

Anal. Calcd. for $C_3Cl_2F_6S$: C, 14.24; Cl, 28.02; F, 45.06; S, 12.67. Found: C, 14.61; Cl, 27.77; F, 44.81; S, 13.00.

2-Bromo-1,1,1,3,3,3-hexafluoro-2-propanesulfonyl Bromide (XXXVIII).—Bromine, 8.0 g. (0.05 mole), was placed in a flask and cooled to -5° in an ice-salt bath. HFTA, 9.1 g. (0.05 mole), was distilled into the flask, and the reaction mixture was allowed to stand at 0° for 3 hr. and then distilled. There was obtained 14.7 g. (86%) of 2-bromo-1,1,1,3,3,3-hexafluoro-2-propanesulfonyl bromide as an orange-red liquid, b.p. $48-49^\circ$ (38 mm.), n_D^{20} 1.4368. The F^{19} n.m.r. spectrum contained a single unsplit resonance line at 0 p.p.m.

Anal. Calcd. for $C_3Br_2F_6S$: C, 10.53; Br, 46.76; F, 33.34; S, 9.36. Found: C, 11.12; Br, 46.67; F, 33.27; S, 9.27.

Oxidation of HFTA with Nitric Oxide.—A 2.5-cm. Vycor tube packed for a length of 25 cm. with quartz rings was connected to a trap cooled by Dry Ice-acetone and the tube was heated to 650° . HFTA dimer, 18.2 g. (0.5 mole), was added dropwise through the tube over a period of 2 hr. A slow stream (about 100 ml./min.) of nitric oxide was also passed through the tube along with the dimer. The condensate in the trap was distilled to give 12.9 g. (78%) of a fraction consisting chiefly of hexafluoroacetone, b.p. -26° . Identification was made by comparing the n.m.r. and infrared spectra of this gas with those of an authentic sample of hexafluoroacetone. Sulfur dioxide was also used in place of nitric oxide for this oxidation, but yields were poorer in this case.

When oxygen was used in place of the nitric oxide, only sulfur dioxide (82%) was condensed in the trap, indicating the carbon

and fluorine portions of HFTA were oxidized to gases not condensed at -78° .

Reduction of HFTA with Hydrogen Sulfide.—A 2.5-cm. Vycor tube packed for a length of 25 cm. with quartz rings was connected to a trap cooled by Dry Ice-acetone. The tube was heated to 650° , and 46 g. (0.125 mole) of HFTA dimer was added dropwise over a period of 4 hr. A slow stream of hydrogen sulfide (about 100 ml./min.) was passed through the tube concurrently with the dimer. The condensate in the trap was distilled to give 32 g. of 1,1,1,3,3,3-hexafluoropropane, b.p. -2 to -1° , identified by comparison of its n.m.r. and infrared spectra with those of a known sample.

Trimethoxyfluoroenylidene phosphorane (XXXI).—A mixture of 6.3 g. (0.032 mole) of thiofluorenone and 100 ml. of pentane was stirred under nitrogen, and 8.0 g. (0.064 mole) of trimethyl phosphite was added dropwise over a period of 10 min. The green color of the thiofluorenone faded and a yellow solid formed. This solid was collected on a filter under nitrogen and washed with pentane. There was obtained 7.3 g. of trimethoxyfluoroenylidene phosphorane as a yellow powder, m.p. $105-107^\circ$. A portion was recrystallized from benzene-hexane and then from hexane to give white needles, m.p. 108° . The infrared spectrum contained bands at 3.3μ ($=CH$), at 3.4 and 3.5μ (saturated CH), in the $6\text{-}\mu$ region (aromatic $-C=C-$), at 7.65μ (possible $P=C$), and in the $9\text{-}\mu$ region ($P-O-C-$).

Anal. Calcd. for $C_{15}H_{17}O_3P$: C, 66.66; H, 5.95; P, 10.75. Found: C, 66.55; H, 5.92; P, 10.90.

Fluorothiocarbonyl Compounds. III.¹ Diels-Alder Reactions

W. J. MIDDLETON

Contribution No. 876 from the Central Research Department, Experimental Station,
E. I. du Pont de Nemours and Company, Wilmington 98, Delaware

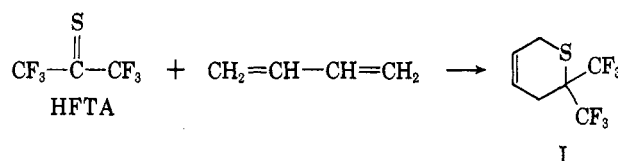
Received October 28, 1964

Hexafluorothioacetone is an exceedingly active dienophile in the Diels-Alder reaction. It forms adducts with butadiene, furan, anthracene, and even styrene under very mild conditions. Other thiocarbonyl compounds such as trifluorothioacetyl fluoride, ethyl trifluorodithioacetate, thiocarbonyl fluoride, and thiophosgene are also active dienophiles.

