Experimental Section[8]

Preparation of the N-Oxides.—The various N-oxides were prepared by procedures available in the literature.[9-11] The purity of the compounds was ascertained by tlc (alumina plates, developing solvents varied from benzene to benzene–ethyl acetate mixtures), mass spectroscopy, and melting points.

Determination of pK_A Values.—All of the pK_A's were determined spectrophotometrically (Cary 14 instrument) using seven different solutions at various H_2SO_4 concentrations. The procedure used was that described by Chia and Trimble.[6] Tables II and III list some of the pertinent uv data.

Determination of Rate Constants.—The appropriate N-oxide was weighed into an nmr tube and 0.4 ml of D_2O was added. The solution was then allowed to come to 31°, and the HA-100 instrument was adjusted. An initial spectrum and integration was then obtained. Addition of 0.1 ml of the appropriate concentration of aqueous NaOD at 31° was then added with shaking. The total time elapsed between addition of the base until the first spectrum is obtained was between 45 to 60 sec. This, as a referee pointed out, and we are certainly aware of it, allows us to get four points for the rapidly exchanging H_2 of the cyano compound. Nevertheless, the data on five different runs are reproducible within the limits indicated in Table I and cover between two and three half-lives.

In all of the other compounds, 10–15 points, covering at least two-half lives, were obtained.

Registry No.—**1,** 25594-31-4; **2,** 6863-76-9; **3,** 23902-69-4; **4,** 6863-77-0; **5,** 2423-65-6; **6,** 13134-48-0; **7,** 25594-37-0; **8,** 13134-49-1.

Acknowledgment.—We wish to thank the Petroleum Research Fund administered by the American Chemical Society for supporting this work under Grant No. 2839-A1.

---

[8] Nmr spectra were obtained with a Varian HA-100 spectrometer. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6E instrument equipped with a solid sample injector. The ionizing voltage employed was 80 V. Elemental analyses were done by Mrs. K. Decker of this department.

[9] H. Shindo, *Chem. Pharm. Bull.*, **8**, 33 (1960).

[10] B. Klein, E. O'Donnell, and J. Auerbach, *J. Org. Chem.*, **32**, 2412 (1967).

[11] A. S. Elina, I. S. Musatova, and G. P. Sirova, *Khim. Geterotsikl. Soedin.*, 725 (1968).

Bis(trifluoromethyl)thioketene. I. Synthesis and Cycloaddition Reactions

MAYNARD S. RAASCH

Contribution No. 1647 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Received December 10, 1969

Bis(trifluoromethyl)thioketene has been synthesized by cracking its dimer prepared from diethyl malonate, thiophosgene, and sulfur tetrafluoride. It is stable enough to be distilled, handled, and stored without special precautions, yet is highly reactive. A tetramer and polymer have been prepared. Described here are reactions of the thioketene with (a) thiocarbonyl compounds to form dithietanes, (b) olefinic compounds and quadricyclenes to yield thietanes, (c) carbodiimides and azines to give 1,3-thiazetidines, (d) 2,3-dimethylbutadiene to form a 2H-thiopyran, and (e) norbornadienes to yield 2,6 adducts. 1,3-Dipolar additions of the thiocarbonyl group take place with diazomethane, benzonitrile oxide, and nitrones. Like nitrones, aryl oximes also give 1,4,2-oxathiazolidines. Two molecules of the thioketene combine with sulfur to form a dithiolane and trithiolane.

