Fluorinated Thiolanes and a Selenolane

C. G. KRESPAN

Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware

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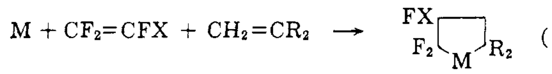
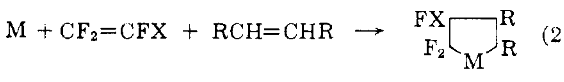
A versatile new synthesis of fluorinated thiolanes has been found in the reaction of sulfur, a fluoroölefin, and another unsaturated reactant at 150°. This synthesis has also been extended to the preparation of a selenolane. Reaction of iodine with tetrafluoroethylene and another olefin appears to offer a similar general route to partially fluorinated 1,4-diiodides.

A one-step synthesis of octafluorothiolane from sulfur and tetrafluoroethylene was described in a previous paper.[1] Modification of this reaction by the addition of an unsaturated third component has now been found to be a general preparative method for partially fluorinated thiolanes. Thus, a mixture of equimolar amounts of sulfur, tetrafluoroethylene, and another unsaturated component combines at 150° in a remarkably specific reaction to form, in yields up to 60%, a thiolane containing one molecule or atom of each of the reactants.

The third component can contain terminal, internal, or aromatic unsaturation, and functional groups such as ester, anhydride, nitrile, hydroxyl, ether, sulfide, and halide will survive the reaction. Furthermore, chloro- and bromotrifluoroethylene can be substituted for tetrafluoroethylene, and even difluorovinylidene chloride will give low yields of thiolanes. Use of selenium rather than sulfur resulted in the formation of the selenolane, but in lower yield than for the corresponding thiolane. Equations 1 and 2 present the synthesis in general terms.


(1)

$$M + CF_2{=}CFX + CH_2{=}CR_2 \longrightarrow \text{FX}\,\text{F}_2\text{(M)R}_2 \quad (1)$$

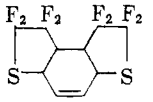

(2)

$$M + CF_2{=}CFX + RCH{=}CHR \longrightarrow \text{FX}\,\text{F}_2\text{(M)R, R} \quad (2)$$

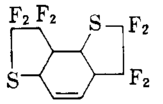
where M = S, Se
X = F, Cl, Br
R = H, CH_3, CN, CO_2CH_3, $OCOCH_3$, OCH_2CH_3, Cl, CH_2OH, CF_3, C_6H_5, etc.

Table I contains examples of the reaction of sulfur and tetrafluoroethylene with a variety of olefinic compounds. Mono- and disubstituted ethylenes react well, but tri- and especially tetrasubstituted ethylenes gave low yields in the few cases tested. Compounds such as acrylonitrile which undergo rapid cyclodimerization with tetrafluoroethylene lead to production of both a thiolane and a cyclobutane.

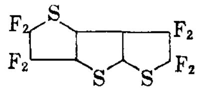
An unusual aspect of this reaction is that aromatic compounds can participate in the same manner as olefins. Styrene appears to react preferentially at the vinyl group, indicating the olefinic unsaturation to have the expected greater susceptibility to attack. In the absence of such reactive centers, however, an aromatic system will itself enter into thiolane ring formation. Under conditions similar to those employed for the reactions in Table I, sulfur and tetrafluoroethylene react with benzene to give a volatile product composed mainly of two isomeric tricyclic compounds that may have structures I and II. These structures are favored over isomers differing only in stereochemistry about asymmetric carbon atoms because of the mechanism postulated for the reaction by which they are formed (see below). Thiophene reacts similarly to give a tricyclic compound that probably has structure III. These preparations and the available evidence for the structures of the products are described in the Experimental.



I



II



III

Table II contains examples of variations in the reaction where substitutions for sulfur and for tetrafluoroethylene have been made. The halotrifluoroethylenes give yields comparable to those from tetrafluoroethylene, but extension to difluorovinylidene chloride leads to greatly diminished efficiency of the reaction. The use of selenium rather than sulfur gives a much slower reaction, a predictable result when the insolubility of selenium in the reaction medium is considered.

Sulfur and tetrafluoroethylene interact at 150° in the presence of a solvent to give octafluorathiolane.[1] This reaction is interpreted as starting with attack on tetrafluoroethylene by the free radical ends of open sulfur chains. After addition of the resulting fluorocarbon radical to a second molecule of tetrafluoroethylene to form a four-carbon chain, ring closure with elimination of sulfur would be sterically favored. The free radical mechanism proposed for the present thiolane synthesis involves intervention in the above mechanism by the second unsaturated reactant as illustrated below.