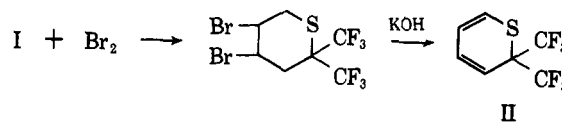
A number of carbonyl compounds, including formaldehyde,² chloral,³ carbonyl cyanide,⁴ diethyl mesoxalate,⁴ hexafluoroacetone,⁵ and hexafluorocyclobutane,⁶ have been shown to function as dienophiles in the Diels-Alder reaction. Among the most active of these are the fluoro ketones.^{5,6}

We have found that thiocarbonyl compounds are also active dienophiles, being several orders of magnitude more reactive than the corresponding carbonyl compounds.⁷

Perfluoro Thio Ketones.—The most reactive dienophiles of all the thiocarbonyl compounds we have examined are the perfluoro thio ketones, in particular hexafluorothioacetone (HFTA). This thio ketone reacts instantaneously with butadiene at -78° to give high yields of 2,2-bis(trifluoromethyl)-3,6-dihydro-2H-thiopyran (I). This reaction is so fast that it can actually be used to titrate butadiene in an inert solvent, using the appearance of the blue color of the thio ketone as the end point of the titration.



The HFTA-butadiene adduct (I) was dehydrogenated in two steps by addition of bromine and elimination of hydrogen bromide to give the thiopyran II. This thiopyran, being a diene itself, reacts with HFTA to form an adduct of uncertain structure. The thiopyran itself appears to be unstable in the monomeric state, for it slowly dimerized over a period of 3 months when stored at room temperature.



Hexafluorothioacetone reacts with surprising ease with certain aromatic compounds to form Diels-Alder adducts. It reacts rapidly with furan at -78° and with anthracene at 0° to give adducts III and IV, respectively.

More impressive yet is the reaction of HFTA with styrene and related compounds. Even at -78° , HFTA reacts rapidly and exothermally with styrene to

(1) Paper II: W. J. Middleton and W. H. Sharkey, *J. Org. Chem.*, **30**, 1384 (1965).

(2) T. L. Gresham and T. R. Steadman, *ibid.*, **71**, 737 (1949).

(3) W. J. Dale and A. J. Sisti, *ibid.*, **76**, 81 (1954).

(4) O. A. Achmatowicz and A. Zamojski, *Bull. acad. polon. sci., Classe III*, **5**, 927 (1957).

(5) J. F. Harris, U. S. Patent 3,136,786 (1964).

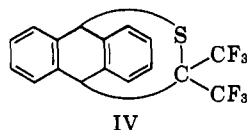
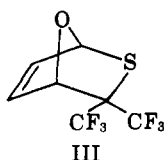
(6) D. C. England, *J. Am. Chem. Soc.*, **83**, 2205 (1961).

(7) W. J. Middleton, E. G. Howard, and W. H. Sharkey, *ibid.*, **83**, 2589 (1961).

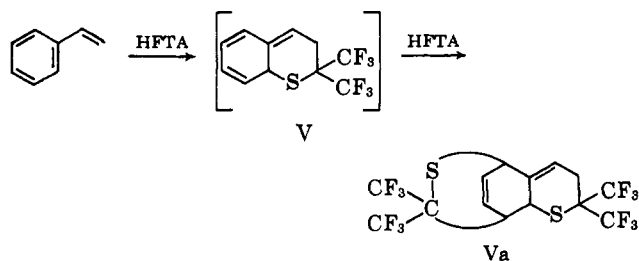
TABLE I
 ADDUCTS OF THIOCARBONYL COMPOUNDS WITH DIENES

Thiocarbonyl compound	Diene	Adduct	Yield.		<i>n</i> _D ²⁰	
			%	B.p. (mm.) (m.p.), °C.		
Hexafluorothioacetone	1,3-Butadiene	I	90	65 (30 mm.)	1.4048	
	2,3-Dimethyl-1,3-butadiene	Ia	90	52 (3 mm.)	1.4487	
	Cyclopentadiene	Ib	85	54.5 (8 mm.)	1.4225	
	2-Chloro-1,3-butadiene	Ic ^a	75	53 (6 mm.)	1.4270	
	1-Methoxy-1,3-butadiene	Id ^a	50	40-45 (1.1 mm.)	1.4139-1.4167	
	Furan	III	73	(20-21)	1.4143	
	Anthracene	IV	100	(123-124)		
	Styrene	Va	33	103-104 (1.2 mm.)	1.4512	
	4-Methoxystyrene	Vb	75	(117-118)		
	1,1-Diphenylethylene	Vc	70	(152-153)		
	2,2-Bis(trifluoromethyl)-2H-thiopyran	Ie	90	53-54 (0.35 mm.)	1.4427	
	Octafluoro-2-butanethione	Anthracene	XVIII	95	(54-55)	
	Trifluorothioacetyl fluoride	Anthracene	XIIa	93	(85)	
		Butadiene	IX	56	39 (10 mm.)	1.4209
2,3-Dimethyl-1,3-butadiene		IXa	67	45 (2 mm.)	1.4343	
Cyclopentadiene		XIa ^a	64	45 (7 mm.)	1.4392	
Pentafluorothiopropionyl fluoride	Anthracene	XIIb	61	(113-114)		
Chlorodifluorothioacetyl fluoride	Hexachlorocyclopentadiene	XIIIa	40	79 (0.25 mm.)	1.5383	
Thiocarbonyl fluoride	Cyclopentadiene	XIb	94	(47.5-48.5)		
	Hexachlorocyclopentadiene	XIIIb	16	(111-115)		
	2,3-Dimethyl-1,3-butadiene	XIV	90	72 (0.8 mm.)	1.4932	
Hexafluorodithiobutylolactone	2,3-Dimethylbutadiene	XV	70	67-68 (0.75 mm.)	1.4673	
Bis(trifluoromethyl) trithio-carbonate	Cyclopentadiene	XVI	70	63 (1.3 mm.)	1.4887	
	Cyclopentadiene	XIc	90	(50-52)		
Thiophosgene	Cyclopentadiene	XVI	90	(50-52)		
Thiofluorenone	2,3-Dimethyl-1,3-butadiene	XVII	84	(125)		

^a Mixture of two isomers.