Organic chemistry has often been characterized as a mature science; yet some simple types of structures are scarcely known. Monomeric thioketenes have been sought for many years. Thioketene formulas appear in the literature as early as 1877,[1] but such compounds were soon realized to be some multiple of the simple formula.[2,3] Staudinger and coworkers unsuccessfully attempted to prepare a thioketene.[4,5] Dimers of aromatic thioketenes have been reported by Schönberg and coworkers[6] and the desaurins[7] can be regarded as thioketenes dimers. Dicyano- and carbomethoxycyanothioketene have not been isolated, but have been trapped as 1,3-[8a] and 1,4-dipolar[8b] adducts. Cyanothioketene has been postulated as an intermediate in the formation of dithiafulvenes from thioamides and chlorocyanoacetylene.[8c] Acidification of $C_6H_5C{\equiv}CSNa$ gave a polymer[9] which may have been derived from phenylthioketene, though this possibility was not mentioned. Subsequently, lithium salts of acetylenic thiols were treated with thiols and with amines to form thio esters and thioamides.[10-12a] Thioketenes were proposed as intermediates in the reaction sequence. Allylbutylthioketene was shown to be an intermediate in the rearrangement of allylthio-1-hexyne by trapping with an amine as a thioamide.[12b] Arylthioketenes have been suggested as intermediates in the photolysis of aryl-substituted 1,2,3-thiadiazoles,[13] and the thermal rearrangement of a dimethylthioketene dimer probably proceeds through the monomer.[14] Attempts to obtain dimethylthioketene by decomposi-

---

[1] T. Norton and A. Oppenheim, *Ber.*, **10**, 703 (1877).

[2] H. Bergreen, *ibid.*, **21**, 337 (1888).

[3] G. Wenzel, *ibid.*, **33**, 2041 (1900); **34**, 1043 (1901).

[4] H. Staudinger, G. Rathsam, and F. Kjelsberg, *Helv. Chim. Acta*, **3**, 853 (1920). H. Staudinger and J. Siegwart, *ibid.*, **3**, 840 (1920); *Ber.*, **49**, 1918 (1916).

[5] H. Staudinger, "Die Ketene," Ferdinand Enke, Stuttgart, 1912, p 128.

[6] A. Schönberg, E. Frese, and K. Brosowski, *Chem. Ber.*, **95**, 3077 (1962).

[7] (a) P. Yates and D. R. Moore, *J. Amer. Chem. Soc.*, **80**, 5577 (1958); (b) R. Gompper and W. Töpfl, *Chem. Ber.*, **95**, 2861 (1962); (c) M. Yokoyama, *J. Org. Chem.*, **35**, 283 (1970).

[8] (a) K. Dickore and R. Wegler, *Angew. Chem.*, **78**, 1023 (1966); *Angew. Chem., Int. Ed. Engl.*, **5**, 970 (1966). (b) R. Gompper and W. Elser, *ibid.*, **79**, 382 (1967); **6**, 366 (1967). (c) T. Sasaki, K. Kanematsu, and K. Shoji, *Tetrahedron Lett.*, 2371 (1969).

[9] M. Schmidt and V. Potschka, *Naturwissenschaften*, **50**, 302 (1963).

[10] P. J. W. Schuijl, L. Brandsma, and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **85**, 889 (1966).

[11] H. E. Wijers, C. H. D. van Ginkel, L. Brandsma, and J. F. Arens, *ibid.*, **86**, 907 (1967); P. J. W. Schuijl and L. Brandsma, *ibid.*, **87**, 38 (1968).

[12] (a) H. E. Wijers, L. Brandsma, and J. F. Arens, *ibid.*, **86**, 670 (1967); (b) H. E. Wijers, C. H. D. van Ginkel, P. J. W. Schuijl, and L. Brandsma, *ibid.*, **87**, 1236 (1968).

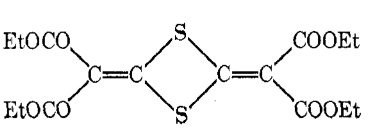
[13] W. Kirmse and L. Horner, *Justus Liebigs Ann. Chem.*, **614**, 4 (1958).