Step A (above) has been found to proceed faster for a highly fluorinated ethylene than for olefins like ethylene and propylene. Hydrocarbon olefins

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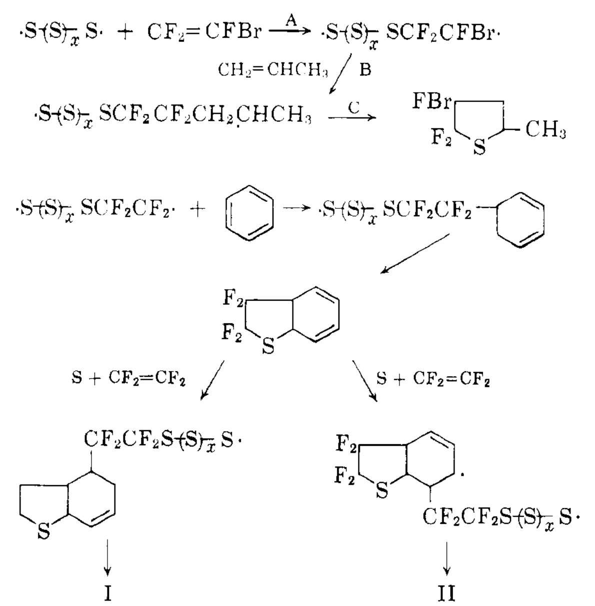
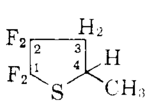
[1] C. G. Krespan and C. M. Langkammerer, *J. Org. Chem.*, **27**, 3584 (1962).

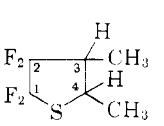


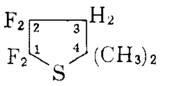
could serve as the olefin used in Step B, however, since they readily add fluorocarbon radicals.[2] This sequence of reactions accounts for the presence of both of the olefins and only monosulfide sulfur in the products. The stepwise nature of the mechanism also fits the observed formation of *trans* as well as *cis* ring junctures when sulfur and tetrafluoroethylene are added to cyclohexene.

The products actually isolated have structures in accord with this mechanism if it is assumed that an unsymmetrical olefin will add a free radical to give the more stable of the new free radicals possible.[3] Polarity of the double bond was not found to have an appreciable effect, since similar products are obtained from such oppositely polarized vinyl compounds as propylene and acrylonitrile. This observation is strong evidence for a free radical rather than an ionic mechanism Attack of sulfur on olefins at temperatures near 150° is considered by Bateman and his co-workers to proceed in general by an ionic mechanism.[4] One of the tests used as evidence for the ionic character of such reactions, catalysis by amines, was applied to the interaction of sulfur, tetrafluoroethylene, and vinyl acetate. This reaction, very slow at 120°, was not noticeably accelerated by the addition of 0.25 equivalent of triethylamine.

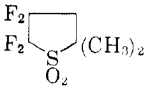
It has been shown[1] that a difluoromethylene group attached to sulfur or selenium gives rise to a n.m.r. band shifted markedly toward lower field, thereby allowing identification of the resonance for —CF_2S— and —CF_2Se— in the present tetrafluorothiolanes and the selenolane. This low field resonance is split into a w-s-s-w group when one of the nonfluorinated ring carbon atoms bears dissimilar substituents—*i.e.*, the methyl group and hydrogen atom in the product from sulfur, tetrafluoroethylene and propylene. The splitting is due to nonequivalence of the two fluorine atoms induced by the presence of the dissimilar substituents on the other carbon atom bonded to sulfur (carbon atom 4 in structure IV). Non-equivalence may arise because the relatively small C—S—C bond angle brings carbon atoms 1 and 4 close together, allowing direct potential interactions to become important, or because an asymmetric inductive effect is readily transmitted through the sulfur atom.[5] The dissimilar substituents in question cannot be located in carbon atom 3, since the resonance associated with the difluoromethylene group adjacent to carbon atom 3 is affected little in this situation. The product, V, with one methyl group on each of carbon atoms 3 and 4, gives, as expected, w-s-s-w patterns for both of the difluoromethylene resonances. The F^{19} spectrum of the product from sulfur, tetrafluoroethylene, and isobutylene fits VI, the structure expected from the proposed mechanism, in that the low field difluoromethylene gives rise to a triplet by coupling with the adjacent difluoromethylene while the latter is a heptuplet resulting from coupling with both methylene and difluoromethylene groups. Similar consideration of the fluorine spectra of the other products leads consistently to structures in accord with equations 1 and 2. The spectra for proton resonances substantiate the structures assigned on the basis of fluorine resonances.