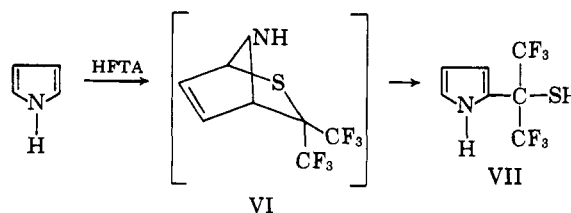
give a 2:1 adduct. Although a mixture of isomers was apparently obtained and no specific structural assignment was made, the spectral evidence indicates that a Diels-Alder-type reaction occurred with the two conjugated diene systems in styrene. We have postulated that the first step of the reaction involves the addition of HFTA to styrene to give a nonaromatic adduct such as V. This adduct is apparently more reactive than styrene and combines with another molecule of HFTA to give the final product, which is the 2:1 adduct (Va or isomer). *p*-Methoxystyrene



and 1,1-diphenylethylene react with HFTA in a similar manner to give corresponding 2:1 adducts. This behavior is in contrast to that of other active dienophiles. For example, *p*-methoxystyrene undergoes a cycloaddition reaction with tetracyanoethylene to give a cyclobutane with the aromatic ring intact.⁸

(8) J. K. Williams, D. W. Wiley, and B. C. McKusick, *J. Am. Chem. Soc.*, **84**, 2210 (1962).

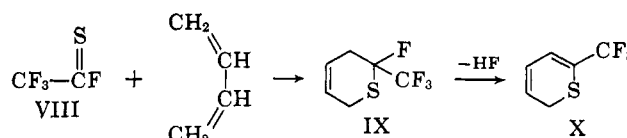
HFTA also reacts with pyrrole at low temperatures to give such products as VII that may involve a Diels-Alder reaction as a first step. However, if the adduct VI does form, it opens up to regenerate the pyrrole ring.



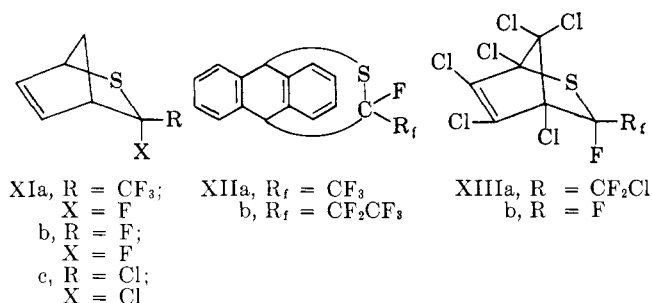
Octafluoro-2-butanethione is also an extremely active dienophile. It forms an adduct with anthracene at 0°, with reaction being complete in only a few seconds.

The adducts prepared from the perfluoro thio ketones are listed in Table I.

Thioacyl Fluorides.—Although less reactive than HFTA, perfluorothioacyl fluorides are nevertheless exceedingly active dienophiles. Trifluorothioacetyl fluoride (VIII) reacts even at -78° with butadiene and dimethylbutadiene to give the corresponding dihydrothiopyrans. These adducts can be isolated, but they are quite unstable because of the ease with which they lose hydrogen fluoride. For example, the trifluorothioacetyl fluoride butadiene adduct (IX) spontaneously lost hydrogen fluoride when stored in a glass vial to give the thiopyran X.

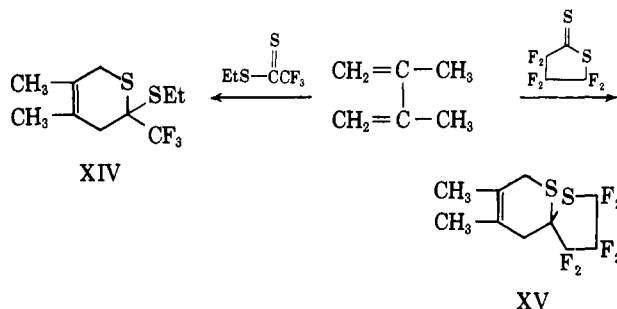


More stable adducts are formed by reaction of the thioacyl fluorides with cyclic dienes. In these adducts, intramolecular loss of hydrogen fluoride is less likely in view of the impossibility of introducing a bridgehead double bond in such systems. Stable adducts were formed from the reaction of trifluorothioacetyl fluoride with cyclopentadiene (XIa) and anthracene (XIIa), from pentafluorothiopropanoyl fluoride with anthracene (XIIb), and from chlorodifluorothioacetyl fluoride with hexachlorocyclopentadiene (XIIIa).