[14] E. U. Elam and H. E. Davis, *J. Org. Chem.*, **32**, 1562 (1967).

tion of cycloadducts of aryl isothiocyanates and 1-dialkylamino-2-methylpropenes were unsuccessful.[15a] No thioketenes were detected in the reaction of atomic sulfur with acetylenes.[15b]

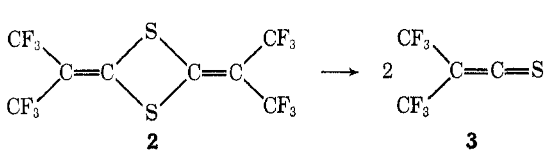
Reports of isolable thioketenes have been few. Carbon subsulfide,[16] $S{=}C{=}C{=}C{=}S$, might be included here. The synthesis of thioketene itself by the pyrolysis of *t*-butyl ethynyl sulfide was reported by Howard.[17] Thioketene could be collected without solvent at −196° but polymerized on warming to −80°. When collected and maintained in cyclohexene at −80°, it could be kept for several hours. The subject of this article, the reactive bis(trifluoromethyl)thioketene[18] (**3**), was announced in 1966. Since then, the hindered di-*t*-butylthioketene[19] and the ylide, $(C_6H_5)_3P{=}C{=}C{=}S$,[20] have been reported.

Synthesis.—Bis(trifluoromethyl)thioketene has been synthesized by preparing and cracking its dimer. From diethyl sodiomalonate and thiophosgene, tetraethyl 1,3-dithietane-$\Delta^{2,\alpha:4,\alpha'}$-dimalonate (**1**) was prepared



1

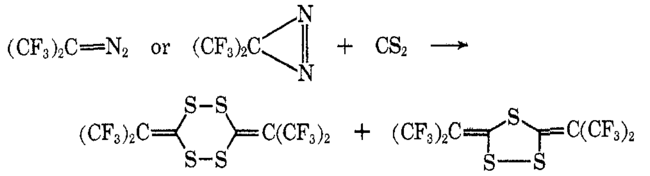
in 70% yield. This is an old compound but had been assigned a different structure.[3] Heating the tetraester with sulfur tetrafluoride in the presence of hydrogen fluoride[21] produced 2,4-bis[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-dithietane (**2**), the dimer



2 **3**

of bis(trifluoromethyl)thioketene. This process was carried out in two steps. If a large amount of hydrogen fluoride was employed, the ester was converted to tar. When a small amount of hydrogen fluoride was used, only two or three of the ester groups were converted to CF_3. However, this partially fluorinated, deactivated mixture of dithietanes could be heated with additional hydrogen fluoride and sulfur tetrafluoride to form **2** in 75% yield.

The dimer is also available through other syntheses. Reaction of bis(trifluoromethyl)ketene[22a] with triphenylphosphine sulfide at 200° formed the dimer in 60% yield. Similar reactions, which probably proceed through a four-membered ring intermediate, have been reported to give only polymeric sulfur products with diphenylketene[4] and chloral.[22b] The decomposition of 2-diazo-1,1,1,3,3,3-hexafluoropropane[23] or 3,3-bis(trifluoromethyl)-3H-diazirine[24a] in carbon disulfide at 150–175° produced the cyclic polysulfides, **4** and **5**.[24b]



4 **5**

Presumably, bis(trifluoromethyl)carbene is formed and adds to carbon disulfide. The adduct then dimerizes to **4** and this, by loss of an atom of sulfur, forms **5**. These compounds are converted into the thioketene dimer by abstraction of sulfur with triphenylphosphine. A similar reaction with carbon disulfide has been reported for diazodiphenylmethane.[6] However, 3,3-bis(chlorodifluoromethyl)-3H-diazirine failed to undergo the reaction because the intermediate carbene rearranged to $CF_2{=}CClCF_2Cl$ by a 1,2 shift of a chlorine atom. Recently, the thioketene dimer has been synthesized by reaction of perfluoroisobutylene with potassium sulfide[25] and the reaction of $(CF_3)_2C{=}C{=}P(C_6H_5)_3$ with sulfur.[26]

Studies with a mass spectrometer equipped with a preheater showed bis(trifluoromethyl)thioketene dimer to be stable to 400°. At 600° the spectrum indicated the presence of 75% of bis(trifluoromethyl)thioketene, 21% of dimer, and 2% of perfluoroisobutylene. For laboratory production of the thioketene, the dimer was sublimed at 1-mm pressure through a platinum tube packed with quartz rings and heated to 750°. This produced the distilled monomer in 70% yield. The pyrolysis could also be carried out at 650° by distilling the dimer through the tube at atmospheric pressure but this formed a small foreshot containing carbon disulfide, tetrakis(trifluoromethyl)allene,[27] and perfluoroisobutylene, identified by mass spectrometry.

