Bis(trifluoromethyl)thioketene. II. Acyclic Derivatives

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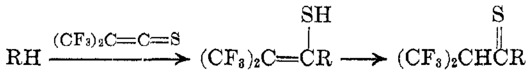
Bis(trifluoromethyl)thioketene adds to alcohols and thiols to form thio esters and to amines to give thioamides. With 1,3-disubstituted triazenes compounds of the formula $ArSC(=NR)CH(CF_3)_2$ are formed. Dimethylanilines give $ArN(CH_3)CH_2SCH=C(CF_3)_2$ and ethers form $ROCHRSCH=C(CF_3)_2$. Silicon and tin hydrides add to yield products with sulfur-metal bonds. Olefinic compounds undergo ene reactions to produce compounds containing the $C=CC-SCH=C(CF_3)_2$ unit. More complex transformations take place with cycloheptatriene, bicyclobutane, and bicyclo[4.2.0]oct-7-ene. C-Thioacylations occur with indole, 1,3,3-trimethyl-2-methyleneindoline, and 6-(dimethylamino)fulvene. Reaction with sulfur diimides yields ketenimines of the formula $(CF_3)_2C=C=NR$.

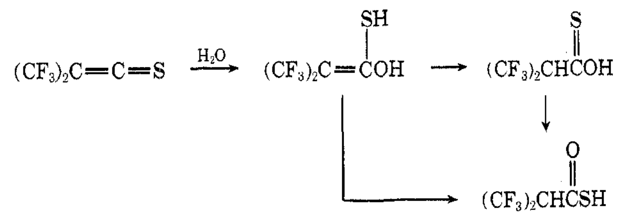
Synthesis and cycloaddition reactions of bis(trifluoromethyl)thioketene were reported in part I.[1] This paper describes acyclic derivatives to illustrate further the range of reactivity of the thioketene.

Addition to Water, Alcohol, and Thiols.—The reactivity of bis(trifluoromethyl)thioketene resides, in most instances, in the thiocarbonyl group, as reflected in its cycloaddition reactions. Normal additions to active hydrogen compounds are therefore believed to proceed through the enethiol.



$$RH \xrightarrow{(CF_3)_2C=C=S} (CF_3)_2C=\overset{\overset{\large SH}{|}}{C}R \longrightarrow (CF_3)_2CH\overset{\overset{\large S}{\|}}{C}R$$

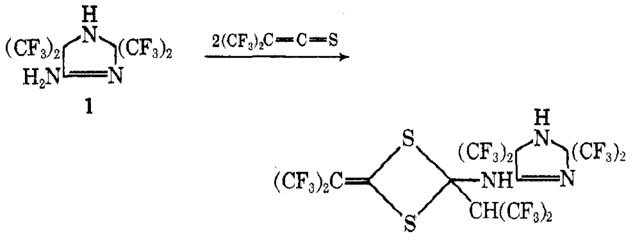
In the special case of water, a thiono acid may be another possible intermediate.



Addition of methanol or ethanol forms $(CF_3)_2CHC(=S)OR$ which, like certain other sulfur compounds,[2] produces white, faintly oxyluminescent fumes in air, a phenomenon that has been attributed to the formation of sulfur monoxide. Thio adducts do not give obvious fumes. Addition of benzeneselenol results in the novel function, $-C(=S)Se-$. Thio esters derived from the thioketene are listed in Table I.

Addition to Hydrogen Bromide.—The thioketene and HBr form $(CF_3)_2CHC(=S)Br$. Few thioacyl bromides are known. Besides thiocarbonyl bromide,[3] a complex thioacyl bromide[4] has been reported.

Thioacylation of Amines.—Catalytic amounts of tertiary amines, except for *N,N*-dimethylanilines, cause the thioketene to dimerize, but with primary and secondary amines addition takes place much more rapidly than dimerization and high yields of thioamides are obtained (Table I). Ordinarily, a second molecule of the thioketene does not add to the thiocarbonyl group of the thioamides to form a 1,3-dithietane. However, in the case of the aminoimidazoline[5] **1**, only the diadduct **2** can be obtained, even when excess imidazoline is used.

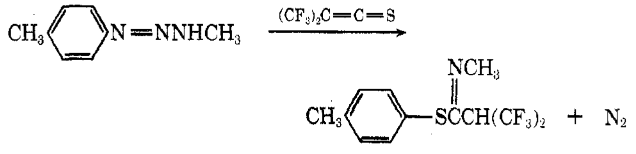


1

(or tautomer)

2

Bis(trifluoromethyl)thioketene and 1-methyl-3-*p*-tolyltriazene result in the unusual reaction shown below, which is also operable with 1,3-di-*p*-tolyltriazene.



Thioacylation of the triazene seems likely as the first step in the reaction sequence and product formation might be rationalized as shown in Scheme I.

Besides physical evidence, proof of structure of the product includes hydrolysis to *p*-toluenethiol. 3,3-Dimethyl-1-*p*-tolyltriazene dimerized the thioketene.

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(1) M. S. Raasch, *J. Org. Chem.*, **35**, 3470 (1970). To the literature synopsis therein may be added: (a) Reaction of alkylthiophenylacetylenes with amines to form phenylthioacetamides is postulated to proceed through phenylthioketene. M. L. Petrov, B. S. Kupin, and A. A. Petrov, *Zh. Org. Khim.*, **5**, 1759 (1969); *J. Org. Chem. USSR*, **5**, 1705 (1969). (b) Pyrolysis of 1,1-diphenyl-2-ethoxy-2-(ethoxythiocarbonylthio)ethylene or ethyl diphenylthionoacetate gave diphenylthioketene dimer. A. Schönberg, W. Knöfel, E. Frese, and K. Praefcke, *Chem. Ber.*, **103**, 949 (1970). (c) Carbomethoxycyanothioketene, generated *in situ*, combines with 2-methylthiobenzhydrazide to form mesoionic 2-(carbomethoxycyanomethylene)-4-methyl-5-phenyl-1,3,4-thiadiazole. R. Grashey, M. Baumann, and R. Hamprecht, *Tetrahedron Lett.*, 5083 (1970). (d) Perfluoroisobutene reacts with sulfur and potassium fluoride to form $(CF_3)_2C=C=S$ dimer. B. L. Dyatkin, S. R. Sterlin, L. G. Zhuravkova, and I. L. Knunyants, *Dokl. Akad. Nauk SSSR*, **183**, 598 (1968); *Proc. Acad. Sci. USSR*, **183**, 1018 (1968). (e) Reaction of perfluoroisobutene with potassium diethyl thiophosphate, potassium thiocyanate, or sodium thiosulfate forms $(CF_3)_2C=C=S$ dimer. I. L. Knunyants, B. L. Dyatkin, S. R. Sterlin, and V. L. Isaev, Russian Patent 246,508 (1969). (f) Perfluoroisobutene and potassium sulfide yield $(CF_3)_2C=C=S$ dimer. D. C. England, U. S. Patent 3,544,591 (1970); *Chem. Abstr.*, **74**, 141735h (1971). (g) Bis(trifluoromethyl)thioketene adds to carbodiimides and azines to give 1,3-thiazetidines. M. S. Raasch, U. S. Patent 3,592,811 (1971); *Chem. Abstr.*, **75**, 99232k (1971). (h) Reaction of lithium 2-phenylethynethiolate with protic substances presumably proceeds through phenylthioketene. R. Raap, *Can. J. Chem.*, **46**, 2251 (1968). (i) Thioketene ions appear in the mass spectra of desaurins. P. Yates, T. R. Lynch, and L. S. Weiler, *ibid.*, **46**, 365 (1968). (j) The potential role of thioketene intermediates in the dimerization of *N*-alkyl-3-isothiazolones to 2,4-dimethylene-1,3-diethietanes is discussed. A. W. K. Chan, W. D. Crow, and I. Gosney, *Tetrahedron*, **26**, 1493 (1970).

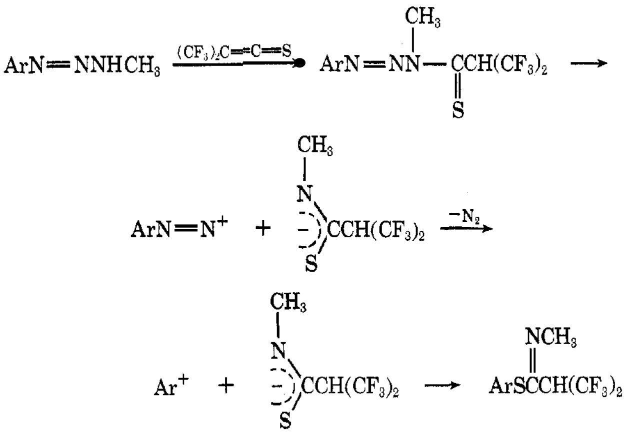
(2) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. IV, Chemical Publishing Co., New York, N. Y., 1962, pp 179, 180.

(3) W. J. Middleton, E. G. Howard, Jr., and W. H. Sharkey, *J. Org. Chem.*, **30**, 1375 (1965); R. Steudel, *Angew. Chem.*, **79**, 649 (1967); *Angew. Chem., Int. Ed. Engl.*, **6**, 635 (1967).

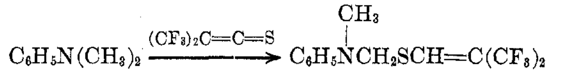
(4) B. R. O'Connor and F. N. Jones, *J. Org. Chem.*, **35**, 2002 (1970).

(5) W. J. Middleton and C. G. Krespan, *ibid.*, **35**, 1480 (1970).

SCHEME I

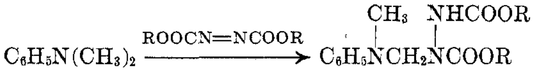


Reaction with *N,N*-Dimethylanilines.—The thioketene adds to *N,N*-dimethylanilines at 10° with attack on one methyl group. The reaction is reminiscent of



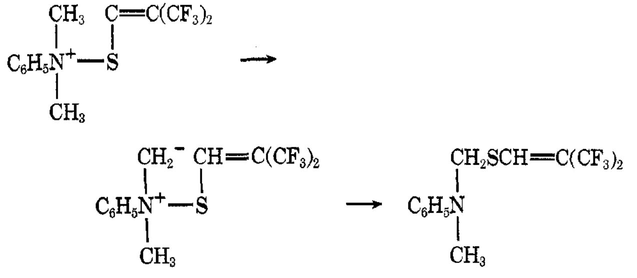
$$\mathrm{C_6H_5N(CH_3)_2 \xrightarrow{(CF_3)_2C{=}C{=}S} C_6H_5\overset{CH_3}{N}CH_2SCH{=}C(CF_3)_2}$$

the addition of azodicarboxylic ester to dimethylaniline, the mechanism of which has been concluded to be ionic.[6]



$$\mathrm{C_6H_5N(CH_3)_2 \xrightarrow{ROOCN{=}NCOOR} C_6H_5\overset{CH_3}{N}CH_2\overset{NHCOOR}{N}COOR}$$

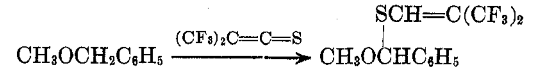
Like the azodicarboxylic ester reaction, the thioketene reaction proceeds more slowly with *N,N*-dimethyl-*m*-nitroaniline than with *N,N*-dimethylaniline, does not go with *N,N*-dimethyl-*p*-nitroaniline under the conditions, and is not stopped by diphenylpicrylhydrazyl. Adapting the rationalization used for the azodicarboxylic ester reaction to the present case, electrophilic attack on the nitrogen atom first takes place, then proton transfer and ylide rearrangement.