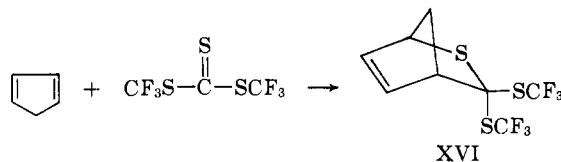


Thiocarbonyl Fluoride.—Like other thioacyl fluorides, thiocarbonyl fluoride is also an active dienophile. However, most of its adducts are extremely unstable. The adduct with cyclopentadiene (XIb) proved to be stable enough for isolation and could be stored in the cold, but it spontaneously polymerized in a few days when stored at room temperature. The instability appears to be associated with the remaining unsaturation in the adduct, for its bromine addition product was stable to storage. An adduct of thiocarbonyl fluoride and hexachlorocyclopentadiene (XIIIb) was also prepared, and this adduct has good stability.

Dithio Esters.—In addition to thio ketones and thioacyl fluorides, fluorine-containing dithio esters are also active dienophiles. Adducts XIV and XV have been prepared by the reaction of ethyl trifluorodithioacetate and perfluorodithiobutylolactone, respectively, with 2,3-dimethylbutadiene at 0°. Even

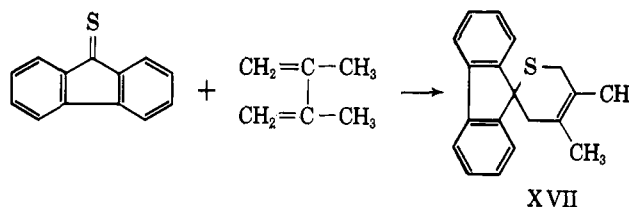


bis(trifluoromethyl) trithiocarbonate, which does not have a fluoroalkyl group directly attached to the thiocarbonyl group, also reacts rapidly with cyclopentadiene at 0° to give an adduct (XVI).



Other Thiocarbonyl Compounds.—Although this investigation has dealt principally with fluorine-

containing thiocarbonyl compounds, it was of interest to determine if fluorine-free thiocarbonyl compounds are active dienophiles. This, indeed, is the case. Thiofluorenone reacts rapidly and exothermically with dimethylbutadiene in pentane at room temperature to give a high yield of the adduct (XVII). Thiophosgene



is also a dienophile. It adds to cyclopentadiene at low temperatures to give an adduct (XIc) that is relatively unstable. As is the case with the thiocarbonyl fluoride-cyclopentadiene adduct, a derivative stable at room temperature is obtained by addition of bromine to the thiophosgene adduct.

Experimental⁹

Elemental analysis of adducts appear in Table II.

Hexafluorothioacetone-Butadiene Adduct¹⁰ (I).—Butadiene, 10.8 g. (0.2 mole), was condensed into a flask cooled to -78° by a Dry Ice-acetone bath. Hexafluorothioacetone was then distilled rapidly into the flask until a faint blue color persisted. The reaction mixture was allowed to warm to room temperature and was then distilled to give 42.4 g. of 2,2-bis(trifluoromethyl)-3,6-dihydro-2H-thiopyran as a colorless oil. The infrared absorption spectrum contains bands at 3.25 (C=CH), 3.4 and 3.5 (saturated CH₂), and 5.95 μ (—CH=CH—). The F¹⁹ n.m.r. spectrum contains a single unsplit resonance band at 4.24 p.p.m. Adducts of hexafluorothioacetone with 2,3-dimethyl-1,3-butadiene (2,2-bistrifluoromethyl-3,6-dihydro-4,5-dimethyl-2H-thiopyran, Ia: infrared, 3.35, 3.40, and 3.50 for CH₂ and CH₃, and 5.95 μ for C=C; F¹⁹ n.m.r. singlet; H¹ n.m.r., three peaks in ratio of 1:1:3), with cyclopentadiene (3,3-bistrifluoromethyl-2-thiabicyclo[2.2.1]hept-5-ene, Ib: F¹⁹ n.m.r., two quartets of equal area), with 2-chloro-1,3-butadiene (2,2-bistrifluoromethyl-4-(and 5-) chloro-3,6-dihydro-2H-thiopyran, Ic: F¹⁹ n.m.r., two singlets indicating a mixture of 4- and 5-chloro isomers), with 1-methoxybutadiene (3,3-bistrifluoromethyl-3-(and 6-) methoxy-3,6-dihydro-2H-thiopyran, Id), and with 2,2-bis(trifluoromethyl)-2H-thiopyran (Ie) were prepared in a similar manner. With the last three unsymmetrical dienes, a mixture of the two possible isomers was formed in each case, as was evidenced by their F¹⁹ n.m.r. spectra.

Hexafluorothioacetone-Furan Adduct (III).—Hexafluorothioacetone was distilled into a flask containing 6.8 g. (0.1 mole) of furan cooled to -78° until a faint blue color persisted. The reaction product solidified at this point. It was sublimed at 25° (0.05 mm.) into a trap cooled to -78° to give 2,2-bis(trifluoromethyl)-3,6-epoxy-3,6-dihydro-2H-thiopyran as a white solid, m.p. 20–21°. The F¹⁹ n.m.r. spectrum of the adduct in methylene chloride solution showed two quadruplets of equal intensity.

The product is not stable to storage at room temperature (25°) in its liquid state. After standing a few hours, the liquid became more viscous, and after 5 days it was a hard glass. This glass appears to be a polymer of the adduct.

Anal. Calcd. for (C₇H₄F₆OS)_n: C, 33.60; H, 1.60; F, 45.60; S, 12.80. Found: C, 33.10; H, 1.65; F, 44.50; S, 13.05.