Monomeric bis(trifluoromethyl)thioketene (**3**) is a reddish orange liquid, bp 52–53°, with spectral absorptions at 5.61 μ (1783 cm^{-1}), 503 mμ (ϵ 8.5), and 239 mμ (ϵ 5590). It is a compound of gratifying reactivity, yet stable enough to distil, handle, and store without special precautions. It may be kept at 25° in glass

---

[15] (a) A. K. Bose and G. L. Mina, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, p 122; G. L. Mina, *Diss. Abstr.*, *B*, **27**, 3862 (1967); R. Oda, A. Miyasu, and M. Okano, *Nippon Kagaku Zasshi*, **88**, 96 (1967). (b) O. P. Strausz, J. Font, E. I. Dedio, P. Kebarle, and H. G. Gunning, *J. Amer. Chem. Soc.*, **89**, 4805 (1967).

[16] B. Lengyel, *Ber.*, **26**, 2960 (1893); A. O. Diallo, *C. R. Acad. Sci.*, **261**, 5386 (1965); W. H. Smith and G. E. Loroi, *J. Chem. Phys.*, **45**, 1778 (1966).

[17] E. G. Howard, Jr., U. S. Patent 3,035,030 (1962).

[18] M. S. Raasch, *Chem. Commun.*, 577 (1966); U. S. Patent 3,275,609 (1966); Abstracts, 3rd Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, Pa., Feb 1968, p 76.

[19] E. U. Elam, F. H. Rash, J. T. Dougherty, V. W. Goodlett, and K. C. Brannock, *J. Org. Chem.*, **33**, 2738 (1968).

[20] C. N. Matthews and G. H. Birum, *Tetrahedron Lett.*, 5707 (1966); U. S. Patent 3,459,804 (1969); G. H. Birum and C. N. Matthews, *J. Amer. Chem. Soc.*, **90**, 3842 (1968); J. J. Daly, *J. Chem. Soc. A*, 1913 (1967).

[21] W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Amer. Chem. Soc.*, **82**, 543 (1960).

[22] (a) D. C. England and C. G. Krespan, *ibid.*, **87**, 4019 (1965); I. L. Knunyants, Y. A. Cheburkov, and M. D. Bargamova, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1389 (1963); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1265 (1963); Y. A. Cheburkov, E. I. Mysov, and I. L. Knunyants, *ibid.*, 1432 (1963). (b) H. Sohr and K. Lohs, *Z. Chem.*, **7**, 153 (1967).

[23] D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Amer. Chem. Soc.*, **88**, 3617 (1966); C. G. Krespan and W. J. Middleton, U. S. Patent 3,242,166 (1966); E. P. Mochalina and B. L. Dyatkin, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 926 (1965); *Bull Acad. Sci. USSR, Div. Chem. Sci.*, 899 (1965).

[24] (a) R. B. Minasyan, E. M. Rokhlin, N. P. Gambaryan, Y. V. Zeifman, and I. L. Knunyants, *ibid.*, 746 (1965). (b) Compounds **4** and **5** have been used to prepare iridium and platinum complexes of bis(trifluoromethyl)thioketene and 1,1-bis(trifluoromethyl)ethene-2,2-dithiolate: M. Green, R. B. L. Osborn, and F. G. A. Stone, *J. Chem. Soc. A*, 944 (1970).