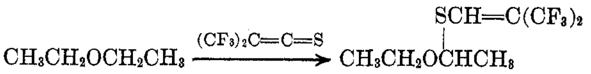
The reaction also proceeds well with *N,N*-dimethyl-*p*-toluidine, and with *N,N,N′,N′*-tetramethylbenzidine to give a diadduct. However, with *N*-ethyl-*N*-methylaniline or *N,N*-dimethyl-1-naphthylamine the reaction is apparently slowed to the point where the sensitive, base-catalyzed dimerization of the thioketene takes precedence.

The $(CF_3)_2C{=}CHS$– group, encountered in the above compounds and many that follow, has in its ^1H nmr spectrum a diagnostic quadruplet, $J = 1.4$–1.6 Hz, at about 7.5 ppm, a position seldom occupied by other absorptions.

Addition to Ethers.—Reaction of the thioketene with ethers is another example of the introduction of a propenylthio group.

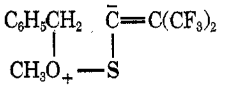


$$\mathrm{CH_3OCH_2C_6H_5 \xrightarrow{(CF_3)_2C{=}C{=}S} CH_3O\overset{SCH{=}C(CF_3)_2}{C}HC_6H_5}$$



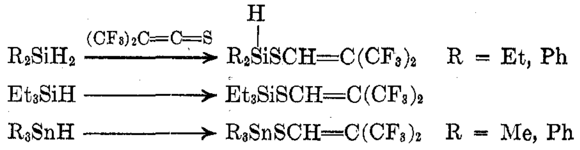
$$\mathrm{CH_3CH_2OCH_2CH_3 \xrightarrow{(CF_3)_2C{=}C{=}S} CH_3CH_2O\overset{SCH{=}C(CF_3)_2}{C}HCH_3}$$

This reaction, like the addition to dimethylaniline, could be represented as proceeding through a dipolar intermediate.



However, the reaction is peroxide catalyzed and is considered to be a free radical reaction. Peroxide catalysis also leads to more complex products.

Adducts with Silicon and Tin Hydrides.—These hydrides also add to the thioketene to form the $(CF_3)_2C{=}CHS$– group with its characteristic nmr.



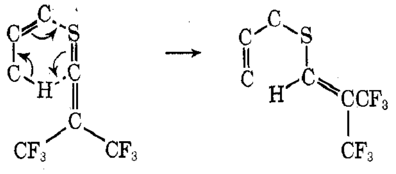
$$\mathrm{R_2SiH_2 \xrightarrow{(CF_3)_2C{=}C{=}S} R_2\overset{H}{Si}SCH{=}C(CF_3)_2 \quad R = Et, Ph}$$
$$\mathrm{Et_3SiH \longrightarrow Et_3SiSCH{=}C(CF_3)_2}$$
$$\mathrm{R_3SnH \longrightarrow R_3SnSCH{=}C(CF_3)_2 \quad R = Me, Ph}$$

The product from trimethylstannane is unstable. The reaction can be compared with the addition of triethylstannane to phenyl isothiocyanate, which adds in the same direction.[7] Presumably it is ionic with nucleophilic attack of hydride hydrogen on carbon, *e.g.*,

$$\mathrm{R_3SnH \xrightarrow{(CF_3)_2C{=}C{=}S} [R_3Sn^+ + S^-CH{=}C(CF_3)_2] \longrightarrow R_3SnSCH{=}C(CF_3)_2}$$

Ene Reactions.—A range of olefinic substances readily undergoes the ene reaction[8] with the thioketene as illustrated in Table II. The olefin attaches to the sulfur atom and in this respect the thioketene resembles hexafluorothioacetone[9a] and aryl thioketones in their reaction with tetramethylallene.[9b]

The ene reaction is usually, though not necessarily, represented as a concerted reaction proceeding through a six-membered transition state.



In the reaction of the thioketene with allene, two linear molecules, to form $(CF_3)_2C{=}CHSCH_2C{\equiv}CH$ some modification of the picture is needed.[10]

If a diradical were an intermediate, cyclization to form a thietane would be a possibility in addition to the ene product. No careful search for the thietanes

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[6] R. Huisgen and F. Jacob, *Justus Liebigs Ann. Chem.*, **590**, 46 (1954).

[7] J. G. Noltes and M. J. Janssen, *J. Organometal. Chem.*, **1**, 346 (1964).

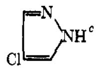
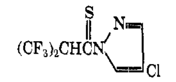
[8] For a review of the ene reaction see H. M. R. Hoffmann, *Angew. Chem.*, **81**, 597 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969).

[9] (a) W. J. Middleton, *J. Org. Chem.*, **30**, 1395 (1965); (b) H. Gotthardt, *Tetrahedron Lett.*, 2343, 2345 (1971).

[10] W. R. Dolbier, Jr., and Sheng-Hong Dai, *Chem. Commun.*, 166 (1971), propose that allene and hexafluorocyclobutanone undergo a concerted reaction passing through a distorted, cyclic, six-membered, dipolar transition state. W. H. Urry, J. H. Y. Niu, and L. G. Lundsted, *J. Org. Chem.*, **33**, 2302 (1968), suggest a zwitterion intermediate in the reaction of allene with hexafluoroacetone. R. L. Adelman, *ibid.*, **33**, 1400 (1968), argues for a four-membered, cyclic, dipolar intermediate for the ene reaction of olefins with hexafluoroacetone.

TABLE I

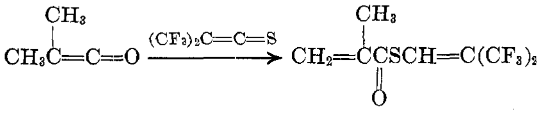
ESTERS AND AMIDES FROM BIS(TRIFLUOROMETHYL)THIOKETENE[d]

Reactant	Reaction conditions	Product	Registry no.	Yield, %	Bp (mm) or mp, °C	$n^{25}D$	Color
CH_3OH	CH_2Cl_2	$(CF_3)_2CH\overset{S}{\overset{\|}{C}}OCH_3$	33830-41-0	69	94-96	1.3588	Pale yellow
C_2H_5OH	CH_2Cl_2	$(CF_3)_2CH\overset{S}{\overset{\|}{C}}OC_2H_5$	867-93-6	84	110-111	1.3622	Pale yellow
C_2H_5SH	CH_2Cl_2	$(CF_3)_2CH\overset{S}{\overset{\|}{C}}SC_2H_5$	33830-42-1	88	62.6 (23)	1.4382	Orange
$(CH_3)_2CHSH$	CH_2Cl_2	$(CF_3)_2CH\overset{S}{\overset{\|}{C}}SCH(CH_3)_2$	33830-43-2	85	62-64 (23)	1.4322	Orange
$C_6H_5CH_2SH$	CH_2Cl_2	$(CF_3)_2CH\overset{S}{\overset{\|}{C}}SCH_2C_6H_5$	33830-44-3	92	65 (0.3)	1.5136	Orange
C_6H_5SH		$(CF_3)_2CH\overset{S}{\overset{\|}{C}}SC_6H_5$	33830-45-4	82	100 (10) Mp 37.5-38.5	1.5044	Orange
p-ClC_6H_4SH[a]	100°, 5 hr	$(CF_3)_2CH\overset{S}{\overset{\|}{C}}SC_6H_4Cl$-$p$	33830-46-5	81	74-75 (0.5) Mp 34		Red-orange
C_6H_5SeH[a]		$(CF_3)_2CH\overset{S}{\overset{\|}{C}}SeC_6H_5$	33830-47-6	96	112-114 (13)	1.525	Magenta
$CH_2{=}CHCH_2NH_2$	CH_2Cl_2	$(CF_3)_2CH\overset{S}{\overset{\|}{C}}NHCH_2CH{=}CH_2$	33830-48-7	64	67-68 (16)	1.4345	Orange
$C_6H_5CH_2NH_2$	CH_2Cl_2	$(CF_3)_2CH\overset{S}{\overset{\|}{C}}NHCH_2C_6H_5$	33830-49-8	49	Mp 64-66 (hexane)		Pale yellow
p-$ClC_6H_4NH_2$	C_6H_6	$(CF_3)_2CH\overset{S}{\overset{\|}{C}}NHC_6H_4Cl$-$p$	7527-43-7	84	Mp 54.5-55.5 (petroleum ether)		Yellow
$C_6H_5NHCH_3$	Hexane	$(CF_3)_2CH\overset{S}{\overset{\|}{C}}\underset{CH_3}{\underset{\|}{N}}C_6H_5$	33820-51-2	83	Mp 77.5-78.5 (hexane)		Pale yellow
p-$CH_3C_6H_4NHCH_3$[a]	CH_2Cl_2	$(CF_3)_2CH\overset{S}{\overset{\|}{C}}\underset{CH_3}{\underset{\|}{N}}C_6H_4CH_3$-$p$	33830-52-3	71	Mp 70-70.7 (CH_3OH)		Yellow
$C_6H_5CH{=}NNHCH_3$[b]	CH_2Cl_2	$(CF_3)_2CH\overset{S}{\overset{\|}{C}}\underset{CH_3}{\underset{\|}{N}}N{=}CHC_6H_5$	33830-53-4	85	Mp 143-144 (CH_3OH)		Yellow
 [c]	CH_2Cl_2		33830-54-5	81	37 (0.1)	1.4872	Red-orange

[a] Eastman Kodak Co., Rochester, N. Y. [b] R. H. Wiley and G. Irick, *J. Org. Chem.*, **24**, 1925 (1959). [c] R. Hüttel, O. Schäfer, and G. Welzel, *Justus Liebigs Ann. Chem.*, **598**, 186 (1956). [d] Satisfactory analytical data (±0.33% for C, H, and S) were reported for all new compounds listed in the table except that no. 8 was analyzed for F instead of S.

was made aside from observing the nmr spectra. The ^{19}F shift for the thietanes[1] is farther downfield than for ene products. Only in the case of α-methylstyrene in Table II were both products observed, probably the result of separate reaction paths rather than a common intermediate.

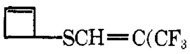
Dimethylketene and butylethylketene react with the thioketene to form acrylate thio esters, whereas



$$CH_3\overset{CH_3}{\overset{|}{C}}{=}C{=}O \xrightarrow{(CF_3)_2C=C=S} CH_2{=}\overset{CH_3}{\overset{|}{C}}\underset{O}{\underset{\|}{C}}SCH{=}C(CF_3)_2$$

ketene and methylketene cycloadd to form thietanes.[1] The greater electron donation to C=C in $(CH_3)_2$-$C{=}C{=}O$ *vs.* $CH_3CH{=}C{=}O$ promotes the ene reaction. This effect has been observed in other ene reactions.[8]

1-Methylcyclopropene, cyclopentene, and cyclohexene readily underwent the ene reaction at 15-25° but cyclobutene required a higher temperature. At 100° a mixture was formed. Purification by glpc was hampered by polymerization on the column but a small amount of material identified as $CH_2{=}CHCH{=}CHSCH{=}C(CF_3)_2$ was obtained. This could arise by ring opening of the primary ene product, shown below.