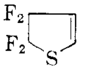

IV


V


VI

Partially fluorinated acyclic sulfides are reported to be oxidized to alkyl fluoroalkyl sulfones with conventional oxidizing agents,[6] and the fluorinated thiolanes might also be expected to give sulfones on oxidation. Warm hydrogen peroxide–acetic acid has been found to convert a number of the thiolanes to sulfones—*i.e.*, 2,2,3,3-tetrafluoro-5,5-dimethylthiolane has given the corresponding sulfone VII with this reagent.


VII


VIII

Other derivatives of the thiolanes are available from conventional reactions, as shown in the formation of the dihydrothiophene VIII by treatment of

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(2) R. N. Haszeldine and A. G. Sharpe, "Fluorine and Its Compounds," Methuen and Co., London, England, 1951, pp. 91, 138.

(3) R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 1199 (1953); 923 (1954).

(4) L. Bateman and C. G. Moore in N. Kharasch's "Organic Sulfur Compounds," Vol. I, Pergamon Press, New York, 1961, pp. 210–228.

(5) The related case of nonequivalence in fluorinated cyclobutanes has been discussed by W. D. Phillips, *J. Chem. Phys.*, **25**, 949 (1956).

(6) A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold, New York, 1958, p. 337.

TABLE I

REACTIONS OF SULFUR, TETRAFLUOROETHYLENE, AND OLEFINS

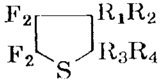
					N.m.r. bands[a]			
Olefin		B.p.	Yield, %	Analysis, %	—SCF₂—	—CF₂—	—CR₁R₂—	—CR₃R₄—
CH_2=CH_2	$R_1 = R_2 = R_3 = R_4 = H$	74° (150 mm.)	15[b]	Calcd. for $C_4H_4F_4S$: C, 30.00; H, 2.52; F, 47.40; S, 20.02. Found: C, 30.43; H, 2.64; F, 48.02; S, 20.14.	(Singlets for —SCF_2— and —CF_2—; not calibrated)			
CH_2=$CHCH_3$	$R_1 = R_2 = R_3 = H$ $R_4 = CH_3$	72° (100 mm.)	40	Calcd. for $C_5H_6F_4S$: C, 34.48; H, 3.47; F, 43.64; S, 18.41. Found: C, 34.96; H, 3.72; F, 44.34; S, 18.51.	(wssw for —SCF_2— and singlet for —CF_2—; not calibrated)			
CH_2=$C(CH_3)_2$	$R_1 = R_2 = H$ $R_3 = R_4 = CH_3$	75° (100 mm.)	43	Calcd. for $C_6H_8F_4S$: C, 38.29; H, 4.28; F, 40.39; S, 17.04. Found: C, 38.45; H, 4.48; F, 40.76; S, 17.12.	794, 803, 813 (triplet)	1777 (heptuplet)	185, 199, 213 (triplet)	233
CH_3CH=$CHCH_3$	$R_1 = R_3 = H^c$ $R_2 = R_4 = CH_3$	82° (100 mm.)	44	Calcd. for $C_6H_8F_4S$: C, 38.29; H, 4.28; F, 40.39; S, 17.04. Found: C, 38.53; H, 4.49; F, 40.71; S, 16.76.	Strong bands; 129, 338, 1292, 1505 (wssw) Weak bands; 461, 669, 851, 1062 (wssw)	2090, 2325, 2431, 2666 (wssw) 1776, 2055, 2128, 2403 (wssw)	CH at 193; CH_3 at 244	CH at 163; CH_3 at 244
C_6H_5CH=CH_2	$R_1 = R_2 = R_3 = H^d$ $R_4 = C_6H_5$	102–103° (10 mm.)	20	Calcd. for $C_{10}H_8F_4S$: C, 50.84; H, 3.41; F, 32.17; S, 13.57. Found: C, 51.48; H, 3.66; F, 32.52; S, 14.24.	(wssw for —SCF_2— and singlet for —CF_2—; not calibrated)			
CH_2=$CHCl$	$R_1 = R_2 = R_3 = H$ $R_4 = Cl$	85° (170 mm.)	36	Calcd. for $C_4H_3ClF_4S$: C, 24.69; H, 1.55; Cl, 18.22; F, 39.06; S, 16.48. Found: C, 24.63; H, 1.72; Cl, 18.14; F, 39.21; S, 16.27.	666, 873, 879, 1070 (wssw)	1926	176	75
CH_2=$CHOCH_2CH_3$	$R_1 = R_2 = R_3 = H$ $R_4 = OCH_2CH_3$	90° (60 mm.)	32	Calcd. for $C_6H_8F_4OS$: C, 35.29; H, 3.92; F, 37.22; S, 15.70.	570, 777, 905, 1117 (wssw)	1876	186	CH at 80; CH_3 at 245; CH_2 at 156

