of benzene was mixed with 1 g. of anhydrous magnesium sulfate and the mixture was refluxed for 3 hr. After filtering and evaporating the solvent, the product was chromatographed. Two products were obtained. The first one (30 mg.), $[\alpha]^{25}_D$ +71 ± 7°, was a material having the same ultraviolet and infrared spectra as the dehydration product (XIII) from α-4,8,13-duvatriene-1-ol-3-one. The second product (40 mg.) had ultraviolet (λ_{max}^{EtOH} = 289 mμ, ε 11,000) and infrared absorption (1659, 1620, 1226, 1140, 968 cm.$^{-1}$) consistent with the structure 1,4,8,13-duvatetraene-3-one. No analyses were obtained due to limited amounts of compounds.

Retroaldol Reaction of β-4,8,13-Duvatriene-1-ol-3-one.—A solution of β-4,8,13-duvatriene-1-ol-3-one in 10% sodium carbonate solution containing a small amount of alcohol was refluxed for 0.5 hr. The solution was extracted with ether and the ether solution was washed, dried, and evaporated. The product was an oil which was further purified by chromatography. The compound had the same infrared, ultraviolet, and nuclear magnetic resonance spectra and molecular weight as 11-isopropyl-4,8-dimethyl-3,7,12-pentadecatriene-2,14-dione (VI), obtained previously from α-4,8,13-duvatriene-1-ol-3-one.

Ozonolysis of β-4,8,13-Duvatriene-1,3-diol.—β-4,8,13-Duvatriene-1,3-diol (665 mg.) in 75 ml. of methylene chloride was ozonized for 30 min. at −78°. The solution was allowed to warm to room temperature and the solvent was evaporated *in vacuo*. Zinc dust was added and the mixture was steam distilled into a saturated solution of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid. The precipitate was filtered and chromatographed on silicic acid to give 311 mg. (35% yield of theoretical on a one mole basis) of levulinaldehyde 2,4-dinitrophenylhydrazone identified *via* infrared and mixed melting point. On the same basis a 55% yield of levulinaldehyde was obtained from a second ozonization of β-duvatrienediol.

Permanganate Oxidation of β-4,8,13-Duvatriene-1,3-diol.—Potassium permanganate (7.75 g., 49 mmoles) in 100 ml. of water was added to 1 g. of β-4,8,13-duvatriene-1,3-diol (3.26 mmoles) mixed with 300 ml. of water. The solution was stirred for 24 hr., then was treated with sulfur dioxide, and extracted with ether. The oil (300 mg.) obtained after evaporation of the ether was treated with diazomethane and the resulting mixture was analyzed by vapor phase chromatography. It was found to contain two major components, along with several minor ones; the two major components were determined to be methyl levulinate and methyl 5-keto-2-isopropylhexanoate by comparison of vapor phase chromatograms of samples enriched by the addition of authentic specimens. The vapor phase chromatograms were done using the same conditions as described previously for the products from the periodate–permanganate oxidation of α-4,8,13-duvatriene-1,3-diol.

Acknowledgment.—The authors are indebted to Richard F. Walsh for technical assistance and Thomas C. James for the extraction of the tobacco. The authors wish to express their appreciation to Drs. M. Senkus, C. E. Teague, and E. E. van Tamelen for their encouragement and helpful suggestions. Dr. W. G. Brown is also to be thanked for his assistance in preparation of the manuscript.

Fluorinated Cyclic Polysulfides and Their Polymers

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Contribution No. 778 from the Central Research Department, Experimental Station,
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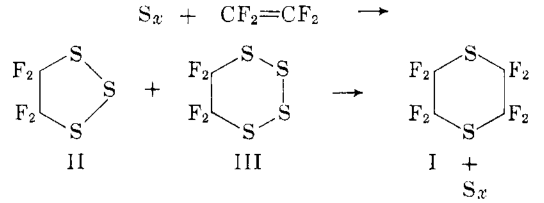
A unique cyclic tetrasulfide, tetrafluoro-1,2,3,4-tetrathiane, has been prepared in good yield directly from sulfur and tetrafluoroethylene. The new cyclic polysulfides, tetrafluoro-1,2,3-trithiolane and octafluoro-1,2,5-trithiepane, have also been isolated. The polymerization of these compounds and their role in the preparation of the thermally stable octafluoro-1,4-dithiane are described.

During earlier studies[1] of the interaction of sulfur with tetrafluoroethylene to produce octafluoro-1,4-dithiane (I), it was observed that polysulfides were also formed, apparently as intermediates to the dithiane. Further investigation of this reaction has now resulted in the characterization of several unusual cyclic and linear polysulfides of tetrafluoroethylene. Unlike reactions of sulfur with hydrocarbons, the number and amount of by-products are small, and individual polysulfides of tetrafluoroethylene are easily obtained.