Hexamethyl Dewar benzene gave an ene reaction, apparently the first reported for this compound.

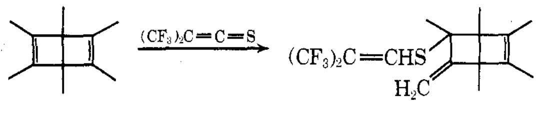
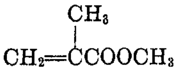
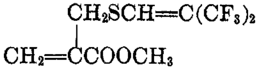
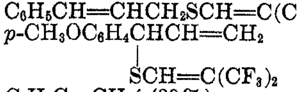
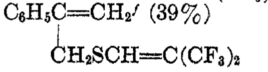
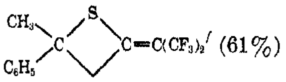
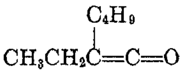
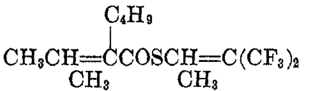
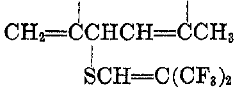
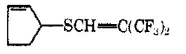
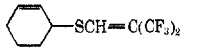
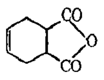
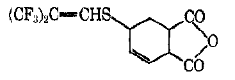
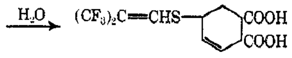
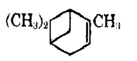
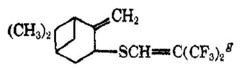
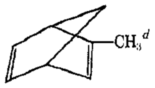
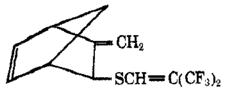
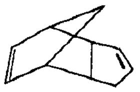
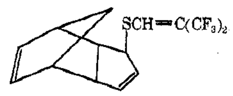
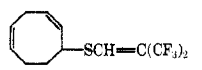
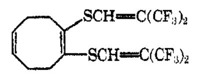
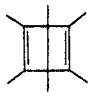
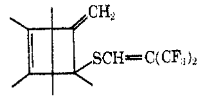


TABLE II

ENE REACTIONS. 3,3,3-TRIFLUORO-2-(TRIFLUOROMETHYL)PROPENYL SULFIDES[i,j]

Reactant	Reacn condn	Product	Registry no.	Bp, °C (mm)	n^{25}D	Yield, %
$CH_2{=}CHCH_3$	100°, 3 hr	$CH_2{=}CHCH_2SCH{=}C(CF_3)_2$	28181-98-8	52.5-53 (15)	1.4048	61
$CH_2{=}C{=}CH_2$	100°, 15 hr	$CH{\equiv}CCH_2SCH{=}C(CF_3)_2$	33830-56-7	62.5-63 (22)	1.4080	>42
$(CH_3)_2C{=}C(CH_3)_2$	24-30°	$CH_2{=}CCH_3C(CH_3)_2SCH{=}C(CF_3)_2$	30589-11-8	58 (7)	1.4200	88
$CH_2{=}CHCH_2Cl$	100°, 16 hr	$ClCH{=}CHCH_2SCH{=}C(CF_3)_2$ 65:35 cis:trans	33835-26-6 33835-27-7	68 (8)	1.4360	27
 $CH_2{=}C(CH_3)COOCH_3$	24°, 16 hr Reflux, 4 hr	 $CH_2{=}C(CH_2SCH{=}C(CF_3)_2)COOCH_3$	33830-58-9	82 (1)	1.4250	27
$C_6H_5CH_2CH{=}CH_2$	100°, 2 hr	$C_6H_5CH{=}CHCH_2SCH{=}C(CF_3)_2$[e]	33835-28-8	73-77 (0.1)	1.5062	70
$p\text{-}CH_3OC_6H_4CH{=}CHCH_3$ (Anethole)	24°, 16 hr	 $p\text{-}CH_3OC_6H_4CH(SCH{=}C(CF_3)_2)CH{=}CH_2$	33830-59-0	Mp 77 (MeOH)		72
$C_6H_5C(CH_3){=}CH_2$	24°, 20 hr	 $C_6H_5C(CH_2SCH{=}C(CF_3)_2){=}CH_2$[f] (39%)	28182-02-7		1.4916	
		 [f] (61%)	23592-39-4	60 (0.05)	1.4875	65
$(CH_3)_2C{=}C{=}O$[a]	0-34°, 2 hr EtOAc	$CH_2{=}CCH_3COSCH{=}C(CF_3)_2$	33872-30-9	80-81 (23)	1.4234	40
 $CH_3CH_2C(C_4H_9){=}C{=}O$[b]	24°, 16 hr Hexane	 $CH_3CH{=}C(C_4H_9)COSCH{=}C(CF_3)_2$	33830-62-5	47-49 (0.1)	1.4417	75
 $CH_3C(CH_3){=}CHCH{=}C(CH_3)CH_3$	24°, 2 hr 100°, 1 hr	 $CH_2{=}C(CH_3)CH(SCH{=}C(CF_3)_2)CH{=}C(CH_3)CH_3$	33830-63-6	84-85 (5)	1.4393	60
 [c]	0°, CH_2Cl_2		33830-64-7	65-68 (11)	1.4210	31
	24°, 1 hr		30631-75-5	97-99 (32)	1.4345	89
	24°, 1 hr		28181-99-9	112-114 (29)	1.4455	72
	C_6H_6, 100°, 20 hr		33830-67-0	Mp 72-73 (CCl_4)		65
			33830-81-8	Mp 157 ($MeNO_2$)		
 (α-Pinene)	24°, 16 hr	 [g]	30589-17-4	69-70 (0.3)	1.4568- 1.4605	85
 [d]	24°, 1 hr		33830-82-9	91 (4.6)	1.4668	83
	24°, 20 hr		28182-01-6	70 (0.1)	1.4773	92
	24°, 3 hr		28182-00-5	49 (0.05)	1.4621	23, 50
			33872-35-4	95 (0.05)	1.4750	34, 15
	24°, 16 hr		33830-85-2	61 (0.4)[h]	1.4514	96

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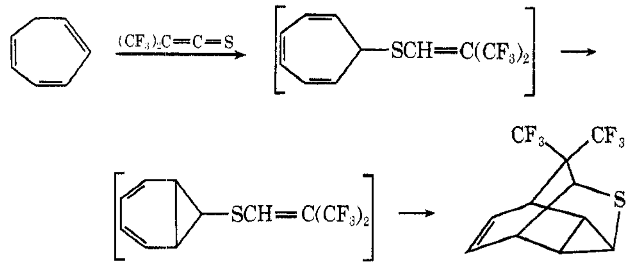
[a] C. W. Smith and D. G. Norton in "Organic Syntheses," Collect. Vol. IV, N. Rabjohn, Ed., Wiley, New York, N. Y., 1963, pp 348–350. [b] Eastman Chemical Products, Inc., Kingsport, Tenn. [c] F. Fisher and D. E. Applequist, *J. Org. Chem.*, **30**, 2089 (1965); R. M. Magid, T. C. Clarke, and C. D. Duncan, *ibid.*, **36**, 1320 (1971). [d] C. A. Cohen, French Patent 1,478,766 (1967); *Chem. Abstr.*, **68**, 12554a (1968). [e] Similarity of nmr spectrum to that of anethole indicates trans form. [f] Compounds separated by glpc on column containing 20% Triton X305 (Rohm and Haas Co.) on firebrick. [g] Two stereoisomers. [h] Distillation bath at 100°. [i] Disclosed in part in M. S. Raasch, U. S. Patent 3,536,765 (1970); *Chem. Abstr.*, **74**, 4232c (1971). [j] Satisfactory analytical data (±0.4%) for C, H, and S were reported for all new compounds listed in the table.

Natural rubber in solution reacted with the thioketene to form a composition containing 30% by weight of the thioketene.

Cycloheptatriene Adduct.—Cycloheptatriene and bis(trifluoromethyl)thioketene, containing a total of five double bonds, react at 25° in a 1:1 ratio to give a compound **3**, revealing only one double bond in its Raman spectrum. This has been rationalized as proceeding through an ene reaction, bond rearrangement to a norcaradiene, and intramolecular Diels–Alder addition of the side chain to the norcaradiene to form the proposed structure **3**.



3

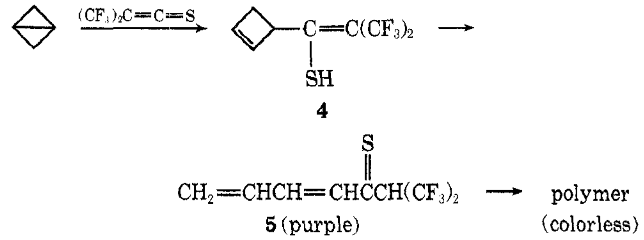
The nmr spectra and other physical data are described in the Experimental Section. A model of the structure poses no problems. The first two steps are analogous to those proposed for the addition of dimethyl acetylenedicarboxylate to cycloheptatriene.[11a] A favorable situation for the intramolecular Diels–Alder addition is assumed, as $(CF_3)_2C{=}CHSCH_3$ and $(CF_3)_2C{=}CHSC_6H_5$ do not add to cycloheptatriene or 2,3-dimethylbutadiene at 100°.

The vinyl sulfides were made by the following sequence and served also as nmr and ir reference compounds.

$$RSCH_2Cl \xrightarrow{Ph_3P} RSCH_2PPh_3Cl \xrightarrow{BuLi} RSCH{=}PPh_3 \xrightarrow{(CF_3)_2CO} RSCH{=}C(CF_3)_2$$

$$R = Me,\ PhCH_2,\ Ph$$

Addition to Bicyclobutane.—Addition of the thioketene to bicyclobutane gave short-lived products in a course different from the conventional ene reaction.

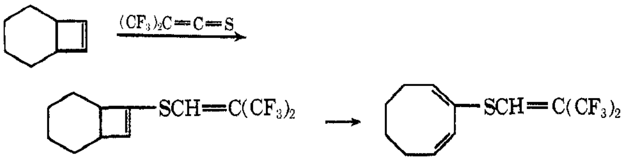


$$CH_2{=}CHCH{=}CH\overset{\overset{\textstyle S}{\|}}{C}CH(CF_3)_2 \longrightarrow \text{polymer}$$

5 (purple) (colorless)

When equivalent amounts of the reactants were mixed at 0° in deuteriochloroform and the solution was placed in a cold ir cell, a strong band was observed for SH at 2550 cm^{-1}, at 1588 cm^{-1} for exocyclic C=C, and at 1562 cm^{-1} for cyclobutene C=C. After 10 min the sample had become purple with weaker SH and C=C bands. After 16 min the SH band had disappeared. The nmr spectra were in accord with the structure **4** (see Experimental Section). With development of the purple color, nmr showed the appearance of the $(CF_3)_2CH$ group, disappearance of cyclobutene CH=CH, and appearance of new unsaturation. The purple color is indicative of a conjugated thiocarbonyl group. From these considerations, structure **5** is proposed for the purple compound, formed by ring opening of the cyclobutene. Clean conversion to **5** was frustrated by concomitant polymerization. The end product was a colorless, tacky polymer.