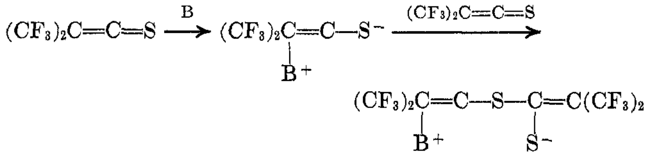
[25] C. G. Krespan and D. C. England, *J. Org. Chem.*, **33**, 1850 (1968).

[26] G. H. Birum and C. H. Matthews, *ibid.*, **32**, 3554 (1967).

[27] D. C. England and C. G. Krespan, *J. Amer. Chem. Soc.*, **88**, 5582 (1966).

bottles for many months with little dimerization. In contrast, hexafluorothioacetone at 25° dimerizes in several hours.[28]

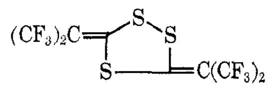
Dimerization of the thioketene back to 2 is brought about rapidly by catalytic amounts of Lewis bases such as tertiary amines and various nitrogen-, oxygen-, and sulfur-containing molecules that do not otherwise react with the thioketene. Presumably, this occurs through the mechanism



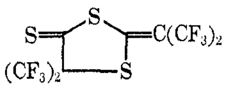
$$(CF_3)_2C{=}C{=}S \xrightarrow{B} (CF_3)_2C{=}\underset{B^+}{C}{-}S^- \xrightarrow{(CF_3)_2C=C=S} (CF_3)_2C{=}\underset{B^+}{C}{-}S{-}\underset{S^-}{C}{=}C(CF_3)_2$$

Loss of B results in dimer if the catalysis is carried out above about −20°. At lower temperatures, polymer is formed through addition of more units of the monomer. The thioketene is polymerized by adding it to acetone at −80°. The white polymer is insoluble in all solvents tried and melts at 245° with cracking back to the monomer. The infrared spectrum shows C=C absorption at 1575 cm^{-1}. A tetramer has also been prepared from the thioketene, but before discussing this, a description of the reaction of the thioketene with sulfur is necessary.

Reaction with Sulfur.—When the thioketene is heated with sulfur at 200°, two adducts, **5** and **6**, are formed in which two molecules of the thioketene are combined



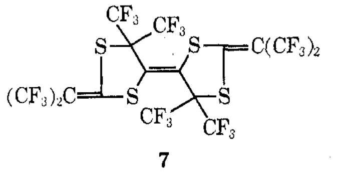
5



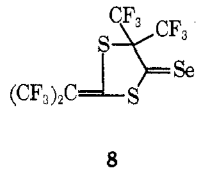
6

with one atom of sulfur. Compound **5** is the same product as obtained from the reaction of 2-diazo-1,1,1,-3,3,3-hexafluoropropane with carbon disulfide. Its ^{19}F nmr spectrum has two close quadruplets at −8.60 and −7.72 ppm referred to $ClCF_2CF_2Cl$ as standard, and infrared C=C absorption at 1550 cm^{-1}. The magenta color of **6** is indicative of the thiocarbonyl group. The ^{19}F nmr shows an A_3B_3 pattern at −7.75 ppm arising from $(CF_3)_2C{=}C$ attached to two sulfur atoms, which are in turn attached to differing groups, and a singlet at +1.63 ppm from the ring CF_3 groups. Infrared C=C absorption is at 1577 cm^{-1}. Alternative structures with a five-membered ring containing C=S would have a 3-carbon sequence in the ring and would show well-separated quadruplets in the ^{19}F nmr. Both **5** and **6** are converted to the thioketene dimer and sulfur on standing in acetone solution.

Bis(trifluoromethyl)thioketene Tetramer.—When the thioketene and selenium were heated together at 200°, a 30% yield of a sparingly soluble bis(trifluoromethyl)thioketene tetramer, mp 130–130.5°, was formed along with a low yield of a purplish liquid mixture. The structure **7** is proposed for this tetramer.