TABLE I (*Continued*)

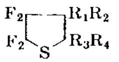
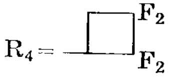
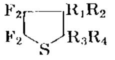
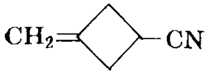
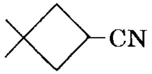
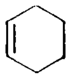
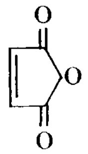
					N.m.r. bands[a]			
Olefin		B.p.	Yield, %	Analysis, %	—SCF_2—	—CF_2—	—CR_1R_2—	—CR_3R_4—
				Found: C, 35.48; H, 4.12; F, 37.10; S, 15.28.				
CH_2=$CHCH_2OH$[e]	$R_1 = R_2 = R_3 = H$ $R_4 = CH_2OH$	102° (20 mm.)	35	Calcd. for $C_5H_6F_4OS$: C, 31.58; H, 3.18, F, 39.97, S, 16.86. Found: C, 31.76; H, 3.51; F, 39.64; S, 16.32.	446, 656, 1051, 1257 (wssw)	1948	(complex)	(complex)
CH_2=$CHOCOCH_3$	$R_1 = R_2 = R_3 = H$[f] $R_4 = OCOCH_3$	106° (50 mm.)	25	Calcd. for $C_6H_6F_4O_2S$: C, 33.18; H, 2.33; F, 35.00; S, 14.76. Found: C, 33.14; H, 2.82; F, 35.44; S, 14.81.	721, 929, 961, 1173 (wssw)	1941	181	CH at 53; CH_3 at 213
CH_2=$CHCH$=CH_2	$R_1 = R_2 = R_3 = H$ R_4 =  (2 racemates)	76–77° (16 mm.) 80° (10 mm.)	45 (combined)	Calcd. for $C_8H_6F_8S$: C, 33.57; H, 2.11; F, 53.11; S, 11.20. Found: C, 34.01; H, 2.36; F, 52.95; S, 12.22. Found: C, 33.81; H, 2.33; F, 52.73; S, 11.94.	(wssw for —SCF_2— and singlet for —CF_2— for each racemate; not calibrated)			
CH_2=$CHCF_3$	$R_1 = R_2 = R_3 = H$ $R_4 = CF_3$	98°	11	Calcd. for $C_5H_3F_7S$: C, 26.32; H, 1.33; F, 58.30; S, 14.05. Found: C, 26.52; H, 1.57; F, 58.31; S, 13.95.	(wssw for —SCF_2— and singlets for CF_3— and —CF_2—; not calibrated)			
CH_2=$CHCO_2CH_3$	$R_1 = R_2 = R_3 = H$[g] $R_4 = CO_2CH_3$	80–81° (20 mm.)	14	Calcd. for $C_6H_6F_4O_2S$: C, 33.18; H, 2.33; F, 35.00; S, 14.76. Found: C, 33.42; H, 3.43; F, 35.33; S, 14.99.	509, 713, 1113, 1322 (wssw)	2006	188	CH at 132 CH_3 at 148
CH_2=$CHCN$	$R_1 = R_2 = R_3 = H$[h] $R_4 = CN$	112° (50 mm.)	20	Calcd. for $C_5H_3F_4NS$: C, 32.43; H, 1.63; F, 41.05; N, 7.59; S, 17.32. Found: C, 32.17; H, 1.85; F, 40.54; N, 7.34; S, 17.78.	651, 860, 920, 1127	2003	184	131