Fluorinated Cyclic Polysulfides.—In order to obtain the primary products formed from tetrafluoroethylene and sulfur, the reaction was conducted at atmospheric pressure in a flow system with a large excess of sulfur. These conditions were attained by passing tetrafluoroethylene through vapors of refluxing sulfur (b.p. *ca.* 445°) and continuously withdrawing volatile product. High yields of polysulfides were obtained by this procedure, and it was possible to isolate 10% of the yellow tetrafluoro-1,2,3-trithiolane (II) and 60% of the pale yellow tetrafluoro-1,2,3,4-tetrathiane (III) with little of the dithiane I having been formed. Both II and III are malodorous oils with b.p. 38–39° (30 mm.) and 59–61° (15 mm.), respectively.



At the high temperature of 445°, some tetrafluoroethylene is lost in cracking reactions in which

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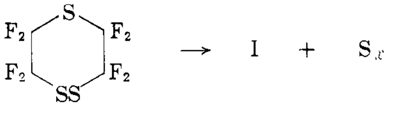
[1] C. G. Krespan and C. M. Langkammerer, *J. Org. Chem.*, **27**, 3584 (1962).

such products as carbon disulfide and thiocarbonyl fluoride are formed. As might be expected from this result, the tetrathiane can be converted cleanly to thiocarbonyl fluoride and sulfur by pyrolysis at 600° or higher in a flow system. The unique cyclic polysulfides II and III, and the linear polysulfides obtained as by-products, are evidently formed initially in the reaction between chains of sulfur atoms and tetrafluoroethylene. Both II and III, when pyrolyzed at 300° for ten hours under autogenous pressure, gave the dithiane I, just as tetrafluoroethylene and sulfur do under these conditions.

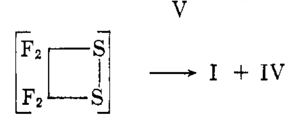
Since preparation of the dithiane I in good yield required reaction times of eight hours or more under pressure, another approach to isolation of intermediates was the use of a short reaction time in a sealed tube. Injection of tetrafluoroethylene at 300° into a pressure vessel containing an equivalent of sulfur followed by an additional hour of heating resulted in the formation of the new octafluoro-1,2,5-trithiepane (IV) in 24% yield along with 37% of I. The trithiepane IV was shown to be another precursor of the dithiane I by a separate pyrolysis at 300° for an extended period.


IV

Higher proportions of sulfur than above gave less of the dithiane I and the trithiepane IV, while the trithiolane II and the tetrathiane III were formed in increasing amounts along with high boiling residue.

The results described above show that tetrafluoroethylene combines with sulfur to form at least three cyclic polysulfides, two of which are formed directly and all of which will gradually eliminate sulfur at 300° to form the dithiane I as the major product. Separate tests have shown I to be stable at 300° and unreactive toward free radicals, so that it can be considered a stable end product under the reaction conditions. The principal route to trithiepane IV and dithiane I in the short-time reactions conducted under pressure should be interaction of intermediate polysulfides with tetrafluoroethylene except, as noted above, for cases where a large excess of sulfur is present for reaction with the tetrafluoroethylene. This follows from the fact that addition of tetrafluoroethylene over a period of time to one or two equivalents of sulfur heated at 300° in a pressure vessel results in the formation of considerable tetrasulfide III and other polysulfides during the early part of the tetrafluoroethylene addition. These products pyrolyze so slowly to I that, during the latter part of the olefin addition, direct reaction of tetrafluoroethylene with polysulfides must occur. Otherwise, the rapid rate of cyclodimerization of tetrafluoroethylene to the inert octafluorocyclobutane would cause lower yields of I than are actually obtained.

This line of reasoning raises the prospect of preparing new polysulfides by addition of tetrafluoroethylene to the fluorinated cyclic sulfides already available. The trithiepane IV proved to be unreactive toward tetrafluoroethylene at 300°, even in the presence of small amounts of sulfur, indicating that IV simply degrades slowly to the dithiane I once it is formed. The higher polysulfides, however, do react readily with tetrafluoroethylene, as was shown by the absorption of one equivalent of the olefin by the tetrathiane III at 150–200° to form a highly regular disulfide polymer (V) in 80% yield.


$$\mathrm{III} + CF_2{=}CF_2 \longrightarrow \underset{\mathrm{V}}{-\!\!(CF_2CF_2SS)\!\!-_n} \rightleftarrows$$
VI

Pyrolysis of V under pressure was shown to give trithiepane IV as well as dithiane I. It is likely that IV also results from the direct addition of tetrafluoroethylene to the trithiolane II, but this reaction has not been demonstrated. Tetrafluoro-1,2-dithietane (VI) has been observed as a product only in the pyrolysis of the polydisulfide V under reduced pressure. Under these conditions the polymer volatilized as species indicated by mass spectrometric analysis to include the 1,2-dithietane VI, but on condensation the volatile material reverted to V.[2]