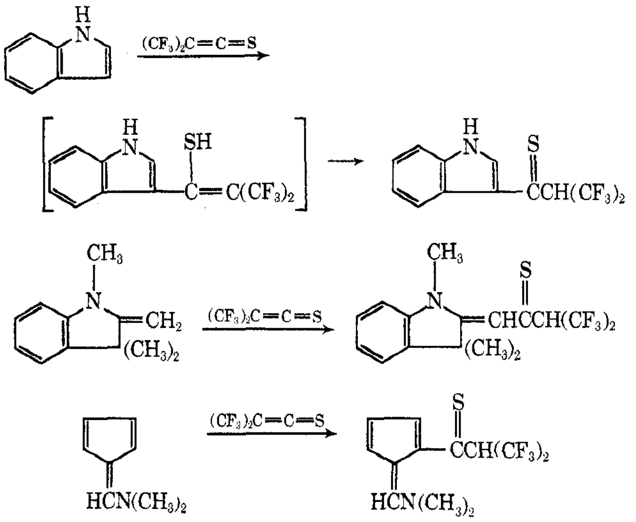
Addition to Bicyclo[4.2.0]oct-7-ene.—The thioketene substitutes on the cyclobutene ring to form a compound **6** that is isomerized by heat with opening of the cyclobutene ring to form a 1,3-cyclooctadiene **7**.



6 **7**

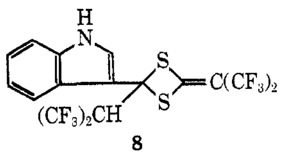
The ^1H nmr of the initial adduct reveals the $(CF_3)_2C{=}CH$ group and one cyclobutene =CH. Incipient isomerization was noted at 50° in an nmr tube. At 95°, isomerization became complete. The final product was identified by nmr and ir spectrum and by oxidation to adipic acid.

C-Thioacylations.—Indole, 1,3,3-trimethyl-2-methyleneindoline, and 6-(dimethylamino)fulvene are thioacylated at 25° by the thioketene.



These colored thioketones can be regarded as vinylogs of thioamides, having one, one, and three vinylene groups, respectively, between the thiocarbonyl group and the nitrogen atom. They are dipole stabilized; *i.e.*, a resonance form can be written in which a negative charge resides on the sulfur atom and a positive charge on the nitrogen.

These thioketones form unstable dithietanes with another mole of the thioketene, *e.g.*,



8

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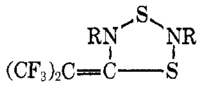
[11] (a) M. J. Goldstein and A. H. Gevirtz, *Tetrahedron Lett.*, 4413 (1965); (b) D. H. Clemens, A. J. Bell, and J. L. O'Brien, *ibid.*, 1487, 1491 (1965).

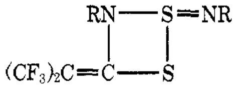
Ketenimines from Sulfur Diimides.—The thioketene reacts with sulfur diimides to give ketenimines in 20–48% yield.

$$\mathrm{RN{=}S{=}NR} \xrightarrow{(\mathrm{CF_3})_2\mathrm{C{=}C{=}S}} (\mathrm{CF_3})_2\mathrm{C{=}C{=}N{-}R}$$

R = Me, *n*-Bu, *tert*-Bu, Ph

No evidence for mechanism is available, as the by-products were resinous. However, the reaction may proceed through a five- or four-membered ring.





Phenyl isothiocyanate reacts with sulfur diimides analogously.[11b]

Experimental Section

The ^{1}H nmr spectra were determined on a Varian A-60 instrument using tetramethylsilane as external standard. The ^{19}F nmr spectra were measured on a Varian A-56/60 instrument using 1,2-difluoro-1,1,2,2-tetrachloroethane as a standard in a capillary tube placed in the sample tube. With this standard, nearly all values for the compounds of this article fall within 1000 Hz downfield (−) for the standard. This standard is 3800 Hz (67.4 ppm) upfield from chlorotrifluoromethane. Raman spectra were measured on Cary Model 81 Laser, ir on Perkin-Elmer Model 21 and uv on Cary 14 spectrometers. Melting and boiling points are uncorrected.

Esters and Amides (Table I).—To the reactant in the solvent specified, stirred and cooled in an ice bath, bis(trifluoromethyl)thioketene was added dropwise at such a rate as to keep the temperature at 15–25°. The reaction with p-$\mathrm{ClC_6H_4SH}$ at 100° was carried out in a sealed glass tube. In simple esters and amides the nmr septuplet (J = 7–8 Hz) for H in $(\mathrm{CF_3})_2\mathrm{CH}$ is at about 4.4 ppm. The ^{19}F nmr shows a doublet around −1.3 to −2.3 ppm.

Use of excessively low temperatures for these reactions should be avoided, as polymer formation may ensue. Thus, adding the thioketene to ethanol at −80° results in 38% conversion to the thioketene polymer.[12]

Hydration.—To 10 ml of concentrated sulfuric acid containing an added 0.5 ml of water was added 5 g of the thioketene with stirring. The thioketene became decolorized in 5 min; 5 g more of the thioketene was added with cooling in ice. The mixture was poured onto ice and the fluoro acid was collected with dichloromethane. After drying ($\mathrm{MgSO_4}$), distillation gave 7.3 g (67%) of 3,3,3-trifluoro-2-(trifluoromethyl)thiopropionic acid: bp 97–99°; $n^{25}\mathrm{D}$ 1.3489; ir 2976 (CH), 2571 (SH), 1709 (C=O), 1330–1100 cm^{-1} (CF); ^{1}H nmr (neat) 4.05 [septuplet, $(\mathrm{CF_3})_2\mathrm{CH}$], 5.02 ppm (s, SH).

Anal. Calcd for $\mathrm{C_4H_2F_6OS}$: C, 22.65; H, 0.95; S, 15.12; neut equiv, 212. Found: C, 23.01; H, 1.06; S, 15.68; neut equiv, 214.

3,3,3-Trifluoro-2-(trifluoromethyl)thiopropionyl Bromide.—About 1.8 ml (4.9 g, 0.06 mol) of HBr was condensed into a glass tube cooled in Dry Ice–acetone and 5.82 g (0.03 mol) of bis(trifluoromethyl)thioketene was added. The tube was sealed and allowed to stand at 24° for 64 hr. Distillation gave 5.54 g (65%) of the purple thioacyl bromide: bp 94–96°; $n^{25}\mathrm{D}$ *ca.* 1.401; ^{1}H nmr (neat) 4.65 ppm (septuplet); ^{19}F nmr −1.15 ppm (d, J = 6.8 Hz).

Anal. Calcd for $\mathrm{C_4HBrF_6S}$: C, 17.47; H, 0.37; S, 11.66. Found: C, 17.85; H, 0.47; S, 11.36.

When triethylamine in dichloromethane was added to a solution of the product in dichloromethane, bis(trifluoromethyl)thioketene dimer[1] was formed.

4-Amino-2,2,5,5-tetrakis(trifluoromethyl)-3-imidazoline Product.—The imidazoline[4] **1** (1.79 g, 0.005 mol), 5 ml of benzene, and 2.14 g (0.011 mol) of bis(trifluoromethyl)thioketene were heated at 100° for 5 hr in a sealed glass tube. The benzene was evaporated and the product was recrystallized from dichloromethane to give 3.13 g (84%) of 4-{2-[2,2,2-trifluoro-1-(trifluoromethyl)ethyl]-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-dithietan-2-ylamino}-2,2,5,5-tetrakis(trifluoromethyl)-3-imidazoline (**2**): mp 122.5–123°; ir 3472 (NH), 3021 (CH), 1681 (C=N), 1634 (C=C), 1565 cm^{-1} (NH deformation); ^{1}H nmr [$(\mathrm{CD_3})_2\mathrm{CO}$] 6.29 [septuplet, J = 11 Hz, $(\mathrm{CF_3})_2\mathrm{CH}$], 6.29 (s, NH), 9.14 ppm (s, broadened, NH); ^{19}F nmr −8.00 [s, $(\mathrm{CF_3})_2\mathrm{C{=}C}$], −4.22 [d, J = 8 Hz, $(\mathrm{CF_3})_2\mathrm{CH}$], +5.50, +10.8 (broadened peaks with evidence of splitting, one peak for each pair of ring $\mathrm{CF_3}$ groups).

Anal. Calcd for $\mathrm{C_{15}H_3F_{24}N_3S_2}$: C, 24.17; H, 0.41; S, 8.60. Found: C, 24.45; H, 0.61; S, 8.69.

No 1:1 adduct could be detected, even when excess imidazoline was used.

Reaction with 3-Methyl-1-*p*-tolyltriazene.—To 5.96 g (0.04 mol) of 3-methyl-1-*p*-tolyltriazene in 20 ml of dichloromethane was added 7.76 g (0.04 mol) of bis(trifluoromethyl)thioketene with stirring and cooling in ice. Nitrogen was evolved. Distillation gave 2.74 g (22%) of *p*-tolyl 3,3,3-trifluoro-2-(trifluoromethyl)-*N*-methylthiolpropionimidate, bp 61–63° (0.4 mm). Recrystallization from methanol left 2.02 g: mp 50–51.3°; ir 2976, 2899 (CH), 1629, 1493 (C=N and aromatic C=C), 846 cm^{-1} (para-disubstituted aromatic); ^{1}H nmr ($\mathrm{CCl_4}$) 2.24 (s, $\mathrm{CH_3}$ on phenyl), 3.26 (s, $\mathrm{CH_3N}$), 3.71 [septuplet, $(\mathrm{CF_3})_2\mathrm{CH}$], 7.71 ppm ($\mathrm{A_2B_2}$ pattern, $\mathrm{C_6H_4}$); ^{19}F nmr −2.57 ppm (d, J = 7 Hz).

Anal. Calcd for $\mathrm{C_{12}H_{11}F_6NS}$: C, 45.71; H, 3.52; N, 4.44; S, 10.17. Found: C, 45.47; H, 3.73; N, 4.61; S, 10.16.

Hydrolysis with a hot solution of KOH in methanol–water resulted in the formation of *p*-toluenethiol, identified by odor, melting point, and mixture melting point (42°) and by comparison of nmr spectrum.