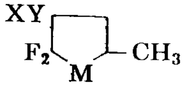
TABLE I (*Continued*)

Olefin		B.p.	Yield, %	Analysis, %	N.m.r. bands[a] —SCF$_2$—	—CF$_2$—	—CR$_1$R$_2$—	—CR$_3$R$_4$—
	R$_1$ = R$_2$ = H R$_3$ + R$_4$ =  (*cis* and *trans* isomers)	86° (1 mm.) 115° (2 mm.)[i]	56 (combined)	Calcd. for $C_8H_7F_4NS$: C, 42.66; H, 3.14; F, 33.75; N, 6.22; S, 14.24. Found: C, 42.84; H, 3.32; F, 33.95; N, 6.62; S, 13.93. Found: C, 42.92; H, 3.40; F, 33.90; N, 6.22; S, 14.37.	(Singlets for —SCF$_2$— and —CF$_2$— for each isomer; not calibrated)			
	R$_1$ = R$_3$ = H[b] R$_2$ + R$_4$ = —(CH$_2$)$_4$—	94° (20 mm.)	23	Calcd. for $C_8H_{10}F_4S$: C, 44.85; H, 4.71; F, 35.48; S, 14.97. Found: C, 45.39; H, 4.83; F, 35.69; S, 14.88.	(Mixture of two racemates indicated by two sets of wssw each for —SCF$_2$— and —CF$_2$—; not calibrated)			
	R$_1$ = R$_3$ = H R$_2$ + R$_4$ = —CO$_2$CO—	m.p. 68–69°	17	Calcd. for $C_6H_2F_4O_3S$: C, 31.31; H, 0.88; F, 33.02; S, 13.93. Found: C, 31.69; H, 1.30; F, 33.51; S, 13.67.	(Both —SCF$_2$— and —CF$_2$— resonances split; not calibrated)			

The reactions were run with about 0.2 mole of each reactant in 10–20 ml. of carbon disulfide as solvent. These mixtures were heated at 150° under autogenous pressure in an 80-ml. stainless steel-lined pressure vessel. Reaction times were about 6 hr. [a] Fine structure evident in all bands. Group intensities fitted assigned structures. [b] Run only 2 hr.; yield could be higher. [c] Mixture of two racemates shown by n.m.r. [d] Aromatic ring confirmed by infrared. Also obtained 1-phenyl-2,2,3,3-tetrafluorocyclobutane in 48% yield. [e] No carbon disulfide used as solvent. [f] Also obtained 2,2,3,3-tetrafluorocyclobutyl acetate in 9% yield. [g] Also obtained methyl 2,2,3,3-tetrafluorocyclobutanecarboxylate in 19% yield. [h] Also obtained 2,2,3,3-tetrafluorocyclobutanecarbonitrile in 31% yield. [i] Product crystallized to give white solid, m.p. 95–96°.

TABLE II

REACTIONS OF SULFUR OR SELENIUM, PERHALOETHYLENES, AND PROPYLENE

Reactants	Product; 	B.p.	Yield, %	Analysis, %	N.m.r. bands[a] —SCF₂—	—CFX—	—CH₂—	—CH(CH₃)—
S, $CF_2{=}CFCl$, $CH_2{=}CHCH_3$	X = F[b] Y = Cl M = S	96° (100 mm.)	30	Calcd. for $C_5H_6ClF_3S$: C, 31.50; H, 3.17; Cl, 18.60; F, 29.90; S, 16.82. Found: C, 31.73; H, 3.15; Cl, 18.45; F, 30.33; S, 17.08.	−321, −115, 1221, 1430 (wssw); 604, 617 (wssw in which satellites were not located)	1985; 2095[c]	190	CH at 142; CH_3 at 240
S, $CF_2{=}CFBr$, $CH_2{=}CHCH_3$	X = F[b] Y = Br M = S	93° (50 mm.)	36	Calcd. for $C_5H_6BrF_3S$: C, 25.54; H, 2.57; Br, 34.00; F, 24.25; S, 13.64. Found: C, 25.84; H, 2.54; Br, 33.78; F, 24.62; S, 13.66.	−508, −302, 1168, 1375 (wssw); 192, 394, 624, 829 (wssw)	1867; 2038[c]	187	CH at 148; CH_3 at 241
S, $CF_2{=}CCl_2$, $CH_2{=}CHCH_3$	X = Y = Cl M = S	79–80° (20 mm.)	2	(Identified by n.m.r. only)	(wssw for —SCF_2— and expected bands for CH_3—, —CH_2—, —CH—; not calibrated)			
Se, $CF_2{=}CF_2$,[d] $CH_2{=}CHCH_3$	X = Y = F M = Se	84–85° (100 mm.)	8	Calcd. for $C_5H_6F_4Se$: C, 27.16; H, 2.74; F, 34.38; Se, 35.7. Found: C, 27.21; H, 3.00; F, 34.02; Se, 35.2.	335, 530, 1017, 1228 (wssw)	2034	198	CH at 143; CH_3 at 234 (doublet, $J = 8$)