The thermal conversion of the disulfide bonds in the trithiepane IV and the polymer V to the monosulfide bonds in octafluoro-1,4-dithiane in good yield is an unusual transformation, even in a fluorocarbon series. Acyclic fluoroalkyl polysulfides are reported to eliminate sulfur at high temperatures to give disulfides as the major products with little monosulfide being formed.[3,4] Therefore, it seems likely that the intramolecular nature of a reaction such as elimination of sulfur from the trithiepane IV to form a sterically favored six-membered ring is the main reason that the dithiane I can be prepared in high yield. If initial dissociation of the sulfur–sulfur bond into thiyl radicals is assumed, the conversion of IV to I must involve attack of thiyl radical on a saturated carbon atom with displacement of sulfur. Such reactions are rare, and the difficulty with which they proceed relative to recombination or reaction with sulfur to form higher polysulfides would account for the low rate of formation of I by pyrolysis of the various precursors. The known photochemical preparation of bis-

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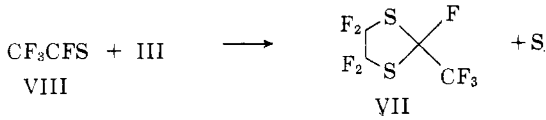
[2] The authors are indebted to Dr. M. W. Farlow of these laboratories for this experiment.

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

[4] M. Hauptschein and A. V. Grosse, *J. Am. Chem. Soc.*, **73**, 5461 (1951).

(trifluoromethyl) sulfide from bis(trifluoromethyl) disulfide appears to be a similar reaction of an acyclic disulfide.[3]

It was previously reported[1] that 2-trifluoromethylpentafluoro-1,3-dithiolane (VII), a product isomeric with the dithiane I, occurred as a by-product in reactions of sulfur with tetrafluoroethylene under pressure. During the present work, another product formed as a result of migration of a fluorine atom was observed. Trifluorothioacetyl fluoride (VIII)[5] consistently appeared as a minor product when sulfur and tetrafluoroethylene reacted in a flow system under one atmosphere of pressure. The rearranged intermediate VIII can serve as the source of the dithiolane VII, as demonstrated by its reaction with the cyclic tetrasulfide III at 300° to form the dithiolane in fair conversion.[6] Octafluoro-1,4-dithiane, on the other hand, was shown not to isomerize to the dithiolane under the conditions of the reaction.



Characterization of the new fluorinated cyclic polysulfides included determination of the nuclear magnetic resonance (n.m.r.) spectra for F^{19}. The dithiane I was previously found to have an n.m.r. spectrum consisting of a single resonance at lower field than usual for CF_2.[1] Since the ring in I must be puckered, the lack of splitting indicates rapid interconversion of the several possible conformations to give an average planar form. The spectrum for the trithiepane IV, however, consisted of two resonances in 1:1 ratio with the one at higher field appearing as a w-s-s-w group (AB pattern). This splliting, a result of non-equivalence of the two fluorine atoms on one of the difluoromethylene groups and consequent strong spin–spin coupling, is evidence that IV exists in one preferred puckered conformation as a mixture of optical isomers. The known hindrance to intramolecular rotation about sulfur–sulfur bonds[7] and the demonstrated rapid inversion in the 1,4-dithiane I lead us to believe the non-equivalent fluorine atoms in IV are on the carbon atoms adjacent to the disulfide group.[8]

Ring size, reported to be an important factor in determining stability of nonfluorinated cyclic disulfides,[9] has also been found to affect similarly the stability of the present fluorinated polysulfides. The tendency to polymerize is apparently so marked in the four-membered dithietane VI that we have been unable as yet to isolate it as the monomer, while the seven-membered trithiepane IV at the other end of the scale shows little tendency to polymerize on heating and requires a relatively strong base (triethylamine) to promote ionic ring-opening. The five-membered trithiolane II and six-membered tetrathiane III are intermediate in reactivity, so that the order of increasing stability is VI<II<III<IV.

The concept of ring size as a major factor in determining stability of the cyclic polysulfides can be related not only to compression of normal bond angles, but also to the strong repulsions between $p\pi$-electrons on adjoining sulfur atoms. These repulsions cause energy minima for those conformations where the dihedral angle for —S—S— is approximately 90–100°.[10,11] Hindrance to intramolecular rotation about sulfur–sulfur bonds develops because of unfavorable interactions in other conformations such as the planar or nearly planar, thereby providing a rationale for the instability of the small rings in VI and II which are forced into such an arrangement. Evidence that the trithiolane II contains a strained, nearly planar ring was found in its n.m.r. spectrum for F^{19}. Unlike the nonequivalence of fluorine atoms in the difluoromethylene group attached to polysulfide observed for the trithiepane IV, the fluorine atoms in II were shown to be equivalent by a spectrum containing only one singlet.

