carbon disulfide, and 150 ml of distilled dimethylformamide was stirred at 25° for 2 hr. Then 58.2 g (0.25 mol) of 2,3-dichlorohexafluoro-2-butene was added, and the reaction was continued for 3 days at 25°. The resulting mixture of solid and orange liquid was diluted with 1.5 l. of water and extracted with two 100-ml portions of petroleum ether. The combined organic layers were dried and distilled to give 23.1 g (34%) of **10**, bp 82° (20 mm), identified by comparison of the infrared and nmr spectra with those of a known sample (see above).

This synthesis was also carried out using sodium sulfide nonahydrate, carbon disulfide, and 2,3-dichlorohexafluoro-2-butene in methanol, but the yield was only 13%.

An attempt to form a sulfonium salt with boiling benzyl bromide failed.

Bis(trifluoromethyl)thioketene Dimer (14).—Powdered potassium sulfide (44 g, 0.4 mol) and 100 ml of dimethylformamide were stirred and cooled in a −80° bath while 40 g (0.2 mol) of octafluoroisobutylene was added as a gas. When addition was complete, the mixture was stirred at 0° for 0.5 hr. Vacuum was then applied and volatile material was collected in a −80° trap while the reaction mixture was heated to 100°. The solid product was isolated by filtration, washed with water, and dried to give 19.5 g (62%) of crystalline bis(trifluoromethyl)thioketene dimer, **14**. Recrystallization from chloroform gave product, mp 85–86°, shown by mixture melting point and infrared spectrum to be identical with an authentic sample.[4]

Yields in this reaction were much lower at higher reaction temperature, presumably because the product is sensitive to attack by potassium sulfide in dimethylformamide. With hydrated sodium sulfide in dimethyformamide, a 44% yield was obtained.

Bis(perfluoro-1,1-dimethylethyl) Trisulfide (15) and Tetrasulfide (16). A.—The dimethylformamide filtrate above, from which thioketene dimer **14** had been separated, was diluted with water to cause separation of about 3 g of oil. The principal component, separated by gas chromatography, was the trisulfide **15**, mp 44–44.5° after recrystallization from chloroform. No functional groups were detected by infrared analysis and no proton by nmr analysis. The F^{19} nmr was a singlet at +63.3 ppm.

Anal. Calcd for $C_8F_{18}S_3$: C, 17.99; S, 18.01. Found: C, 18.18; S, 18.10.

B.—The assumption that trisulfide **15** is formed from a reaction initiated by fluoride ion was confirmed by the greatly increased yields obtained with sulfur plus potassium or cesium fluoride in place of potassium sulfide.

A mixture of 152 g (1.0 mol) of cesium fluoride, 64 g (2.0 g-atoms) of sulfur, and 250 ml of dimethylformamide was stirred while 700 g (3.5 mol) of octafluoroisobutylene was added as a gas. The exothermic reaction was maintained at 60–70° by controlling the rate of addition. When the sulfur was consumed during the addition, more was added to give a total of 112 g (3.5 g-atoms) of sulfur used. The mixture was then poured into water in a hood (caution; toxic gas evolved), and the mixture was extracted with petroleum ether. The organic extract was washed with water, dried, and cooled to −80° to precipitate 142 g (21%) of thioketene dimer **14**. Distillation of the filtrate gave 326 g (35% based on olefin, 52% based on sulfur) of trisulfide **15**, bp 96–100° (50 mm), which solidified on cooling and was shown to be identical with the earlier sample. A 20-g fraction boiling up to 123° (50 mm) probably contained the tetrasulfide **16**.

A similar run carried out with potassium fluoride in place of cesium fluoride gave a low yield of tetrasulfide **16** in a solid fraction with bp 123–138° (45 mm). Recrystallization at −80° from petroleum ether and then from chloroform gave **16**, mp 74–77°. F^{19} nmr showed a singlet at +63.3 ppm.

Anal. Calcd for $C_8F_{18}S_4$: C, 16.98; S, 22.66. Found: C, 17.36; S, 22.04.

Registry No.—**1**, 2342-08-7; **3**, 2924-06-3; **4**, 2924-05-2; **6**, 16005-65-5; **9**, 16005-61-1; **10**, 16005-62-2; **11**, 16031-09-7; **14**, 7445-61-6; **15**, 16005-64-4; **16**, 16065-65-9.

Fluoro Olefins. II. Isomerization of β-Substituted Perfluoro Olefins. Kinetic *vs.* Equilibrium Control[1]

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The scope of the synthetic sequence for the preparation of β-substituted perfluoro olefins from triphenylphosphine, sodium chlorodifluoroacetate, and polyfluorinated ketones has been extended to the polyfluorinated ketone, 1-phenylpentafluoropropanone. The product mixture consisted of 2-phenylheptafluoro-1-butene and *cis*- and *trans*-2-phenylheptafluoro-2-butene. The latter arises by a fluoride ion catalyzed isomerization of 2-phenylheptafluoro-1-butene to the isomeric internal fluoro olefin. The product ratio of external olefin to internal olefin and the *trans*/*cis* ratio of the internal olefin were found to be highly dependent upon the choice of alkali metal chlorodifluoroacetate and reaction time. With sodium and potassium chlorodifluoroacetate, the isomerization yielded an initial *trans*/*cis* (k_2/k_1) kinetic ratio of 1.2 and 2.0, respectively, which is markedly different from the equilibrium ratio of ~6.7. The effect of added alkali metal fluoride salts greatly accelerated the decomposition of the alkali metal chlorodifluoroacetates in the Wittig reaction and enhanced the equilibration of the *trans*–*cis* isomers in the order Cs ≫ Rb > K ≫ Na. Two mechanisms are suggested to explain the initial kinetic ratio of *trans*/*cis* isomers. The first mechanism involves a linear transition state with or without the intermediacy of a "discrete" fluoro carbanion. The second mechanism involves a six-membered cyclic transition state consisting of fluoro olefin and alkali metal fluoride.

The importance of fluoride ion has been well demonstrated in a wide variety of ionic reactions of perfluoro- and polyfluorinated olefins.[3] Owing to its unique reactivity as a strong nucleophile in unsaturated fluorine systems, it has been employed as a catalyst for anionic polymerizations, condensation and addition reactions, and rearrangements of polyfluorinated olefins. The major part of its applicability in these cases is to form

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[1] (a) Presented in part at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, Abstracts, p 9K; (b) taken in part from the Doctoral Dissertation of F. E. H., the University of Iowa, Aug 1966; (c) preliminary report, D. J. Burton and F. E. Herkes, *Tetrahedron Lett.*, No. 50, 4509 (1965).

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[3] For an excellent review, see R. D. Chambers and R. H. Mobbs, *Advan. Flourine Chem.*, **4**, 50 (1965).