(9) Fluorine n.m.r. spectra were obtained with a Varian Associates high-resolution n.m.r. spectrometer operating at 56.4 Mc./sec. Spectra were calibrated in terms of displacement in parts per million from the F¹⁹ resonance of 1,2-difluoro-1,1,2,2-tetrachloroethane used as an external standard. Negative frequency displacements are for resonances occurring at lower field than the reference. Proton resonance spectra were obtained with a Varian Associates A-60 spectrometer. Spectra were calibrated in terms of lower field displacement in parts per million from the proton resonance of tetramethylsilane used as an internal reference.

(10) W. J. Middleton, U. S. Patent 3,073,845 (1963).

TABLE II
 ANALYSES OF ADDUCTS

Adduct	Formula	Carbon, %		Hydrogen, %		Fluorine, %		Sulfur, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
I	C ₇ H ₆ F ₆ S	35.60	36.52	2.60	2.67	48.20	47.92	13.50	13.87
Ia	C ₉ H ₁₀ F ₆ S	40.80	40.99	3.80	3.97	43.20	42.28	12.10	12.41
Ib	C ₈ H ₈ F ₆ S					45.90	45.87		
Ic	C ₇ H ₅ ClF ₆ S	31.10	31.44	1.90	1.88	13.10 ^a	13.22 ^a	11.80	12.75
Id	C ₈ H ₈ F ₆ OS	36.09	36.13	3.03	3.26	42.83	42.79	12.04	12.27
Ie	C ₁₀ H ₄ F ₁₂ S ₂	28.85	29.32	0.95	1.19	54.78	54.92	15.42	15.61
III	C ₇ H ₄ F ₆ OS	33.60	33.78	1.60	1.79	45.66	45.84	12.80	12.71
IV	C ₁₇ H ₁₀ F ₆ S	56.67	56.95	2.80	3.00	31.64	31.60	8.90	8.82
Va	C ₁₄ H ₈ F ₁₂ S ₂	35.40	36.52	1.72	2.19	48.69	48.62	13.69	13.89
Vb	C ₁₆ H ₁₀ F ₁₂ OS ₂	36.15	36.96	2.02	2.08	45.75	45.98	12.90	13.44
Vc	C ₂₀ H ₁₂ F ₁₂ S ₂	44.12	44.40	2.23	2.68	41.88	41.65	11.78	11.84
IX	C ₈ H ₆ F ₄ S	38.72	38.89	3.25	3.34	40.82	41.00	17.22	17.34
IXa	C ₈ H ₁₂ F ₄ S	44.80	45.11	4.72	5.10	35.50	35.21	14.90	14.12
XIa	C ₇ H ₆ F ₄ S	42.44	42.30	3.05	3.25	38.36	38.08	16.17	16.32
XIb	C ₈ H ₆ F ₂ S	48.64	48.37	4.10	4.19	25.60	25.07	12.60	12.36
XIc	C ₈ H ₆ Cl ₂ S	39.77	40.04	3.34	3.42	39.16 ^a	38.76 ^a	17.70	17.77
XIIa	C ₁₆ H ₁₀ F ₄ S	62.93	62.69	3.25	3.62	24.49	23.91	10.33	10.03
XIIb	C ₁₇ H ₁₀ F ₆ S	56.67	56.70	2.80	3.16	31.64	31.55	8.90	8.90
XIIIa	C ₇ Cl ₇ F ₃ S	58.90 ^a	58.91 ^a			13.53	13.31	7.62	7.75
XIIIb	C ₈ Cl ₆ F ₂ S	59.95 ^a	59.76 ^a			10.70	10.76		
XIV	C ₁₂ H ₁₀ F ₈ S	46.85	47.16	5.90	6.20	22.24	22.28	25.01	25.23
XV	C ₁₀ H ₁₀ F ₆ S ₂	39.00	39.40	3.00	2.93	37.00	36.89	20.70	21.02
XVI	C ₈ H ₆ F ₆ S ₃							30.80	30.32
XVII	C ₁₉ H ₁₉ S	81.97	81.73	6.52	6.67			11.52	11.64
XVIII	C ₁₈ H ₁₀ F ₈ S	52.66	53.16	2.46	3.08	37.04	36.85	7.81	7.69

^a Chlorine analysis.

Hexafluorothioacetone-Anthracene Adduct (IV).—A suspension of 26.7 g. (0.15 mole) of anthracene in 100 ml. of carbon disulfide was cooled to 0°, and 17 ml. of hexafluorothioacetone was distilled into the stirred suspension. The solution was then evaporated to dryness to give 54 g. of white, crystalline residue (crude yield 100%). The product was recrystallized from pentane to give 47 g. of 12,12-bis(trifluoromethyl)-9,10-dihydro-9,10-epithiomethanoanthracene as long white needles.

12-Trifluoromethyl-12-pentafluoroethyl-9,10-dihydro-9,10-epithiomethanoanthracene (XVIII) was prepared in a similar manner from the reaction of anthracene with octafluoro-2-butanethione in carbon disulfide.