On the basis of the foregoing, the cyclic tetrasulfide III should have one or more preferred puckered conformations. Its n.m.r. spectrum for F^{19} indicates that this is so by exhibiting only a w-s-s-w pattern, each branch of which contains five distinguishable peaks. The inference drawn is that III exists as a mixture of several conformers which are not readily interconverted. The fact that III has a sharp melting point despite the presence of several forms is analogous to the behavior noted for the *n*-hexadecyl polysulfides.[12] The barrier to interconversion of the various conformers of III must nevertheless be higher than for acyclic polysulfides, since the polymer $—(—CF_2CF_2S—S—S—S—)—_n$ obtained from III shows no pronounced spin coupling in its n.m.r. spectrum.

The inherent lability of sulfur–sulfur bonds, which allows ring-opening reactions such as polymerization to proceed readily with the present cyclic polysulfides, has caused considerable confusion in the past in identification of hydrocarbon polysulfides. Many products reported as cyclic monomers are actually polymers.[13] At least one authentic cyclic trisulfide is reported in the litera-

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[5] See W. J. Middleton, E. G. Howard, and W. H. Sharkey, *J. Am. Chem. Soc.* **83**, 2589 (1961), for the preparation of this compound and its cyclic dimer.

[6] This experiment was carried out by Dr. C. G. Bottomley of these laboratories.

[7] C. C. Woodrow, M. Carmack, and J. G. Miller, *J. Chem. Phys.*, **19**, 951 (1951).

[8] G. Claeson, G. M. Androes, and M. Calvin, *J. Am. Chem. Soc.*, **83**, 4357 (1961), report similar results with a nonfluorinated cyclic disulfide.

[9] M. Calvin and J. A. Barltrop, *ibid.*, **74**, 6153 (1952).

[10] L. Pauling, *Proc. Nat. Acad. Sci. U. S.*, **35**, 495 (1949).

[11] O. Foss in N. Kharasch's "Organic Sulfur Compounds," Vol. I, Pergamon Press, New York, N. Y., 1961, pp. 77–80.

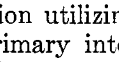
[12] J. E. Baer and M. Carmack, *J. Am. Chem. Soc.*, **71**, 1215 (1949).

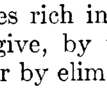
[13] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. III, Chemical Publishing Co., New York, N. Y., 1960, pp. 368, 369.

ture,[14] but such trisulfides are rare, and to our knowledge no cyclic tetrasulfide was previously known.

It is now generally conceded that sulfur chains are linear rather than branched,[14,15] in spite of the ease with which sulfur is often eliminated. The n.m.r. spectrum of the fluorinated cyclic trisulfide II provides a new type of evidence against the unsymmetrical branched structure with a dangling sulfur atom, since it indicates a symmetrical structure in which all the fluorine atoms are equivalent. Similarly, the n.m.r. spectrum of the tetrasulfide III is best explained by a structure with the sulfur atoms in a linear arrangement.

Correlation of our results with work in the literature shows that fluorinated four-membered heterocycles containing 1,2-sulfur atoms are unstable unless the ring also contains a double bond. Tetrafluoro-1,3-dithietane (IX) has been reported to be stable under normal conditions.[5] In contrast, we have found the sulfur–sulfur bond in tetrafluoro-1,2-dithietane (VI) to be so weak that VI could not be isolated, indicating that, even when this four-membered ring bears such strongly electron-withdrawing substituents as fluorine atoms, the planar configuration involving a disulfide group is very unfavorable. These findings may be compared to results obtained with the relatively stable 3,4-bis-(polyfluoroalkyl)-1,2-dithietenes (X),[16] which are also characterized by a planar four-membered ring containing a disulfide group and bearing electronegative substituents that are not substantially involved in resonance with the ring. The stability of the dithietenes, taken in conjunction with the behavior of the dithietane VI, shows the sulfur–sulfur bond in the planar ring of X to be remarkably strong and indicates that an unusual interaction of the unshared electrons on the sulfur atoms and π-electrons of the double bond is present.


IX


X

Fluorinated Linear Polysulfides.—Strong evidence was previously obtained that sulfur and tetrafluoroethylene, both electrophiles, interact primarily by a free radical mechanism.[17] A highly simplified mechanism can now be written for this reaction utilizing cyclic polysulfides rich in sulfur as primary intermediates which give, by further reaction with tetrafluoroethylene or by elimination of sulfur, lower polysulfides and ultimately octafluoro-1,4-dithiane. However, the reaction is actually complex in that equilibria of sulfur with various polysulfides are involved, cracking with cleavage of carbon–carbon bonds can occur, rearrangement of fluorine atoms is observed, and, most importantly, the various cyclic polysulfides form polymers and copolymers which can further react with tetrafluoroethylene or condense with elimination of sulfur.

Although the initial reaction of sulfur with tetrafluoroethylene is free radical in nature, and polymerization of the intermediate cyclic polysulfides can apparently also be accomplished by free radicals, these polymerizations were most readily carried out with weak bases under conditions such that replacement of fluorine did not occur. Sulfur chains, known to be susceptible to cleavage by various anions,[18] are particularly so when the end groups are electronegative. Thus even mild bases such as acetonitrile, ethanol, and acetone sufficed as initiators for the anionic polymerization of the trithiolane II and the tetrathiane III. The more stable trithiepane IV required a stronger base, triethylamine. These polymerizations were mildly exothermic and could be conducted at room temperature, but the highest molecular weights and cleanest polymers were obtained at −40 to −80°.