The reactions were run on a 0.2-mole scale in 20 ml. of carbon disulfide as solvent. These mixtures were heated at 150° under autogenous pressure in an 80-ml. stainless steel-lined pressure vessel for 6 hr. [a] Fine structure evident in all bands. Group intensities fitted assigned structures. [b] Mixture of two racemates shown by n.m.r. [c] Similar intensities; not correlated with w-s-s-w groups. [d] Also added 0.05 mole of iodine; allowed to react for 15 hr.

2-acetoxy-4,4,5,5-tetrafluorothiolane with phosphorus pentoxide.

An attempt to cause phosphorus to interact with tetrafluoroethylene and propylene in the presence of iodine resulted instead in the formation of a 1,4-diiodide (IX). This reaction is analogous to the addition of tetrafluoroethylene diiodide to tetrafluoroethylene to form 1,4-diiodoöctafluorobutane,[7] except that preferential addition of $ICF_2CF_2\cdot$ to an olefin such as propylene rather than to tetrafluoroethylene occurs. This specificity is the same as that observed in the thiolane synthesis and suggests that a large number of partially fluorinated 1,4-diiodides would be available in one step from iodine, tetrafluoroethylene, and another olefin.

$ICF_2CF_2CH_2CHICH_3$

IX

Experimental[8]

2-Cyano-4,4,5,5-tetrafluorothiolane.—A mixture of 8.0 g. (0.25 g.-atom) of sulfur, 30 g. (0.30 mole) of tetrafluoroethylene, 10.6 g. (0.20 mole) of inhibited acrylonitrile, and 20 ml. of carbon disulfide was heated in an 80-ml., stainless steel-lined shaker tube at 150° for 7 hr. under autogenous pressure. Distillation of the product gave 9.4 g. (31% yield based on acrylonitrile of 2,2,3,3-tetrafluorocyclobutanecarbonitrile, b.p. 89–91° (120 mm.), and 7.4 g. (20% yield based on acrylonitrile) of 2-cyano-4,4,5,5-tetrafluorothiolane, b.p. 112° (50 mm.).

The infrared spectrum of the thiolane contained absorption attributable to saturated C—H, C≡N, and C—F bonding. The thiolane was analyzed and characterized by n.m.r. (Table I).

2-(2′,2′,3′,3′-Tetrafluorocyclobutyl)-4,4,5,5-tetrafluorothiolane.—A mixture of 6.4 g. (0.20 g.-atom) of sulfur, 30 g. (0.30 mole) of tetrafluoroethylene, 8 g. (0.15 mole) of butadiene, and 20 ml. of carbon disulfide was heated in an 80-ml. pressure vessel at 150° for 5 hr. Distillation gave a few grams of mixed low-boiling products and 19.4 g. (45% yield based on tetrafluoroethylene or butadiene) of 2-(2′,2′,3′,3′ - tetrafluorocyclobutyl) - 4,4,5,5 - tetrafluorothiolane, b.p. 106° (80 mm.) to 91° (16 mm.). The volatile product was refractionated to give pure samples of the two possible racemates; 5.7 g. (13% yield) of one, b.p. 76–77° (16 mm.), and 5.2 g. (12% yield) of the other, b.p. 80° (10 mm.). These racemates were analyzed (Table I). Their infrared and n.m.r. spectra fitted the assigned structure and showed the compounds to be similar but not identical.

2-Methyl-4-bromo-4,5,5-trifluorothiolane.—A mixture of 6.4 g. (0.20 g.-atom) of sulfur, 40 g. (0.25 mole) of bromotrifluoroethylene, 11 g. (0.26 mole) of propylene, and 20 ml. of carbon disulfide was heated in an 80-ml. pressure vessel at 150° for 6 hr. Distillation of the product gave 16.9 g. (36% yield based on sulfur) of 2-methyl-4-bromo-4,5,5-trifluorothiolane, b.p. 93° (50 mm.); $n^{25}D$ 1.4637, and 12 g. of residual oil. Elemental analyses of the product (Table II) indicated the thiolane structure. N.m.r. indicated the

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(7) R. N. Haszeldine, *Nature*, **167**, 139 (1951).