Reaction with 1,3-Di-*p*-tolyltriazine.—To 2.25 g (0.01 mol) of 1,3-di-*p*-tolyltriazene[13] in 10 ml of dichloromethane was added 1.94 g (0.01 mol) of bis(trifluoromethyl)thioketene. Nitrogen was slowly evolved. After 20 hr the solvent was removed under vacuum and the residue was steam distilled. The product was filtered off, dried, and recrystallized from methanol to give 1.3 g (33%) of *p*-tolyl 3,3,3-trifluoro-2-(trifluoromethyl)-*N*-*p*-tolylthiolpropionimidate: mp 67–67.5°; ir 3077, 3030 (=CH), 2976, 2915, 2857 (CH), 1639, 1623, 1506, 1493 (C=N and aromatic C=C), 854 cm^{-1} (para-disubstituted aromatic); ^{1}H nmr ($\mathrm{CDCl_3}$) 2.32 (2 overlapping $\mathrm{CH_3}$ peaks 0.02 ppm apart), 3.98 [septuplet, $(\mathrm{CF_3})_2\mathrm{CH}$], 6.97, 7.25 ppm (centers of overlapping $\mathrm{A_2B_2}$ patterns for two $\mathrm{C_6H_4}$ groups); ^{19}F nmr −2.94 ppm (d, J = 7 Hz).

Anal. Calcd for $\mathrm{C_{18}H_{15}F_6NS}$: C, 55.24; H, 3.86; S, 8.19. Found: C, 55.53; H, 3.91; S, 8.29.

Reaction with *N*,*N*-Dimethylanilines. A. *N*,*N*-Dimethylaniline.—*N*,*N*-Dimethylaniline (4.84 g, 0.04 mol) in 15 ml of petroleum ether (bp 30–60°) was stirred and cooled in ice and 7.76 g (0.04 mol) of bis(trifluoromethyl)thioketene was added dropwise. A reddish color developed with each drop and then faded. The crystals that separated were filtered off and rinsed with petroleum ether. Concentration of the mother liquor gave more for a total of 9.4 g (75%) of *N*-methyl-*N*-[3,3,3-trifluoro-2-(trifluoromethyl)propenylthiomethyl]aniline. Recrystallization from petroleum ether (18 ml) left 8.2 g: mp 51–52°; ir 3077 (=CH), 2959, 2915, 2857 (CH), 1608 [$(\mathrm{CF_3})_2\mathrm{C{=}C}$], 1582, 1511, 1493 (aromatic C=C), 1408 cm^{-1} ($\mathrm{NCH_3}$); ^{1}H nmr ($\mathrm{CCl_4}$) 2.90 (s, $\mathrm{CH_3}$), 4.87 (s, $\mathrm{CH_2}$), 7.0 (m, $\mathrm{C_6H_5}$), 7.45 ppm [quadruplet, J = 1.4 Hz, $(\mathrm{CF_3})_2\mathrm{C{=}CH}$]; ^{19}F nmr −4.81, −6.92 ppm (quadruplets, components of former split to doublets, J = 1.4 Hz).

Anal. Calcd for $\mathrm{C_{12}H_{11}F_6NS}$: C, 45.71; H, 3.52; S, 10.17. Found: C, 45.98; H, 3.72; S, 9.93.

The compound is stable at 4° but decomposes after several weeks at 24°. It is not basic enough to dissolve in aqueous hydrochloric acid but the hydrochloride was made by passing HCl into an ethereal solution of the amine, mp 103–106°.

Anal. Calcd for $\mathrm{C_{12}H_{11}F_6NS \cdot HCl}$: Cl, 10.08. Found: Cl, 10.03.

B. *N*,*N*-Dimethyl-*p*-toluidine.—The thioketene (7.76 g, 0.04 mol) was added with cooling to 5.40 g (0.04 mol) of *N*,*N*-dimethyl-*p*-toluidine in 15 ml of dichloromethane. The product was distilled to give 4.76 g (36%) of *N*-methyl-*N*-[3,3,3-trifluoro-2-(trifluoromethyl)propenylthiomethyl]-*p*-toluidine: bp 60° (0.2 mm); $n^{25}\mathrm{D}$ 1.5001; ^{1}H nmr (neat) 1.95 (s, p-$\mathrm{CH_3}$), 2.47 (s, $\mathrm{NCH_3}$), 4.37 (s, $\mathrm{CH_2}$), 6.48 ($\mathrm{A_2B_2}$ pattern, p-$\mathrm{C_6H_4}$), 7.23 ppm [quadruplet, J = 1.4 Hz, $(\mathrm{CF_3})_2\mathrm{C{=}C}$]; ^{19}F nmr −4.84, −7.15 ppm (quadruplets, components of former split to doublets).

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(12) M. S. Raasch, U. S. Patent 3,275,609 (1966).

(13) P. Jacobson, *Justus Liebigs Ann. Chem.*, **427**, 152 (1922).

Anal. Calcd for $C_{13}H_{13}F_6NS$: C, 47.41; H, 3.98; S, 9.74. Found: C, 47.79; H, 4.24; S, 9.80.

C. ***N,N*-Dimethyl-*m*-nitroaniline.**—A solution of 0.03 mol of each of the reactants in 25 ml of dichloromethane was allowed to stand for 2 days, then extracted with 10% HCl to remove unreacted *N,N*-dimethyl-*m*-nitroaniline. The solution was evaporated on a steam bath to drive out the thioketene dimer. The residue was recrystallized from cyclohexane containing a little dichloromethane to give 3.76 g (35%) of *N*-methyl-3-nitro-*N*-[3,3,3-trifluoro-2-(trifluoromethyl)propenylthiomethyl]aniline: mp 58°; ^{1}H nmr 3.13 (s, CH_3), 5.04 (s, CH_2), 6.8–7.8 ppm (m, $=CH + C_6H_5$).

Anal. Calcd for $C_{12}H_{10}F_6N_2O_2S$: C, 40.00; H, 2.80; S, 8.90. Found: C, 40.30; H, 3.12; S, 9.01.

D. ***N,N,N',N'*-Tetramethylbenzidine.**—To a solution of 1.20 g (0.05 mol) of *N,N,N',N'*-tetramethylbenzidine in 12 ml of dichloromethane was added 3.88 g (0.02 mol) of the thioketene with cooling in ice. Part way through the addition a product precipitated (monoadduct?) and then dissolved as addition continued. Evaporation of the solvent and recrystallization of the residue from cyclohexane gave 2.3 g (73%) of *N,N'*-bis[3,3,3-trifluoro-2-(trifluoromethyl)propenylthiomethyl]-*N,N'*-dimethylbenzidine: mp 132–132.5°; ^{1}H nmr ($CDCl_3$) 3.11 (s, CH_3), 5.09 (s, CH_2), 7.32 (aromatic A_2B_2 pattern), 7.67 ppm [quadruplet, $J = 1.4$ Hz, $(CF_3)_2C{=}CH$].

Anal. Calcd for $C_{24}H_{20}F_{12}N_2S_2$: C, 45.85; H, 3.21; S, 10.20. Found: C, 45.76; H, 3.37; S, 9.97.

Reaction with Ethers. A. Benzyl Methyl Ether.—To 6.10 g (0.05 mol) of freshly distilled benzyl methyl ether was added 6.79 g (0.035 mol) of the thioketene. After 16 hr at 24° the product was distilled to give 6.7 g (60%) of α-[3,3,3-trifluoro-2-(trifluoromethyl)propenylthio]benzyl methyl ether: bp 65° (0.2 mm); $n^{25}D$ 1.4699; ir 3049 (=CH), 2941, 2841 (CH), 1623 (linear C=C), 1502 cm^{-1} (aromatic C=C); ^{1}H nmr (neat) 3.05 (s, CH_3), 5.19 (s, CH of benzyl), 6.95 (m, C_6H_5), 7.40 ppm [quadruplet, $J = 1.4$ Hz, $(CF_3)_2C{=}CH$]; ^{19}F nmr −6.51, −4.03 ppm (quadruplets, $J = 7$ Hz, components of latter split to doublets, $J = 1.4$ Hz).

Anal. Calcd for $C_{12}H_{10}F_6OS$: C, 45.56; H, 3.19; S, 10.14. Found: 45.12; H, 3.27; S, 10.52.

B. **Ethyl Ether.**—Bis(trifluoromethyl)thioketene (7 g) and 7 ml of ethyl ether were allowed to stand for 2 days. The solution was then cooled in ice and 3.24 g (46%) of the thioketene dimer[1] was filtered off. Distillation of the filtrate gave 2.33 g (24%) of ethyl 1-[3,3,3-trifluoro-2-(trifluoromethyl)propenylthio]ethyl ether, bp 70° (17 mm). The compound was purified for analysis by glpc over Triton X 305 (Rohm and Haas Co.) on diatomite: $n^{25}D$ 1.3953; ir 3058 (=CH), 2985, 2941, 2899 (CH), 1616 (C=C), 1379 cm^{-1} (CCH_3); ^{1}H nmr (neat) 0.86 (t, CH_3CH_2), 1.27 (d, CH_3CH), 3.28 (AB part of ABX_3, CH_2), 4.53 (quadruplet, CH_3CH), 7.58 ppm [quadruplet, $(CF_3)_2C{=}CH$]; ^{19}F nmr −3.56, −5.82 ppm (quadruplets).

Anal. Calcd for $C_8H_{10}F_6OS$: C, 35.83; H, 3.76; S, 11.95. Found: C, 35.48; H, 4.02; S, 11.99.

A mixture, 0.62 g, bp 29–42° (0.12 mm), was also formed.

When run in the presence of 3 drops of 40% peracetic acid, the reaction was rapid but produced more of a mixture.

Reactions with Hydrides. A. Diethylsilane.—To 2.64 g (0.03 mol) of diethylsilane was added 5.82 g (0.03 mol) of bis(trifluoromethyl)thioketene with occasional cooling. After the color of the thioketene had disappeared, the product was cooled and 1.63 g of the thioketene dimer was filtered off. Distillation of the filtrate gave 2.14 g (25%) of diethyl[3,3,3-trifluoro-2-(trifluoromethyl)propenylthio]silane: bp 75–76° (16 mm); $n^{25}D$ 1.4119; ^{1}H nmr (neat) 4.43 (broadened peak, SiH), 7.33 ppm [quadruplet for $(CF_3)_2C{=}CH$, $J = 1.6$ Hz]; ^{19}F nmr −3.05, −5.98 ppm (quadruplets, components of former split to doublets, $J = 1.6$ Hz).

Anal. Calcd for $C_8H_{12}F_6SSi$: C, 34.03; H, 4.29; S, 11.36. Found: C, 33.53; H, 4.09; S, 11.75.

B. **Triethylsilane.**—Addition of 5.82 g (0.03 mol) of the thioketene to 3.48 g (0.03 mol) of triethylsilane at 25–30° and distillation gave 6 g (64%) of triethyl[3,3,3-trifluoro-2-(trifluoromethyl)propenylthio]silane: bp 64° (28 mm); $n^{25}D$ 1.4242; ir 2976, 2924, 2890 (CH), 1600 cm^{-1} (C=C); ^{1}H nmr 7.42 ppm [quadruplet, $J = 1.6$ Hz, $(CF_3)_2C{=}CH$]; ^{19}F nmr −3.25, −6.18 ppm (quadruplets, components of former split to doublets, $J = 1.6$ Hz).

Anal. Calcd for $C_{10}H_{16}F_6SSi$: C, 38.68; H, 5.20; S, 10.33. Found: C, 38.67; H, 5.00; S, 10.53.