Stabilization of III for periods of several weeks was attained by storage of the purified monomer in acid-washed glassware at 0°, and IV required no special precautions. However, the trithiolane II polymerized so readily that a change in its viscosity was noticeable within an hour in spite of the precautions taken to prevent polymerization.

Polymers prepared from II and IV, even at low temperatures, had relatively low molecular weights as gaged by the brittleness of films pressed from the polymer. High molecular weight, tough white homopolymer (XI) was obtained from III, but this material was unstable under ordinary conditions. Films pressed from XI eliminated sulfur and embrittled on standing, most rapidly when exposed to light. Since the sulfur appeared as a separate crystalline phase on the polymer surface, an equilibrium governed by concentrations would be continuously displaced toward lower polysulfides and insoluble sulfur at 25°. Inherent viscosities also dropped markedly when polymer solutions were exposed to light and slowly even when the solutions were kept in the dark. In accord with these evidences of mobility of sulfur–sulfur bonds, films of XI that had eliminated sulfur on standing and embrittled could be reheated to 100° and pressed to reform nonbrittle, high molecular weight polymer. Gross decomposition of XI occurred at 250° or higher, as a result of which large amounts of III and some of II were formed.

$$\text{III} \longrightarrow \underset{\text{XI}}{-(-CF_2CF_2-S-S-S-S-)-_n}$$

XI undergoes a relatively sharp transition at about 56° from an opaque plastic to a clear rubbery

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[14] (a) O. Foss, *Acta Chem. Scand.*, **4**, 404 (1950); (b) O. Foss in N. Kharasch's "Organic Sulfur Compounds," Vol. I, Pergamon Press, New York, N. Y., 1961, pp. 75–77.

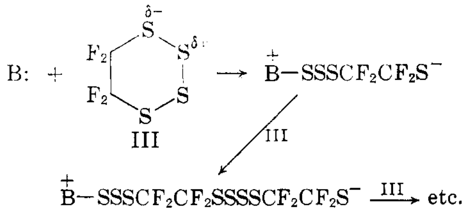
[15] L. Schotte, *Arkiv. Kemi.*, **9**, 361 (1956).

[16] C. G. Krespan, *J. Am. Chem. Soc.*, **83**, 3434 (1961).

[17] C. G. Krespan, *J. Org. Chem.*, **27**, 3588 (1962).

[18] O. Foss in N. Kharasch's "Organic Sulfur Compounds," Vol. I, Pergamon Press, New York, N. Y., 1961, p. 84.

material. This property as well as the singlet observed in the n.m.r. spectrum for F^{19} indicate XI to have the regular structure shown rather than a mixed polysulfide structure. This is explicable as a result of preferential attack by base at the highly polarized sulfur–sulfur bonds adjacent to fluoroalkyl groups.



On the other hand, reaction of the tetrathiane III with tetrafluoroethylene to form —(—CF_2CF_2S—S)—$_n$ (V) must involve the isolated sulfur–sulfur bond, since V has been shown to have a regular disulfide structure by its reaction with amines.[19] On the basis of the stability of fluoroalkylated disulfides compared to higher polysulfides, it seems likely that the 2,3-sulfur–sulfur bond in III is the weakest and tends to dissociate on heating to give a free radical addition to tetrafluoroethylene.

Experimental[20]

Tetrafluoro-1,2,3,4-tetrathiane (III) and Tetrafluoro-1,2,3-trithiolane (II).—The preparation of cyclic polysulfides by reaction of tetrafluoroethylene with the vapors of boiling sulfur at atmospheric pressure was carried out as follows. The apparatus was a 1-l. round-bottom glass reactor provided with an inlet tube delivering the tetrafluoroethylene into the sulfur vapors and an upright outlet neck 35 cm. in length and 25 mm. i.d., the latter serving also as condenser for the sulfur vapors. Nine hundred grams (28 g.-atoms) of sulfur was placed in the reactor, blanketed with nitrogen, and heated to the refluxing point, about 445° at atmospheric pressure. Then 480 g. (4.8 moles) of tetrafluoroethylene was passed through the sulfur vapors over a period of 4 hr. Heating was regulated so that the temperature of the escaping reaction products at the head of the outlet tube was 280–300°. The products were passed through an air-cooled downward condenser and collected in an acid-washed receiver. Volatile products not condensed in the receiver were collected in a trap cooled at −80°. There was 211 g. of residual sulfur in the reactor.