(8) Melting and boiling points are uncorrected. 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 and the H^1 resonance of benzene. Negative frequency displacements are for resonances occurring at lower field than the internal references.

presence of both possible racemates of the assigned structure.

Reaction of Sulfur, Tetrafluoroethylene, and Thiophene.—A mixture of 8.0 g. (0.25 g.-atom) of sulfur, 25 g. (0.25 mole) of tetrafluoroethylene, and 25 ml. of thiophene was heated in an 80-ml. pressure vessel at 150° for 3 hr. Distillation of the reaction mixture gave 6.9 g. of crude product, b.p. 75–80° (1 mm.), and 28 g. of residual oil. Redistillation of the crude product gave 5.2 g. (13% yield based on tetrafluoroethylene) of a tricyclic compound, b.p. 52–53° (0.2 mm.).

Anal. Calcd. for $C_8H_4F_8S_3$: C, 27.59; H, 1.16; F, 43.64; S, 27.62; mol. wt., 348. Found: C, 27.94; H, 1.87; F, 43.74; S, 28.03; mol. wt., 324.

The infrared spectrum contained absorption peaks for saturated C—H and C—F, but none for C═C. N.m.r. revealed the presence of two kinds of tetrafluorothiolane rings in equal amounts, indicating a structure such as III for the product (see Discussion).

Reaction of Sulfur, Tetrafluoroethylene, and Benzene.—A mixture of 32.0 g. (1.00 g.-atom) of sulfur, 160 ml. of benzene, and 50 g. (0.50 mole) of tetrafluoroethylene was heated in a 400-ml. pressure vessel at 150°. The tube was repressured over a period of 1.5 hr. with an additional 41 g. (0.41 mole) of tetrafluoroethylene at a rate sufficient to maintain the pressure at 350–500 lb./sq. in.; then the reaction mixture was heated another 4 hr. Distillation of the reaction mixture gave 5.5 g. (5% yield based on tetrafluoroethylene) of octafluorothiolane, b.p. 40–43°,[1] 6.1 g. of a mixture of by-products, b.p. 42–70° (4.5 mm.), and 44.1 g. (28% yield based on tetrafluoroethylene) of a mixture of tricyclic compounds, b.p. 97–102° (2 mm.). The residue was 49 g. of dark tar.

The high-boiling product crystallized readily. Recrystallization from carbon tetrachloride, then from 95% ethyl alcohol, gave white crystals, m.p. 72–73°.

Anal. Calcd. for $C_{10}H_6F_8S_2$: C, 35.09; H, 1.77; F, 44.41; S, 18.74; mol. wt., 342. Found: C, 34.76; H, 2.12; F, 43.92; S, 18.92; mol. wt., 300.

The infrared spectrum had absorption bands for saturated C—H, unsaturated C—H, and C—F. The presence of unsaturation was confirmed by a positive permanganate test. N.m.r. indicated principally two compounds containing tetrafluorothiolane rings and also showed hydrogen on saturated and unsaturated carbon. Structures I and II are considered the most probable ones for the isomeric products (see Discussion).

2-Acetoxy-4,4,5,5-tetrafluorothiolane.—When the thiolane syntheses were scaled up, yields usually increased. The following example can be compared to the run of 0.2-mole size in Table I where the yield was 25%.

A mixture of 19.2 g. (0.60 g.-atom) of sulfur, 61 g. (0.61 mole) of tetrafluoroethylene, 51.6 g. (0.60 mole) of inhibited vinyl acetate, and 60 ml. of carbon disulfide was heated in a 400-ml. pressure vessel at 150° for 11 hr. Distillation of the product gave 7.6 g. of liquid, mainly 2,2,3,3-tetrafluorocyclobutyl acetate, boiling at 60° (50 mm.) to 86° (20 mm.), and 73.6 g. (56% yield based on vinyl acetate) of 2-acetoxy-4,4,5,5-tetrafluorothiolane, b.p. 86–87° (20 mm.); $n^{25}\text{D}$ 1.4099. This product was characterized by analysis and n.m.r. (Table I).