C. **Diphenylsilane.**—Diphenylsilane (5.52 g, 0.03 mol) and 5.82 g (0.03 mol) of thioketene were allowed to stand for 16 hr. Distillation gave 3.75 g (33%) of diphenyl[3,3,3-trifluoro-2-(trifluoromethyl)propenylthio]silane: bp 92–94° (0.05 mm); $n^{25}D$ 1.5226; ^{1}H nmr (neat) 5.10 (s, SiH), 6.6–7.2 ppm (m, C_6H_5 and −CH=); ^{19}F nmr −3.58, −6.72 ppm (quadruplets, components of former split to doublets, $J = 1.6$ Hz).

Anal. Calcd for $C_{16}H_{12}F_6SSi$: C, 50.78; H, 3.20; S, 8.47. Found: C, 51.04; H, 3.40; S, 8.32.

D. **Triphenylstannane.**—To a solution of 3.51 g (0.01 mol) of triphenylstannane in 10 ml of dichloromethane was added 2.04 g (0.0105 mol) of the thioketene. A white solid was filtered off and the solvent was removed from the filtrate, finally under vacuum. The residue crystallized after several days and was recrystallized from petroleum ether in several crops to give 2.95 g (54%) of triphenyl[3,3,3-trifluoro-2-(trifluoromethyl)propenylthio]stannane: mp 63–64°; ir 3058 (=CH), 1613 (olefinic C=C), 1585, 1570 (aromatic C=C), 730, 696 cm^{-1} (monosubstituted aromatic); ^{1}H nmr (CCl_4) =CH− peak in the aromatic multiplet at 7–7.7 ppm; ^{19}F nmr −4.38, −7.80 ppm (quadruplets, components of former split to doublets, $J = 1.6$ Hz).

Anal. Calcd for $C_{22}H_{16}F_6SSn$: C, 48.48; H, 2.96; S, 5.88. Found: C, 48.86; H, 3.07; S, 5.78.

Trimethylstannane.—To 4.95 g (0.03 mol) of trimethylstannane[14] in 10 ml of hexane was added, with cooling in ice, 5.82 g (0.03 mol) of the thioketene. The reaction was vigorous. The hexane was removed at 25° and 11 mm. The liquid compound was unstable to heat and deposited a solid on standing. However, an nmr spectrum taken immediately after removal of the hexane showed the compound to be trimethyl[3,3,3-trifluoro-2-(trifluoromethyl)propenylthio]stannane: ^{1}H nmr (neat) 0.47 (s, CH_3), 7.57 ppm [quadruplet, $(CF_3)_2C{=}CH$]; ^{19}F nmr −4.50, −7.40 ppm (quadruplets, components of former split to doublets).

Ene Reactions. A. General Conditions.—Where a temperature of 24° is indicated in Table II, bis(trifluoromethyl)thioketene was added to the olefin while it was stirred and cooled in ice if necessary to hold the temperature down. The solution was then allowed to stand at room temperature. Reactions at 100° were run in sealed glass tubes. Structures were established by nmr. The $(CF_3)_2C{=}CHS$– group shows a characteristic quadruplet ($J = 1.4$ Hz) for H at 7.1–8.2 ppm. The ^{19}F nmr has a quadruplet ($J =$ *ca.* 6.4 Hz) at −2.98 to −5.05 ppm with components split to doublets ($J = 1.4$ Hz) and a second, unsplit quadruplet at −5.20 to −7.35 ppm.

B. **With 1,5-Cyclooctadiene.**—In the reaction of the thioketene with 1,5-cyclooctadiene to produce mono- and diadducts (Table II), the first yields recorded were produced by using the reactants in the molar ratio of 1:1.1 while the second yields were obtained from a reactant ratio of 1:4. The structure of the diadduct is established by nmr by the presence of three ring −CH= groups rather than four.

C. **With Cyclobutene.**—Cyclobutene[15] (1.9 g, 0.035 mol), 5 ml of dichloromethane, and 7 g (0.036 mol) of the thioketene were sealed in a glass tube and heated at 100° for 1 hr. Distillation gave 2.38 g, bp 38–43° (2.2 mm), and 2.77 g, bp 51–61° (0.1 mm). Analytical glpc on the low boiler indicated a 71% component, but in preparative glpc over 20% fluoroalkyl pyromellitate on firebrick most of the product polymerized on the column. A small amount of material identified as $CH_2{=}CHCH{=}CHSCH{=}C(CF_3)_2$, 1,3-butadienyl 3,3,3-trifluoro-2-(trifluoromethyl)propenyl sulfide, was obtained: $n^{25}D$ 1.4683; ir 3058 (=CH), 1605 (C=CS), 1570 cm^{-1} (conjugated diene); ^{1}H nmr (neat) 4.6–5.1 (m, CH_2=), 5.6–6.3 (m, 3 CH=), 7.17 ppm [quadruplet, $J = 1.4$ Hz, $(CF_3)_2C{=}CH$]; ^{19}F nmr −3.78, −6.28 ppm (quadruplets, $J = 6.5$ Hz, components of former split to doublets, $J = 1.4$ Hz).

Anal. Calcd for $C_8H_6F_6S$: C, 38.70; H, 2.44; S, 12.92. Found: C, 37.87; H, 2.78; S, 12.93.

The reaction mixture was not examined further.

Cycloheptatriene Adduct.—Bis(trifluoromethyl)thioketene (7.76 g, 0.04 mol) was added to 3.68 g (0.04 mol) of cycloheptatriene with stirring and occasional cooling. Distillation gave 8.4 g, bp 83–86° (2 mm). Recrystallization from methanol left 5.9 g (51%) of 5,5-bis(trifluoromethyl)-3-thiatetracyclo[4.4.0.0^{2,10}.0^{4,9}]dec-7-ene (**3**): mp 70–70.6°; Raman 1613 cm^{-}

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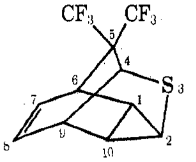
[14] A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **69**, 2692 (1947).

[15] J. D. Bacha and J. K. Kochi, *Tetrahedron*, **24**, 2215 (1968).

(C=C), ir 3049 (=CH), 2994 (CH), 1629, 1616 cm^{-1} (w, C=C); ^{1}H nmr (CDCl$_3$) (see positions below) 1.47 (quartet, 2-H), 1.94, 2.10 (m's, 1-H + 10-H), 3.26 (d with broadening, 4-H), 3.53 (tt, 9-H), 3.96 (peak broadened by CF$_3$'s, 6-H), 6.20 (t, split to d, 8-H), 7.22 ppm (t, 7-H) (decoupling 7-H and 8-H affected 6-H and 9-H but not 4-H); ^{19}F nmr +2.20, −6.74 ppm [quadruplets, J = 12 Hz, former split to d, J = 2 Hz, positions show (CF$_3$)$_2$C=C not present].



Anal. Calcd for $C_{11}H_8F_6S$: C, 46.15; H, 2.82; S, 11.20. Found: C, 46.21; H, 2.88; S, 11.17.

(Methylthiomethyl)triphenylphosphonium Chloride.—Chloromethyl methyl sulfide[16] (33 g, 0.34 mol) and 90 g (0.34 mol) of triphenylphosphine were warmed together on a steam bath until the mixture solidified. Recrystallization from nitromethane gave 76 g (62%) of the salt in two crops, mp 219.5–220.5°.

Anal. Calcd for $C_{20}H_{20}ClPS$: C, 66.93; H, 5.62; S, 8.93. Found: 66.88; H, 5.82; S, 8.89.

Methyl 3,3,3-Trifluoro-2-(trifluoromethyl)propenyl Sulfide.—To 35.9 g (0.1 mol) of powdered (methylthiomethyl)triphenylphosphonium chloride suspended in 200 ml of tetrahydrofuran was added with stirring and cooling in ice 65 ml of 15% butyllithium in hexane (0.1 mol). Hexafluoroacetone was then passed in with continued cooling until there was no further evidence of reaction. All the liquid was distilled from the reaction mixture at 30 mm and collected in a Dry Ice trap. Fractionation gave a foreshot, bp 70–128.5°, and 8.3 g of the sulfide, bp 128.5°, n^{25}D 1.3850. The foreshot was washed with water, dried, and distilled to give 3.9 g more of the sulfide, bp 127–128°, for a total yield of 58%: ir 3067 (=CH), 2950, 2857 (CH), 1608 (C=C), 1326 cm^{-1} (SCH$_3$); ^{1}H nmr (neat) 2.20 (s, CH$_3$), 7.48 ppm [quadruplet, J = 1.4 Hz, (CF$_3$)$_2$C=CH]; ^{19}F nmr −3.67, −6.11 ppm (quadruplets, J = 6.3 Hz, components of high field one split to doublets, J = 1.4 Hz).

Anal. Calcd for $C_5H_4F_6S$: C, 28.59; H, 1.92; S, 15.26. Found: C, 28.85; H, 2.18; S, 15.37.

(Benzylthiomethyl)triphenylphosphonium Chloride.—Benzyl chloromethyl sulfide[17] (45 g, 0.26 mol) and 69 g (0.26 mol) of triphenylphosphine were heated on a steam bath for 16 hr. The solid was broken up and washed with ether, yield 105 g (93%). The product was recrystallized from 315 ml of water to give 97 g (85%) of the salt in two crops, mp 216–217.5° after drying in air and under vacuum at 80°.

Anal. Calcd for $C_{26}H_{24}ClPS$: C, 71.79; H, 5.56; S, 7.37. Found: C, 71.92; H, 5.89; S, 7.40.

Benzyl 3,3,3-Trifluoro-2-(trifluoromethyl)propenyl Sulfide.—To 43.5 g (0.1 mol) of (benzylthiomethyl)triphenylphosphonium chloride suspended in 200 ml of tetrahydrofuran was added with cooling 70 ml (0.108 mol) of 15% butyllithium in hexane. Hexafluoroacetone was passed in, the solution was filtered, and the solvent was boiled off. Petroleum ether was added to the residue and the solid was filtered off. The filtrate was distilled to give 8.2 g (29%) of the sulfide: bp 117–119° (17 mm); n^{25}D 1.4735; ^{1}H nmr (neat) 3.38 (s, CH$_2$), 6.83 (s, C$_6$H$_5$), 7.15 ppm [quadruplet, J = 1.4 Hz, (CF$_3$)$_2$C=CH]; ^{19}F nmr −4.28, −6.80 ppm (quadruplets, components of high field one split to doublets, J = 1.4 Hz).

Anal. Calcd for $C_{11}H_8F_6S$: C, 46.15; H, 2.82; S, 11.20. Found: C, 46.35; H, 3.12; S, 10.89.

(Phenylthiomethyl)triphenylphosphonium Chloride.—Chloromethyl phenyl sulfide[12] (64 g, 0.4 mol) and 105 g (0.4 mol) of triphenylphosphine were warmed on a steam bath for 45 min. The solid was washed with acetone to give 135 g (80%) of the phosphonium salt. Recrystallization from nitromethane gave 121 g (72%) in two crops, mp 232–234° dec.

Anal. Calcd for $C_{25}H_{22}ClPS$: C, 71.35; H, 5.27; S, 7.62. Found: C, 71.26; H, 5.42; S, 7.56.