Hexafluorothioacetone-4-Methoxystyrene Adduct (Vb).—A stirred solution of 13.4 g. (0.1 mole) of 4-methoxystyrene in 24 ml. of chloroform was cooled to -78° and hexafluorothioacetone was added dropwise until a faint blue color persisted for about 30 sec. The reaction mixture was warmed to room temperature and evaporated to dryness under reduced pressure. The residue was recrystallized from hexane to give 37.3 g. of the 2:1 adduct as white prisms, m.p. 117–118.5°, λ^{KBr} 3.35 and 3.50 (saturated CH) and 6.05 μ (C=C). The proton n.m.r. spectrum of a carbon tetrachloride solution indicated no resonance above 6 (aromatic CH region), two multiplets each of relative area 1 centered at 5.88 and 4.92 (olefin CH), and the balance of the resonance between 3.2 and 4.2 p.p.m., relative area 8 (saturated CH and OCH₃). The F¹⁹ n.m.r. resonance showed two pairs of quadruplets centered at -3.97 and -2.66 ($J = 10$ c.p.s.) and -0.96 and -0.28 p.p.m. ($J = 11$ c.p.s.).

Hexafluorothioacetone-1,1-Diphenylethylene Adduct (Vc).—A solution of 1.8 g. of 1,1-diphenylethylene in 10 ml. of pentane was added dropwise to 1.82 g. (0.01 mole) of hexafluorothioacetone cooled to -78°. The blue color faded and a white solid precipitated. The solid was collected on a filter, washed with cold pentane, and recrystallized from cyclohexane to give 2.5 g. of adduct as colorless crystals, m.p. 152–153°. The hydrogen n.m.r. spectrum indicated a ratio of aromatic to olefinic to saturated hydrogens of 5:2:5.

Hexafluorothioacetone-Styrene Adduct (Va).—Styrene was added dropwise to 9.1 g. (0.05 mole) of hexafluorothioacetone cooled to -78° until the blue color faded. The reaction product was distilled to give 7.1 g. of the 2:1 adduct as a colorless, viscous oil, b.p. 103–104 (1.2 mm.). The n.m.r. hydrogen and fluorine spectra indicated a mixture of isomers were present. The hydrogen spectrum indicated a ratio of olefinic to saturated hydrogens of 3:5.

Pentafluorothioproponyl Fluoride-Anthracene Adduct (XIIb).—A mixture of 0.91 g. (0.005 mole) of pentafluorothioproponyl fluoride, 0.89 g. (0.005 mole) of anthracene, and 10 ml. of carbon disulfide was sealed in a glass tube and allowed to stand at room temperature for 20 hr. The tube was cooled and opened, and the reaction mixture was evaporated to dryness. The residue was recrystallized twice from pentane to give 12-fluoro-12-pentafluoroethyl-9,10-dihydro-9,10-epithiomethanonanthracene as colorless prisms, m.p. 113–114°.

12-Fluoro-12-trifluoromethyl-9,10-dihydro-9,10-epithiomethanoanthracene (XIIa), 27.2 g., was prepared in a similar manner from 16 g. of trifluoroethyl fluoride and 21.6 g. of anthracene.

Trifluoroethyl Fluoride-Butadiene Adduct (IX).—A flask containing 5.4 g. (0.1 mole) of butadiene was cooled to -78°. Trifluoroethyl fluoride was distilled into the flask until a faint yellow color persisted, 13.2 g. being required. Distillation of the reaction product gave 10.3 g. of 2-fluoro-2-trifluoromethyl-3,6-dihydro-2H-thiopyran as a colorless oil. The F¹⁹ n.m.r. spectrum of this compound contained a quadruplet and a doublet of relative areas 1:3.

Adducts of trifluoroethyl fluoride with 2,3-dimethyl-1,3-butadiene (2-fluoro-2-trifluoromethyl-3,6-dihydro-4,5-dimethyl-2H-thiopyran, IXa) and cyclopentadiene (3-fluoro-3-trifluoromethyl-2-thiabicyclo[2.2.1]hept-5-ene, XIa) (F¹⁹ n.m.r. indicated a mixture of two isomers in the ratio of about 2:7) were prepared in a similar manner.

The adducts of butadiene and dimethylbutadiene appeared to be unstable to storage. A sample of the butadiene adduct stored at room temperature for 1 week lost hydrogen fluoride and etched the glass container badly. The material from the container was redistilled to give 6-trifluoromethyl-2H-thiopyran as a colorless oil, b.p. 39° (10 mm.). The F¹⁹ n.m.r. spectrum showed a single unsplit resonance band in the CF₃ region. The infrared spectrum showed bands at 6.10 and 6.35 μ .

Anal. Calcd. for C₈H₆F₃S: C, 43.40; H, 3.00; F, 34.30; S, 19.30. Found: C, 43.60; H, 3.55; F, 34.10; S, 19.55.

Thiocarbonyl Fluoride-Cyclopentadiene Adduct (XIb).—Thiocarbonyl fluoride, 14 g. (0.17 mole), was slowly distilled into a flask containing 11.2 g. (0.17 mole) of freshly distilled cyclopentadiene cooled initially to -78°. During the addition, the reaction mixture was stirred and kept below -20°. When the addition was complete, the reaction mixture was allowed to warm to room temperature and then evacuated to 1 mm. by means of an oil pump. During the evacuation, the reaction mixture

solidified to a white granular mass (25 g.). A sample was sublimed at 0.1 mm. for analysis. The fluorine n.m.r. spectrum shows an AB pattern with one side split farther into doublets. The infrared spectrum (3.25, 3.35, 3.40, and 6.55 μ) is also consistent for the proposed structure, 3,3-difluoro-2-thiabicyclo[2.2.1]hept-5-ene.