The volatile fraction consisted of 60 g. of low boiling liquid, shown by fractionation and analysis by infrared and n.m.r. to consist mainly of thiocarbonyl fluoride, b.p. *ca.* −60°; trifluorothioacetyl fluoride, b.p. *ca.* −25°; bis(trifluoromethyl) disulfide and carbon disulfide, b.p. 29–31° for the azeotrope; and bis(trifluoromethyl) trisulfide, b.p. 84–85°. The main product was 1098 g. of liquid containing some solid material. Rapid distillation of this condensate at < 5 mm. gave 813 g. of yellow oil. Fractionation of this oil through an acid-washed packed column into acid-washed receivers afforded two products. The first was 97 g. (10% yield) of tetrafluoro-1,2,3-trithiolane, b.p. 26–32° (15 mm.), a yellow oil with a pronounced tendency to polymerize. An analytical sample was prepared by redistillation at 38–39° (30 mm.). The n.m.r. spectrum for F^{19} consisted of a single sharp resonance for —CF_2S—, indicating the ring to be planar.

Anal. Calcd. for $C_2F_4S_3$: C, 12.24; F, 38.74; S, 49.02. Found: C, 12.63; F, 40.46; S, 49.09.

The major product was 480 g. (44% yield) of pale yellow tetrafluoro-1,2,3,4-tetrathiane, b.p. 59–61° (15 mm.), m.p. 12.5°, n^{25}_D 1.5447. The n.m.r. spectrum for F^{19}, unchanged over several fractions, consisted of four apparent w-s-s-w groups, all centered near +1160 c.p.s. and possessed of similar coupling constants, but with varying intensities. These resonances occurred at +791, +809, +815, and +824 c.p.s.; +1027, +1031, +1043, and +1051 c.p.s.; +1262, +1270, +1282, and +1286 c.p.s.; and +1500, +1510, +1518, and +1534 c.p.s. The n.m.r. spectrum taken at 56.4 Mc./sec. exhibited five w-s-s-w groups. The tetrathiane apparently exists as a mixture of isomers. Since three optically inactive forms are believed to be present in linear tetrasulfides,[12] several preferred conformations may also be found in the cyclic tetrathiane. The pattern became distinctly less sharp but did not collapse to one line when the spectrum was taken at 100°, indicating a high barrier to axial-equatorial inversion.

Anal. Calcd. for $C_2F_4S_4$: C, 10.52; F, 33.31; S, 56.18. Found: C, 10.60; F, 34.70; S, 56.14.

Additional amounts of tetrafluoro-1,2,3,4-tetrathiane contaminated with tetrafluoro-1,2,3-trithiolane were available from pyrolysis of the distillation residue at 250° or higher, so that total yield of the tetrathiane could be made to exceed 60%.

The reaction of sulfur vapor with tetrafluoroethylene was carried out at lower temperatures by reducing the pressure inside the reactor. Cyclic polysulfides were obtained at temperatures as low as 360° (200 mm.), but in poor yield.

Octafluoro-1,2,5-trithiepane (IV).—Use of a shorter reaction time than that employed in the previously described synthesis of octafluoro-1,4-dithiane[1] resulted in the synthesis of octafluoro-1,2,5-trithiepane.

A mixture of 32.0 g. (1.0 g.-atom) of sulfur and 75 ml. of carbon disulfide was heated under autogenous pressure in a 400-ml. shaker tube at 300° while 99 g. (1.0 mole) of tetrafluoroethylene was injected continuously[21] over a 2-hr. period. The reaction mixture was heated an additional hour at 300°. Distillation afforded two fractions. The more volatile fraction, b.p. 36–77°, was cooled to −80° and filtered. The solid thus isolated, a liquid at 25°, was stirred for 8 hr. with 10% sodium hydroxide, dried, and distilled to give 48.2 g. (37%) yield of octafluoro-1,4-dithiane, b.p. 80–81°, identified by its n.m.r. spectrum. The second fraction was 35.1 g. (24% yield based on tetrafluoroethylene) of octafluoro-1,2,5-trithiepane, b.p. 40–42° (20 mm.). A colorless analytical sample was prepared, b.p. 71–72° (100 mm.). The n.m.r. spectrum for F^{19} showed a single peak for —CF_2S— at +700 c.p.s. and a w-s-s-w of equal area at +850, +1077, +1135, and +1366 c.p.s. The latter grouping, most likely arising from difluoromethylene groups adjacent to disulfide, indicates that the ring has a preferred orientation in a puckered configuration.

Anal. Calcd. for $C_4F_8S_3$: C, 16.22; F, 51.31; S, 32.47. Found: C, 16.59; F, 51.13; S, 32.38.

Reaction of Tetrafluoroethylene with Excess Sulfur under Pressure.—Monomeric cyclic sulfides richer in sulfur than octafluoro-1,2,5-trithiepane were obtained by increasing the ratio of sulfur to tetrafluoroethylene from 1:1 to 2:1 or higher A. A mixture of 64.0 g. (2.0 g.-atoms) of sulfur and 75 ml. of carbon disulfide was heated at 300° under autogenous pressure in an agitated 400-ml. pressure tube while 100 g.

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[19] Details of this study will be part of a forthcoming publication.