Phenyl 3,3,3-Trifluoro-2-(trifluoromethyl)propenyl Sulfide.—The reaction and isolation were carried out on a 0.1-mol scale as described for the benzyl compound except that 65 ml of the butyllithium solution was used. Distillation gave 15.7 g (58%) of the sulfide: bp 107–108.5° (28 mm); n^{25}D 1.4725; ^{1}H nmr (neat) 7.03 (s, C$_6$H$_5$), 7.33 ppm [quadruplet, J = 1.4 Hz, (CF$_3$)$_2$C=CH]; ^{19}F nmr −4.05, −6.05 ppm (quadruplets, components of high field one split to doublets, J = 1.4 Hz).

Anal. Calcd for $C_{10}H_6F_6S$: C, 44.12; H, 2.22; S, 11.78. Found: C, 44.47; H, 2.44; S, 11.76.

Addition to Bicyclobutane.—The thioketene was added to an equivalent of bicyclobutane[18] in CDCl$_3$ at 0° and the nmr of the colorless solution was immediately taken: 2.50 (AB pattern, J = 14 Hz, high field pair split to m, low field pair split to d, J = 4 Hz, CH$_2$), 4.23 (broadened peak, CH), 4.30 (quadruplet, J_{H-CF_3} = 11 Hz, a notable value, SH), 5.75, 6.17 ppm (m's, CH=CH); ^{19}F nmr −8.93 (quintuplet, J = 11 Hz, formed by overlap of CF$_3$CF$_3$ and HCF$_3$ splittings of same J value), −12.0 ppm (quadruplet, $J_{CF_3CF_3}$ = 11 Hz). These data and the ir data in the discussion are consistent for 1-(3-cyclobutenyl)-3,3,3-trifluoro-2-(trifluoromethyl)-1-propenethiol (4).

The thioketene (14.4 g, 0.074 mol) was added to 4 g (0.074 mol) of bicyclobutane in 10 ml of dichloromethane at 0–5°. Vacuum flash distillation at room temperature of a portion into a Dry Ice trap caused the compound to turn purple. Distillation with a bath at 55–60° gave 8.2 g (45%) of purple liquid, bp 32–36° (3.5 mm), and a residue of 5.7 g of resin.

Anal. Calcd for $C_8H_6F_6S$: C, 38.70; H, 2.44; S, 12.92. Found: C, 38.26; H, 2.44; S, 12.88.

The ^{1}H nmr showed that some of the primary adduct was still present. A septuplet was present at 4.60 ppm [(CF$_3$)$_2$CH] and the CH=CH multiplets were largely replaced with a multiplet between them. A clean conversion of the primary adduct into 1,1,1-trifluoro-2-(trifluoromethyl)-4,6-heptadiene-3-thione (5) was thwarted because of concomitant polymerization.

Addition to Bicyclo[4.2.0]oct-7-ene.—Bis(trifluoromethyl)thioketene (6.79 g, 0.035 mol) was added with stirring and cooling to 3.78 g (0.035 mol) of bicyclo[4.2.0]oct-7-ene.[19] The temperature was kept at about 25°: ^{1}H nmr of crude product (neat) 1.8–2.8 (multiple absorptions), 3.43 (s, fused CH nearest S), 5.22 (s, =CH of cyclobutene ring), 7.50 ppm [quadruplet, J = 1.4 Hz, (CF$_3$)$_2$C=CH]. These data indicate that the initial product is 7-[3,3,3-trifluoro-2-(trifluoromethyl)propenylthio]-bicyclo[4.2.0]oct-7-ene (6). Distillation gave 8 g (75%) of the isomerized product, 2-[3,3,3-trifluoro-2-(trifluoromethyl)propenylthio]-1,3-cyclooctadiene (7): bp 73° (0.06 mm); n^{25}D 1.4982; ir 3067 (=CH), 2959, 2890, 2865 (CH), 1608 (substituent C=C), 1597 cm^{-1} (conjugated cyclic C=C); ^{1}H nmr (neat) 1.4, 1.85 (two peaks with splittings, 8 H, similar to saturated region of 1,3-cyclooctadiene spectrum), 5.98 (AB pattern, J = 15 Hz, CH=CH), 5.45 (overlapped peak for 3rd =CH), 7.32 ppm [quadruplet, J = 1.4 Hz, (CF$_3$)$_2$C=CH]; ^{19}F nmr −4.20, −6.63 ppm (quadruplets, J = 6.4 Hz, components of former split to doublets, J = 1.4 Hz).

Anal. Calcd for $C_{12}H_{12}F_6S$: C, 47.68; H, 4.00; S, 10.61. Found: C, 47.98; H, 4.04; S, 10.73.

Ozone was passed into 1.65 g of the compound in 35 ml of dichloromethane at −80°. The solution was allowed to warm to 24°, 4 ml of 30% hydrogen peroxide in 25 ml of acetic acid was added, and the mixture was warmed on a steam bath for 1 hr. Peroxide was destroyed by adding 5% Ru on C and the filtered solution was evaporated to dryness. The residue was rinsed with ether to leave 0.6 g (75%) of crude adipic acid, mp and mmp 152–153° after recrystallization from ethyl acetate.

Addition to Indole.—To 3.51 g (0.03 mol) of indole dissolved in 10 ml of chloroform was added 1.94 g (0.01 mol) of bis(trifluoromethyl)thioketene. After 16 hr the solution was cooled and filtered to give 1.81 g (58%) of red crystals of 2,2,2-trifluoro-1-(trifluoromethyl)ethyl-3-indolylthione: mp 199–200° after recrystallization from chloroform in 92% return; ir 3279 (NH), 3077 (=CH), 2933 (CH), 1610, 1585, 1506, 1490 (conjugated cyclic C=C), 754 cm^{-1} (ortho-disubstituted aromatic); ^{1}H nmr [(CD$_3$)$_2$CO] 5.41 [septuplet, (CF$_3$)$_2$CH], 6.2–7.1 (m, 3 H), 8.23 (d, proton in 2 position), 8.3–8.6 (m, 1 H), 11.10 ppm (broad, NH) (addition of D$_2$O caused the NH peak to disappear and the doublet at 8.23 ppm to be converted to a singlet); ^{19}F nmr (tetrahydropyran) −3.24 ppm (d, J = 7 Hz).

Anal. Calcd for $C_{12}H_7F_6NS$: C, 46.30; H, 2.27; S, 10.30. Found: C, 46.45; H, 2.36; S, 10.20.

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[19] R. S. H. Liu, *ibid.*, **89**, 112 (1967).

The compound in dichloromethane dissolved by reaction with another mole of the thioketene to form the unstable dithietane **8**. The product could be obtained in somewhat impure, pale yellow form by crystallization from the solvent: ir 3497 (NH), 3086 (=CH), 1618 (exocyclic C=C), 1534, 1490, 1477 cm^{-1} (cyclic, conjugated C=C); ^{19}F nmr (Me_2CO) −2.94 [d, $(CF_3)_2CH$], −7.71 ppm [s, $(CF_3)_2C{=}C$].

Addition to 1,3,3-Trimethyl-2-methyleneindoline.—To 5.19 g (0.03 mol) of 1,3,3-trimethyl-2-methyleneindoline (Eastman Kodak Co.) in 10 ml of dichloromethane, stirred and cooled in ice, was added 7.5 g (0.038 mol) of the thioketene at *ca.* 20°. Thioketene dimer was filtered off and the solvent was evaporated. The residue was recrystallized from methanol to give 5.87 g (53%) of orange 2,2,2-trifluoro-1-(trifluoromethyl)ethyl (1,3,3-trimethyl-2-indolinylidene)methylthione: mp 114–114.5°; ir 3030 (=CH), 2983, 2924 (CH), 1538, 1515, 1471 cm^{-1} (C=C); visible max (isooctane) 446 mμ (ϵ 29,920); uv max (isooctane) 253 mμ (ϵ 10,430); ^{1}H nmr (CCl_4) 1.44 [s, $(CH_3)_2C$], 3.42 (s, CH_3N), 4.42 [septuplet, $(CF_3)_2CH$], 6.42 (s, =CH), 7.17 ppm (m, 4 H, aromatic); ^{19}F nmr −2.55 ppm (d).

Anal. Calcd for $C_{16}H_{15}F_6NS$: C, 52.45; H, 4.13; S, 8.75. Found: C, 52.64; H, 4.09; S, 8.96.

Addition to 6-(Dimethylamino)fulvene.—To 6.05 g (0.05 mol) of 6-(dimethylamino)fulvene[20] in 35 ml of CCl_4 was added dropwise 9.70 g (0.05 mol) of the thioketene with stirring and cooling to keep the temperature at 25–30°. The product crystallized out and was filtered at 5° and rinsed with cold CCl_4. The product (6.6 g) was recrystallized from CCl_4 to give 5.9 g (37%) of purple 5-(dimethylaminomethylene)-1,3-cyclopentadien-1-yl-2,2,2-trifluoro-1-(trifluoromethyl)ethylthione: mp *ca.* 118° dec; ir 3067 (=CH), 2941 (CH), 1642, 1515 cm^{-1} (C=C); ^{1}H nmr (CD_3CN) 2.65 [s, $(CH_3)_2N$], 4.83 [septuplet, J = 8 Hz, $(CF_3)_2CH$], 5.70 (t, J = 4 Hz, H in 3 position) 6.32 (d, J = 4 Hz, H in 2 or 4 position), 6.52 (d, J = 4 Hz, H in 4 or 2 position), 8.26 ppm (septuplet, J = 0.7 Hz, exocyclic =CH); ^{19}F nmr −3.13 ppm (d, J = 8 Hz).

Anal. Calcd for $C_{12}H_{11}F_6NS$: C, 45.71; H, 3.52; S, 10.17. Found: C, 46.11; H, 3.64; S, 10.28.

Bis(trifluoromethyl)ketenimines.[21] **A. From Dimethylsulfur Diimide.**—To 2.7 g (0.03 mol) of dimethylsulfur diimide[22] in 5 ml of dichloromethane was added dropwise at 20° with stirring 11.64 g (0.06 mol) of bis(trifluoromethyl)thioketene. After 1 hr the volatile material was pulled off at 20 mm and caught in a Dry Ice trap. The pot was finally heated with steam. Fractionation gave 1.94 g (17%) of *N*-[3,3,3-trifluoro-2-(trifluoromethyl)propenylidene]methylamine: bp 55–56° (184 mm); $n^{25}{}_D$ 1.3345; ir 2967, 2899 (saturated CH), 2110 cm^{-1} (C=C=N); ^{1}H nmr (neat) 1.85 ppm (s); ^{19}F nmr −9.80 ppm (s).

Anal. Calcd for $C_5H_3F_6N$: C, 31.43; H, 1.58; N, 7.33. Found: C, 31.18; H, 1.83; N, 7.30.

B. From Di-*n*-butylsulfur Diimide.—The reaction was carried out with di-*n*-butylsulfur diimide[23] as described above. After 2 days, the volatile material was flashed into a Dry Ice trap at 1 mm. Distillation gave a 20% yield of the *n*-butylamine derivative: bp 75° (61 mm); $n^{25}{}_D$ 1.3623; ir 2967, 2890 (saturated CH), 2114 cm^{-1} (C=C=N); ^{19}F nmr −10.1 ppm (s).