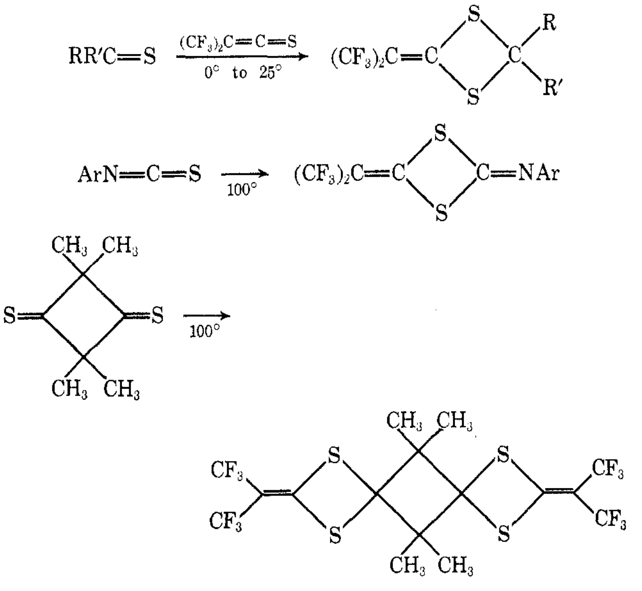
7



8

The ^{19}F nmr spectrum consists of a singlet for the CF_3 groups attached to the ring and an A_3B_3 pattern indicative of $(CF_3)_2C{=}C$ attached to two sulfur atoms which are attached to two differing groups. The central, symmetrically *trans*-substituted double bond does not show in the ir but is revealed in the Raman spectrum at 1520 cm^{-1}. The $(CF_3)_2C{=}C$ group shows characteristic absorption at 1576 cm^{-1} in the ir and Raman spectra. The melting point and sparing solubility of the compound also indicate a symmetrical structure. These data would also fit an alternative structure consisting of two fused six-membered rings with the double bond between the two common carbon atoms but this structure seems unlikely from the method of synthesis. The tetramer may form from the intermediate production of **8** which is the analog of **6**, obtained from the thioketene and sulfur. Thermal loss of selenium then might occur with formation of the ethylene, just as certain thiones lose sulfur to form ethylenes when heated.[29] However, refluxing the sulfur analog **6** (bp 191°) alone or in the presence of metals did not remove the more strongly bound sulfur to give the tetramer.

Dithietanes.—Just as bis(trifluoromethyl)thioketene will combine with itself to form a dithietane, so it will unite with a diversity of other thiocarbonyl compounds to form dithietanes in high yield. The types of operable compounds are illustrated by Table I. The structure of the products is shown by a singlet in the ^{19}F nmr spectrum and C=C absorption in the ir.



The dithietanes vary widely in stability. The least stable is the one formed from yellow *o*-phenylene trithiocarbonate (Table I, no. 12). The white dithietane is obtained at 10° but on standing at 25° it dissociates back into its components. The compound from methyl methylxanthate (no. 9) is not stable enough to distil at reduced pressure. The dithietane from $(C_6H_5)_2C{=}S$ dissociates at 140°. The remaining compounds did not reveal instability during purification.

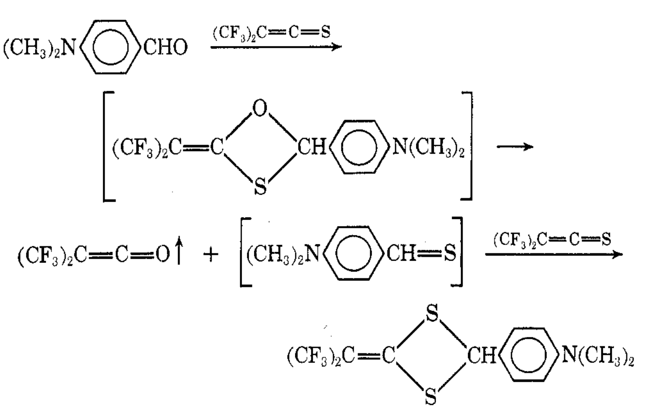
Sulfur–Oxygen Exchange with Carbonyl Compounds.—Though the thioketene unites with thiocarbonyl compounds to form dithietanes, it does not combine with ordinary carbonyl compounds to form oxathie-