[20] Melting and boiling points are uncorrected. Nuclear magnetic resonance (n.m.r.) spectra were obtained by means of a high-resolution n.m.r. spectrometer and associated electromagnet, both manufactured by Varian Associates, operating at 40 Mc./sec. and approximately 10,000 gauss. Spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the F^{19} resonance of 1,1,2,2-tetrachloro-1,2-difluoroethane. Negative frequency displacements are for resonances occurring at lower field than the reference.

[21] In handling tetrafluoroethylene under pressure, precautions must be taken to exclude oxygen and other potential initiators so that explosive decomposition does not occur. See footnote in C. G. Krespan, R. J. Harder, and J. J. Drysdale, *J. Am. Chem. Soc.*, **83**, 3424 (1961).

(1.0 mole) of tetrafluoroethylene was injected continuously over a period of 2.5 hr. After another hour at 300°, the tube was cooled and a small amount of gas was bled off. Distillation of the crude liquid product gave three fractions: (1) 84 ml. of a colorless liquid, b.p. 30–46°; (2) 14.5 g. of a yellow oil, b.p. 56–57° (50 mm.); and (3) 54.4 g. of a yellow oil, b.p. 60—90° (30 mm.). There was also obtained (4) 25 g. of a waxy distillation residue and (5) 3.8 g. of a pale yellow solid which formed during distillation as a coating on the stillhead condenser.

Fraction (1) was cooled to −80° and filtered at that temperature. The liquid phase was mainly carbon disulfide. The phase solid at −80° which was liquid at 25°, was stirred with 10% sodium hydroxide and the liquid lower layer was separated, dried over sodium hydroxide pellets, and distilled to give 27.0 g. (20% yield) of octafluoro-1,4-dithiane, b.p. 79–81°, identified by comparison of the n.m.r. spectrum for F^{19} with that of an authentic sample.

Fraction (2) gave on redistillation a forerun contaminated with the readily polymerizable tetrafluoro-1,2,3-trithiolane, then 8.2 g. (6% yield) of octafluoro-1,2,5-trithiepane, b.p. 71–72° (100 mm.), identified by n.m.r.

Fraction (3) was redistilled to give 10 g. (5% yield based on tetrafluoroethylene) of impure tetrafluoro-1,2,3-trithiolane, b.p. 45–49° (50 mm.), 21.8 g. (10% yield based on tetrafluoroethylene) of a yellow oil consisting chiefly of tetrafluoro-1,2,3,4-tetrathiane, b.p. 65–100° (90 mm.), and 20 g. of a viscous, light-colored residue.

B. Procedure A, above, when used with a larger excess of sulfur and a shorter reaction period, gave even higher proportions of sulfur-rich cyclic sulfides. Into a mixture of 128 g. (4.0 g.-atoms) of sulfur and 75 ml. of carbon disulfide in an agitated tube heated at 300° was injected 102 g. (1.0 mole) of tetrafluoroethylene over a 20-min. period. The reaction mixture was then heated at 300° for an additional 20 min. Distillation of the reaction mixture gave a volatile fraction, b.p. 35–46°, from which was isolated as described above 6.8 g. (5% yield) of octafluoro-1,4-dithiane, b.p. 80–81°. The residue was strongly heated to volatilize 85 g. of yellow oil, b.p. 50–110° (50 mm.). Redistillation of this oil gave 13 g. (7% yield) of tetrafluoro-1,2,3-trithiolane contaminated with a small amount of octafluoro-1,2,5-trithiepane, b.p. 50–75° (50 mm.), identified by n.m.r. The major volatile product was 50.5 g. (22% yield) of crude tetrafluoro-1,2,3,4-tetrathiane, b.p. 70–85° (30 mm.), also identified by its n.m.r. spectrum for F^{19}.

Poly(tetrafluoro-1,2-dithietane) (V).—A 400-ml. shaker tube charged with 76.0 g. (0.33 mole) of tetrafluoro-1,2,3,4-tetrathiane, 40 g. (0.40 mole) of tetrafluoroethylene, and 50 ml. of carbon disulfide was heated under autogenous pressure at 150° for 5 hr., then at 200° for 1 hr. After having been cooled, the reaction vessel contained about 0.1 mole of gas. The mixture of solid product and carbon disulfide was slurried with 200 ml. of petroleum ether and filtered. The solid thus isolated, after having been rinsed with petroleum ether and dried, weighed 86 g. (79% yield). Fractionation of the polymer on the basis of solubility in 700 ml. of chloroform gave 48.8 g. of insoluble polymer A and 34.1 g. of soluble polymer B, precipitated by addition of methanol to the chloroform solution. The total fractionated polymer, 82.9 g., corresponds to a 76% yield. A saturated solution of polymer B in chloroform exhibited a n.m.r. spectrum for F^{19} consisting essentially of a single resonance for —CF$_2$S— with minor amounts of impurities present.

Anal. Calcd. for $(C_2F_4S_2)_n$: C, 14.63; F, 46.30; S, 39.07. Found for A: C, 14.75; F, 45.77; S, 39.97. Found for B: C, 14.74; F, 45.66; S, 40.18.