When this product was stored at room temperature for several days or heated above its melting point for a few minutes, it polymerized to a white elastomer.

A stable dibromide was prepared from this adduct. Bromine was added dropwise to a solution of 1.48 g. (0.01 mole) of the adduct in 2 ml. of carbon tetrachloride until a slight bromine color remained. The reaction mixture was cooled, and the solid that precipitated was collected on a filter. Recrystallization from pentane gave 1.89 g. of the bromine adduct as colorless prisms, m.p. 58–59°.

Anal. Calcd. for $C_6H_6Br_2F_2S$: C, 23.4; H, 2.0; Br, 51.9; F, 12.3; S, 10.4. Found: C, 23.9; H, 2.2; Br, 52.2; F, 12.0; S, 10.4.

Thiocarbonyl Fluoride–Hexachlorocyclopentadiene Adduct¹¹ (XIIIb).—A sealed Carius tube containing 12 ml. (measured at –78°) of thiocarbonyl fluoride and 60 g. of hexachlorocyclopentadiene was heated at 160° for 48 hr. The tube was cooled and opened, and the unchanged starting materials were removed by distillation. There was obtained 12.3 g. of residual crystalline product, m.p. 111–115°. Analysis indicated this product to be hexachloro-3,3-difluoro-2-thiabicyclo[2.2.1]hept-5-ene.

Chlorodifluoroacetyl Fluoride–Hexachlorocyclopentadiene Adduct¹¹ (XIIIa).—A sealed Carius tube containing 7.5 g. of chlorodifluoroacetyl fluoride and 13.7 g. of hexachlorocyclopentadiene was heated at 150° for 8 hr. The tube was cooled and opened, and the contents were distilled to give 8.24 g. (40%) of hexachloro-3-chlorodifluoromethyl-3-fluoro-2-thiabicyclo[2.2.1]hept-5-ene as a colorless oil, b.p. 79° (0.25 mm.), n_D^{25} 1.5383.

Thiophosgene–Cyclopentadiene Adduct (XIc).—Freshly distilled cyclopentadiene, 63.3 g. (0.55 mole), was placed in a 300-ml. flask and cooled to –78°. Thiophosgene, 33 g. (0.5 mole), was added dropwise with stirring. A white solid formed when about one-half of the thiophosgene had been added. The reaction mixture was warmed to 0° and the rest of the thiophosgene was added dropwise. When the color of the thiophosgene had faded completely, the reaction mixture was allowed to warm to room temperature and evacuated to 1 mm. to remove excess cyclopentadiene. The remaining white residue was recrystallized from pentane to give 81 g. (90%) of 3,3-dichloro-2-thiabicyclo[2.2.1]hept-5-ene as a white, waxy, crystalline solid, m.p. 50–52°.

This adduct was unstable to storage at room temperature. A stable derivative was made by the addition of bromine. A solution of 6.8 g. (0.0425 mole) of bromine in 10 ml. of carbon tetrachloride was added dropwise to a solution of 7.7 g. (0.0425 mole) of 3,3-dichloro-2-thiabicyclo[2.2.1]hept-5-ene in 10 ml. of carbon tetrachloride. The bromine color faded very rapidly. When the addition was complete, the reaction mixture was cooled to –50°, and the white solid that precipitated was collected on a filter, washed with cold pentane, and recrystallized from pentane. There was obtained 12.4 g. of the bromine adduct as white prisms, m.p. 73–74°.

Anal. Calcd. for $C_6H_6Br_2Cl_2S$: C, 21.14; H, 1.78; Cl, 20.80; S, 9.40; Br, 46.90. Found: C, 21.6; H, 2.05; Cl, 21.13; S, 9.51; Br, 46.63.

Thiofluorenone–Dimethylbutadiene Adduct (XVII).—A mixture of 4.9 g. of thiofluorenone,¹² 2.05 g. (0.025 mole) of 2,3-dimethylbutadiene, and 100 ml. of pentane was stirred under nitrogen at room temperature for 30 min. The green color of the thiofluorenone faded to light yellow after about 3 min. The light yellow solid that precipitated was collected on a filter and washed with pentane. Recrystallization from cyclohexane and hexane gave 5.8 g. of 2-(9-fluorenylidene)-3,6-dihydro-2H-thiopyran (XVII) as colorless prisms, m.p. 125°.

Ethyl Trifluorodithioacetate–Dimethylbutadiene Adduct (XIV).—A mixture of 4.5 g. (0.055 mole) of 2,3-dimethylbutadiene and 5.22 g. (0.03 mole) of ethyl trifluorodithioacetate was stirred at

0° for 7 hr. and then allowed to warm to room temperature and stand overnight. The reaction mixture was distilled to give 6.9 g. of 2-trifluoromethyl-2-ethylthio-3,6-dihydro-4,5-dimethyl-2H-thiopyran as a colorless oil.

Hexafluorodithiobutyrolactone–2,3-Dimethylbutadiene Adduct (XV).—2,3-Dimethylbutadiene, 1.0 g. (0.012 mole), was added dropwise to 2.26 g. (0.01 mole) of hexafluorodithiobutyrolactone cooled to 0° by an ice bath. An exothermic reaction ensued, and the red color faded rapidly. The reaction mixture was distilled to give 2.16 g. of 2,2,3,3,4,4-hexafluoro-8,9-dimethyl-1,6-dithiaspiro[4.5]dec-8-ene as a light yellow oil.