2,2,3,3-Tetrafluoro-2,3-dihydrothiophene.—A mixture of 11.7 g. (0.54 mole) of 2-acetoxy-4,4,5,5-tetrafluorothiolane and 14 g. (0.1 mole) of phosphorus pentoxide was heated from 160° to 190° over a period of 2 hr. while liquid was continually withdrawn overhead at 90–95°. The product, which weighed 5.8 g. (68% yield crude), was redistilled to give 4.0 g. (47% yield) of 2,2,3,3-tetrafluoro-2,3-dihydrothiophene, b.p. 96°.

Anal. Calcd. for $C_4H_2F_4S$: C, 30.38; H, 1.28; F, 48.06; S, 20.28. Found: C, 30.84; H, 1.49; F, 48.70; S, 20.07.

The infrared spectrum contained bands for a double bond (6.24 μ) and unsaturated hydrogen (3.20 μ). Absorption in the ultraviolet indicative of a vinyl sulfide occurred at $\lambda_{\max}^{\text{isooctane}}$ 239 mμ (ε 3,630). Proton resonances in the n.m.r. spectrum occurred at +32 and +67 c.p.s. (1:1), and fluorine resonances came at +1210 and +1786 c.p.s. (1:1).

2,2,3,3-Tetrafluoro-5,5-dimethylthiolane 1,1-Dioxide.—A mixture of 9.85 g. (0.052 mole) of 2,2,3,3-tetrafluoro-5,5-dimethylthiolane, 15 ml. (0.15 mole) of 30% hydrogen peroxide, and 50 ml. of glacial acetic acid was heated on a steam bath for 10 hr. Distillation of the reaction mixture afforded 4.33 g. (38% yield) of the sulfone, b.p. 77–78° (6 mm.).

Anal. Calcd. for $C_6H_8F_4O_2S$: C, 32.73; H, 3.66; F, 34.52; S, 14.56. Found: C, 33.16; H, 4.06; F, 34.79; S, 14.72.

An absorption band attributable to a sulfone group was found in the infrared spectrum at 7.45 μ. One of two strong bands at 8.4 μ and 8.7 μ must also be due to this group, the other arising from C—F absorption. The n.m.r. spectrum for F^{19} contained a triplet centered at +1651 c.p.s. (J = 15) and a band at +2024 c.p.s. The latter band arises from the difluoromethylene group attached to sulfur; oxidation of the sulfide to sulfone has caused a shift of +1221 c.p.s. in this resonance. The former band, whose resonance was split by the adjacent methylene group into a triplet, in turn split the methylene resonance into a triplet centered at +196 c.p.s. (J = 15). The methyl resonance occurred at +237 c.p.s.

1,1,2,2-Tetrafluoro-1,4-diiodopentane.—A mixture of 15 g. (0.15 mole) of tetrafluoroethylene, 8 g. (0.19 mole) of propylene, 19.0 g. (0.075 mole) of iodine, 20 ml. of carbon disulfide, and 4.7 g. (0.15 mole) of red phosphorus was heated at 160° for 11 hr. under autogenous pressure in an attempt to prepare a phosphorus heterocycle. However, distillation of the reaction mixture gave as the volatile product 7.0 g. (24% yield based on iodine) of 1,1,2,2-tetrafluoro-1,4-diiodopentane, b.p. 80–81° (12 mm.); $n^{23}\text{D}$ 1.5035.

Anal. Calcd. for $C_5H_6F_4I_2$: F, 19.19; I, 64.11. Found: F, 19.46; I, 63.67.

The n.m.r. spectrum for F^{19} contained a band at −265 c.p.s. for the iododifluoromethyl group and a w-s-s-w at +1366, +1544, +1614, and +1799 c.p.s. for the difluoromethylene group. This w-s-s-w must arise from nonequivalence of the fluorine atoms of the difluoromethylene group perhaps due to restricted rotation. The individual bands had considerable fine structure, as did the band for the adjacent methylene group centered at +182 c.p.s. The methyl resonance was a doublet at +209 and +215 c.p.s. due to splitting by the adjacent tertiary hydrogen. The tertiary hydrogen was in turn split into a quadruplet by the methyl group; further splitting by the adjacent methylene group led to a sextuplet centered at +116 c.p.s. (J = 6) due to overlapping. The proton resonances showed the expected relative intensities, as did the fluorine resonances.

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