This polymer was shown to consist almost entirely of regular —(—CF$_2$CF$_2$SS—)—$_n$ chains by its reaction with morpholine.[19]

Pyrolysis of Fluorinated Cyclic Polysulfides.—A 100-ml. shaker tube was charged with 114 g. (0.50 mole) of tetrafluoro-1,2,3,4-tetrathiane and heated at 300° for 10 hr. under autogenous pressure. Distillation of the liquid product afforded a fraction, b.p. 78–80°, which was stirred for 8 hr. with aqueous ammonia, dried and redistilled. There was thus obtained 28.3 g. (43% yield) of product, b.p. 79–81°, shown by n.m.r. analysis to be octafluoro-1,4-dithiane containing a small amount of the isomeric 2-trifluoromethylpentafluoro-1,3-dithiolane.

A similar pyrolysis of 176 g. (0.90 mole) of partially polymerized tetrafluoro-1,2,3-trithiolane gave 46.5 g. (39% yield) of octafluoro-1,4-dithiane containing considerably more isomer.

Pyrolysis of octafluoro-1,2,5-trithiepane (40.0 g., 0.14 mole) at 300° for 10 hr. followed by distillation gave 15.7 g. (42% yield) of octafluoro-1,4-dithiane and 4.1 g. (10%) of recovered trithiepane.

Poly(tetrafluoro-1,2,3,4-tetrathiane) (XI).—Tetrafluoro-1,2,3,4-tetrathiane was polymerized by adding 200 g. (0.88 mole) of the monomer over a 30-min. period to 1200 ml. of rapidly stirred acetonitrile maintained at −40°. The precipitated polymer was isolated by filtration and washed successively with 300-ml. portions of ethanol, ether, ether, pentane, and pentane. The dried product weighed 170 g. (85% yield).

A 100-g. portion of the polymer was dissolved in 400 ml. of chloroform and reprecipitated by pouring the solution into 500 ml. of vigorously stirred, cold (0°) pentane. After having been washed with two 500-ml. portions of pentane and dried, the recovered polymer weighed 94 g. (80% yield over-all).

The inherent viscosity $[\eta]$ of this product was found to be 1.03 in 0.1% solution in toluene at 25° if the solution was made up in the dark. A solution prepared under conditions of normal laboratory illumination gave η 0.79, indicating that some cleavage of the polymer chain had occurred. A similar polymer was prepared in 80% yield by addition of the monomer to stirred acetone at room temperature followed by reprecipitation from toluene. The crystalline melting point of various samples as judged by clarification on a melting point block was 55–60°. Tough, cold-drawable films could be obtained by pressing freshly prepared samples at 90–100°. A saturated solution of the polymer intoluene gave an n.m.r. spectrum for F^{19} containing a peak at +770 c.p.s.

Anal. Calcd. for $(C_2F_4S_4)_n$: C, 10.52; F, 33.31; S, 56.18. Found: C, 10.70; F, 34.07; S, 55.97.

Pyrolysis of Poly(tetrafluoro-1,2,3,4-tetrathiane).—A 500-ml. steel tube was charged with 61 g. (0.27 mole) of poly(tetrafluoro-1,2,3,4-tetrathiane) and heated at 300° for 10 hr. under autogenous pressure. Distillation of the liquid product gave, after a small forerun, 20.1 g. (56% yield) of octafluoro-1,4-dithiane, b.p. 78–80°, identified by n.m.r. spectroscopy.

Poly(octafluoro-1,2,5-trithiepane).—Octafluoro-1,2,5-trithiepane did not give insoluble polymer when added to acetonitrile either at 25° or −40°, even when dimethyl sulfoxide was present as a catalyst. However, catalytic amounts of triethylamine in the acetonitrile at −40° caused precipitation of poly(octafluoro-1,2,5-trithiepane) in 80% yield. Films pressed from this polymer at 100° were weak indicating low molecular weight. The polymer was not soluble in toluene or chloroform.

Poly(tetrafluoro-1,2,3-trithiolane).—A solution of 164 g. (0.84 mole) of tetrafluoro-1,2,3-trithiolane in 210 ml. of pentane was cooled to −80°. To this solution was added a solution of 0.1 g. of trimethyl phosphite in 0.7 g. of pentane, and the mixture was allowed to stand for 1 hr. at −80°. The solvent was decanted and the solid poly(tetrafluoro-1,2,3-trithiolane) which had formed was dissolved in toluene and reprecipitated with pentane. A second similar treatment followed by washing with pentane yielded 30 g. (18% yield) of polymer having an inherent viscosity of 1.21 in 0.1% solution in toluene at 25°. The polymer could be pressed to an opaque white film, which clarified at 95–100°.

Anal. Calcd. for $(C_2F_4S_3)_n$: C, 12.24; F, 38.74; S, 49.02. Found: C, 12.16; F, 39.34; S, 48.86.