Bis(trifluoromethyl) Trithiocarbonate–Cyclopentadiene Adduct (XVI).—Cyclopentadiene was added dropwise to 1.36 g. (0.05 mole) of bis(trifluoromethyl) trithiocarbonate until the red color was discharged. The reaction mixture was distilled to give 1.1 g. of 3,3-bis(trifluoromethylthio)-2-thiabicyclo[2.2.1]hept-5-ene as a light yellow oil.

2,2-Bis(trifluoromethyl)-4,5-dibromotetrahydrothiopyran.—A solution of 30.4 g. (0.19 mole) of bromine in 10 ml. of carbon tetrachloride was added dropwise to a solution of 45 g. of 2,2-bis(trifluoromethyl)-3,6-dihydro-2H-thiopyran in 100 ml. of carbon tetrachloride cooled in an ice bath. The reaction mixture was evaporated to dryness, and the residue was washed with cold pentane and then recrystallized from pentane to give 72 g. (92%) of 2,2-bis(trifluoromethyl)-4,5-dibromotetrahydrothiopyran as large colorless prisms, m.p. 69–69.5°.

Anal. Calcd. for $C_7H_6Br_2F_6S$: Br, 40.30; S, 8.10. Found: Br, 40.12; S, 8.07.

2,2-Bis(trifluoromethyl)-2H-thiopyran.—A solution of 90% potassium hydroxide in 100 ml. of ethanol was added dropwise with stirring to a solution of 59.4 g. (0.15 mole) of 2,2-bis(trifluoromethyl)-4,5-dibromotetrahydrothiopyran in 250 ml. of ethanol cooled in an ice bath. A white solid precipitated immediately. After the addition, the reaction mixture was stirred for 10 min. and then poured into 1500 ml. of water containing 10 ml. of concentrated hydrochloric acid and 30 ml. of methylene chloride. The lower organic layer was separated, washed with water, and dried over sodium sulfate. Distillation gave 21.0 g. (60%) of 2,2-bis(trifluoromethyl)-2H-thiopyran as a colorless liquid, b.p. 49° (34 mm.), n_D^{25} 1.4360, and 5 g. of 2,2-bis(trifluoromethyl)-4-bromo-3,4-dihydro-2H-thiopyran, b.p. 44–45° (4.5 mm.). The F^{19} and H n.m.r. spectrum of each product was consistent with the proposed structure. The thiopyran showed infrared bands at 6.15 and 6.26 μ . The bromodihydrothiopyran contained a strong band at 6.1 μ .

Anal. Calcd. for $C_7H_6F_6S$: C, 35.90; H, 1.72; F, 48.68; S, 13.70. Found: C, 36.10; H, 1.99; F, 48.59; S, 13.56.

Anal. Calcd. for $C_7H_5BrF_6S$: C, 26.68; H, 1.60; Br, 25.37; F, 36.18; S, 10.18. Found: C, 27.27; H, 1.56; Br, 24.50; F, 36.19; S, 10.48.

A sample of the thiopyran dimerized when stored at room temperature for 4 months. A sample of this dimer was recrystallized from chloroform to give colorless plates, m.p. 117°.

Anal. Calcd. for $C_{14}H_8F_{12}S_2$: C, 35.90; H, 1.72; F, 48.66; S, 13.70; mol. wt., 468. Found: C, 35.90; H, 1.94; F, 47.61; S, 13.76; mol. wt., 465.

Reaction of HFTA with Pyrrole.—HFTA, 15 ml. at –78°, was distilled into a receiver containing 6.7 g. (0.1 mole) of pyrrole cooled to –78°. The reaction mixture was allowed to warm to room temperature and was then distilled. There was obtained 2.2 g. of a 1:1 adduct as a light yellow oil, b.p. 33° (1.75 mm.), n_D^{25} 1.4337; 1.1 g. of a 2:1 adduct, b.p. 58° (0.8 mm.), n_D^{25} 1.4240; and 10 g. of a black tarry residue.

Anal. Calcd. for 1:1 adduct, $C_7H_6F_8NS$: C, 33.73; H, 2.02; F, 45.84; N, 5.65; S, 12.98. Found: C, 33.62; H, 2.09; F, 45.57; N, 5.79; S, 12.99.

Anal. Calcd. for 2:1 adduct, $C_{10}H_8F_{12}NS_2$: C, 27.85; H, 1.17; F, 52.87; N, 3.25; S, 14.87. Found: C, 28.27; H, 1.28; F, 52.37; N, 3.61; S, 15.03.

The infrared spectrum of the 1:1 adduct showed bands at 3.9 μ for SH, 2.85 μ for NH, and several other strong bands that could be assigned to the pyrrole nucleus. The F^{19} n.m.r. spectrum contained a single unsplit resonance line. The infrared spectrum of the 2:1 adduct was similar, but showed no band for SH. The F^{19} spectrum showed two absorptions of equal area, one being a singlet and the other a doublet.

(11) We are indebted to Dr. B. C. Anderson for this preparation.

(12) E. Campaigne and W. B. Reid, *J. Am. Chem. Soc.*, **68**, 769 (1946).