Anal. Calcd for $C_8H_9F_6N$: C, 41.20; H, 3.89; N, 6.01. Found: C, 41.12; H, 3.78; N, 5.80.

C. From Di-*tert*-butylsulfur Diimide.—The reaction was carried out with di-*tert*-butylsulfur diimide[24] as described under A. After 4 hr the product was distilled directly to give a 48% yield of the *tert*-butylamine derivative,[21,25] bp 66–68° (108 mm); $n^{25}{}_D$ 1.3524; ir 2985 (saturated CH), 2096 cm^{-1} (C=C=N); uv max (isooctane) 268 mμ (ϵ 287); ^{1}H nmr (neat) 1.08 ppm (s); ^{19}F nmr −10.6 ppm (s).

Anal. Calcd for $C_8H_9F_6N$: C, 41.20; H, 3.89; N, 6.01. Found: C, 41.41; H, 4.17; N, 6.16.

D. From Diphenylsulfur Diimide.—The diphenylsulfur diimide was made by a modification of Cramer's procedure.[26] Aniline (56 g, 0.6 mol) in 100 ml of dichloromethane was cooled in Dry Ice–acetone and 11 g (0.1 mol) of sulfur tetrafluoride was passed in. The mixture was allowed to warm to 24° and the aniline hydrofluoride was filtered off. The solvent was boiled off, finally under vacuum on a steam bath. Petroleum ether was added to precipitate tar and the decanted solution was distilled to give 10.1 g (94%) of diphenylsulfur diimide, bp 105° (0.1 mm).

The reaction was carried out as under A and after 16 hr distillation gave a 38% yield of *N*-[3,3,3-trifluoro-2-(trifluoromethyl)propenylidene]aniline:[27] bp 60° (8 mm); ^{1}H nmr (neat) 6.75 ppm (m); ^{19}F nmr −10.2 ppm (s). Hydrolysis in warm, aqueous acetone gave $(CF_3)_2CHCONHC_6H_5$,[28] mp and mmp 171–172°.

Registry No.—**2**, 33830-86-3; **3**, 33872-36-5; **4**, 33830-87-4; **7**, 33830-88-5; 3,3,3-trifluoro-2-(trifluoromethyl)thiopropionic acid, 33830-89-6; 3,3,3-trifluoro-2-(trifluoromethyl)thiopropionyl bromide, 33830-90-9; *p*-tolyl 3,3,3-trifluoro-2-(trifluoromethyl)-*N*-methylthiolpropionimidate, 33830-91-0; *p*-tolyl 3,3,3-trifluoro-2-(trifluoromethyl)-*N*-*p*-tolylthiolpropionimidate, 33830-92-1; *N*-methyl-*N*-[3,3,3-trifluoro-2-(trifluoromethyl)propenylthiomethyl]aniline, 33890-40-3; 33830-93-2 (HCl); *N*-methyl-*N*-[3,3,3-trifluoro-2-(trifluoromethyl)propenylthiomethyl]-*p*-toluidine, 33830-94-3; *N*-methyl-3-nitro-*N*-[3,3,3-trifluoro-2-(trifluoromethyl)propenylthiomethyl]aniline, 33830-95-4; *N*,*N'*-bis[3,3,3-trifluoro-2-(trifluoromethyl)-propenylthiomethyl]-*N*,*N'*-dimethylbenzidine, 33830-96-5; α-[3,3,3-trifluoro-2-(trifluoromethyl)propenylthio]benzyl methyl ether, 33830-97-6; ethyl 1-[3,3,3-trifluoro-2-(trifluoromethyl)propenylthio]ethyl ether, 33830-98-7; triethyl[3,3,3-trifluoro-2-(trifluoromethyl)-propenylthio]silane, 33872-37-6; diphenyl[3,3,3-trifluoro-2-(trifluoromethyl)propenylthio]silane, 33830-99-8; triphenyl[3,3,3-trifluoro-2-(trifluoromethyl)propenylthio]stannane, 33831-00-4; $CH_2{=}CHCH{=}CHSCH{=}C(CF_3)_2$, 33831-01-5; (methylthiomethyl)triphenylphosphonium chloride, 1779-54-0; methyl 3,3,3-trifluoro-2-(trifluoromethyl)propenyl sulfide, 33831-03-7; (benzylthiomethyl)triphenylphosphonium chloride, 33831-04-8; benzyl 3,3,3-trifluoro-2-(trifluoromethyl)propenyl sulfide, 33831-05-9; (phenylthiomethyl)triphenylphosphonium chloride, 13884-92-9; phenyl 3,3,3-trifluoro-2-(trifluoromethyl)propenyl sulfide, 33831-07-1; adipic acid, 124-04-9; 2,2,2-trifluoro-1-(trifluoromethyl)ethyl-3-indolylthione, 33831-08-2; 2,2,2-trifluoro-1-(trifluoromethyl)ethyl (1,3,3-trimethyl-2-indolinylidene)methylthione, 33831-09-3; 5-(dimethylaminomethylene)-1,3-cyclopentadien-1-yl-2,2,2-trifluoro-1-(trifluoromethyl)ethylthione, 33831-10-6; *N*-[3,3,3-trifluoro-2-(trifluoromethyl)propenylidene]methylamine, 23386-63-2; *N*-[3,3,3-trifluoro-2-(trifluoromethyl)propenylidene]-*n*-butylamine, 23386-64-3; *N*-[3,3,3-trifluoro-2-(trifluoromethyl)propenylidene]-*tert*-butylamine, 23409-78-1; diphenylsulfur diimide, 3839-89-2; *N*-[3,3,3-trifluoro-2-(trifluoromethyl)propenylidene]aniline, 1519-73-9; $(CF_3)_2CHCONHC_6H_5$, 786-39-0; bis(trifluoromethyl)thioketene, 7445-60-5.

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[21] M. S. Raasch, U. S. Patent 3,462,489 (1969); *Chem. Abstr.*, **71**, 90831g (1969).

[22] Made according to B. Cohen and A. G. MacDiarmid, *J. Chem. Soc. A*, 1780 (1966), except that ten times as much methylamine as specified was used; 66% yield.

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[24] See ref 11b.

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Hydroxide Displacement of the Sulfone Linkage in Thioxanthen-9-one 10,10-Dioxides to Benzophenone-2′-hydroxy-2-sulfinic Acids. Intramolecular Cyclization to Xanthones

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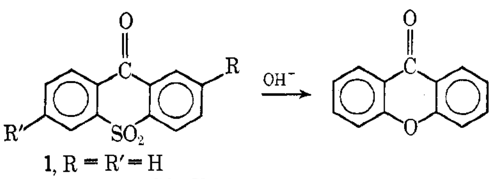
2-H, 2,6-diCOOH, 2-Cl, 2-CH_3, 2-CH_3O, and 2-NO_2 thioxanthen-9-one 10,10-dioxides were synthesized and treated, at reflux, with 2% NaOH–65% dioxane–H_2O. For these systems, facile hydroxide displacement of the sulfone linkage was found to occur exclusively on the more electrophilic ring to give the novel benzophenone-2′-hydroxy-2-sulfinic acids. Further, in alkaline media, these sulfinic acids generally undergo unique intramolecular cyclization to xanthones. The structures of the sulfinic acids were established by replacement of the sulfinic acid group with a chloromercury group followed by replacement of the latter with hydrogen to afford 2-hydroxybenzophenones.

Because thioxanthen-9-one 10,10-dioxides may possess some interesting physiologial properties, synthetic procedures leading to the preparation of a variety of substituted parent (**1**) systems have been reported.[3] Further, the well-known[4] colored solutions resulting from treatment of thioxanthen-9-one 10,10-dioxides with reducing agents in alkaline media have been investigated,[5] and epr data[6] have verified that formation of radical anions are responsible for the observed colors. While studying these color reactions in alkaline systems, the partial conversion of **1** to xanthone (**3**) was observed.[5a] Additional investigations relating to this transformation have not been reported and this interesting cleavage reaction has remained unexplained.



1, R = R′ = H
4, R = R′ = COOH

During the course of our recent studies[7] relating to the cyclization of diphenyl sulfone-2-carboxylic acids to thioxanthen-9-one 10,10-dioxides, we found that the heterocyclic moiety of the 2,6-dicarboxylic acid (**4**) of **1** was unstable to treatment with dilute aqueous sodium hydroxide. Since our results, along with those reported by Heymann, suggested a general lack of stability of the thioxanthen-9-one 10,10-dioxide nucleus in alkaline media, we undertook a more detailed investigation of this reaction system and report our findings in this paper.

For the purpose of this study, six thioxanthene-9-one 10,10-dioxides were prepared and refluxed with 2% sodium hydroxide–65% dioxane–water[8a] solution (Table I). All compounds underwent ring opening at the sulfone linkage[8b] under these conditions, and, following acidification, the corresponding novel hydroxybenzophenonesulfinic acids were obtained (Table II, A). In addition, except for the nitro compound **6**, xanthones were also isolated from the reaction mixtures (Table II, B). Nitro compound **6** gave only the 2′-hydroxy-5′-nitro-2-sulfinobenzophenone (**12**). Further, when the pure hydroxybenzophenonesulfinic acids were refluxed with 3% aqueous sodium hydroxide, all except **12** were converted to their corresponding xanthone products shown in Table III. Under these reaction conditions, the refractory nitro compound, **12**, remained unchanged even after reflux for 48 hr. The

TABLE I
THIOXANTHEN-9-ONE 10,10-DIOXIDES REACTED AT REFLUX IN 2% SODIUM HYDROXIDE–65% DIOXANE–H_2O

Reactant	mmol[a]	R′	R	Reaction time, hr	% Unreacted
1	16	H	H	4	61.5
4	6	COOH	COOH	0.25[b]	45.0
				5	7.5
5	14	H	Cl	4	50.2
6	14	H	NO_2	2	0.0
7	15	H	CH_3	18	23.0
8	15	H	CH_3O	18	28.8

[a] All reactions were run in 500 ml of solution except **4** which was run in 50 ml. [b] Yields in Table II were obtained for this reaction time.

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(2) (a) Taken in part from the M.S. theses of M. J. B. and R. M.; (b) the senior thesis of P. D.; (c) the Ph.D. dissertation of G. S.

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(5) (a) H. Heymann, *J. Amer. Chem. Soc.*, **71**, 260 (1949); (b) E. A. Fehnel, *ibid.*, **71**, 1065 (1949).

(6) E. T. Kaiser and L. Kevan, Ed., "Radical Ions," Interscience, New York, N. Y., 1968, Chapter 8, and references cited therein.

(7) O. F. Bennett and P. Gauvin, *J. Org. Chem.*, **34**, 4165 (1969).

(8) (a) All of the thioxanthen-9-one 10,10-dioxides were completely soluble in this solvent system, while many exhibited limited solubility in only aqueous hydroxide. (b) One referee of this manuscript has observed base-induced ring opening of the thioxanthen-9-one (**2**) ring system using Huang-Minlon conditions. Unlike the sulfone systems, he reports that ring opening in the sulfides does not lead to new, ring-closed products.