---

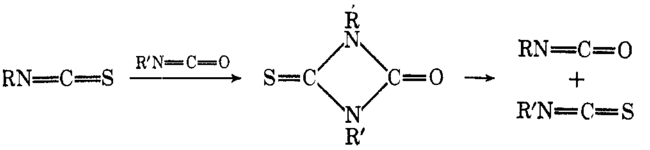
[28] W. J. Middleton, E. G. Howard, and W. H. Sharkey, *J. Org. Chem.*, **30**, 1375 (1965).

[29] E. Campaigne, *Chem. Rev.*, **39**, 50 (1946).

tanes. However, in an unexpected reaction with the electron-rich carbonyl compound *p*-dimethylaminobenzaldehyde at 10°, $(CF_3)_2C{=}C{=}O$ was evolved and a dithietane was formed. Intermediate formation of the oxathietane is postulated with spontaneous dissociation of this into $(CF_3)_2C{=}C{=}O$ and *p*-dimethylaminothiobenzaldehyde. The latter then combines with the thioketene to form the dithietane shown above. The reaction also takes place with *p*-diethylaminobenzaldehyde, *p*-dimethylaminocinnamaldehyde, and *p,p'*-bis(dimethylamino)benzophenone. Thus, the latter gives the same dithietane as the corresponding thioketone.



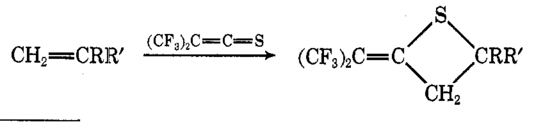
Sulfur–oxygen exchange also takes place between isothiocyanate and isocyanate esters at 200°.[30] This has been represented as occurring through the following sequence.

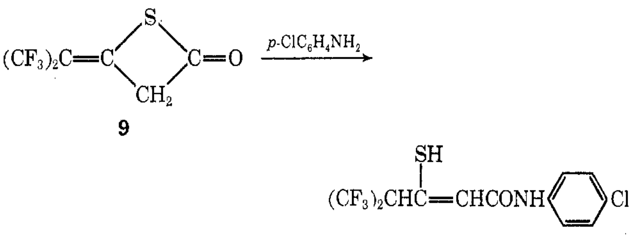


The possibility that a 1,3-oxathietane might be involved seems not to have been evaluated for this reaction or for $COS \leftrightarrows CO_2 + CS_2$.

Thietanes.—The facile reaction of the thioketene with thiocarbonyl compounds to form dithietanes is equaled by its addition to certain olefin types to form thietanes. Methyleneadamantane, styrenes, ketene, and methylketene are operable as well as the electron-rich unsaturates comprising vinyl ethers, sulfides, and esters, and N-vinylcarbazole. The scope of the reaction appears greater than that of hexafluorothioacetone which is reported to form thietanes with vinyl ethers and sulfides.[31] Under photochemical conditions, the relatively unreactive thiobenzophenone will also yield thietanes with certain olefins.[32]

Examples of unsaturates that give thietanes are listed in Table II. The direction of cycloaddition is such that the sulfur atom becomes attached to the carbon atom bearing the substituent(s). The structures have been assigned by a combination of chemical and nmr methods in two cases while in the remaining examples nmr comparisons have been used. At 0°, ketene forms the β-thiolactone **9** which reacts with *p*-chloroaniline to yield an enethiol. For **9**, the ^{19}F nmr shows two quadruplets with the components of the low-field one characteristically split into apparent triplets by the CH_2 group. The CH_2 group shows a band with multiple splitting. For **10**, the ^1H nmr reveals a septuplet at 3.72 ppm [$(CF_3)_2CH$] and singlets at 6.31 (=CH), 7.44 (hydrogen-bonded SH), and 9.38 (NH). Hydrogen bonding of SH with either N or O would form a six-membered ring.

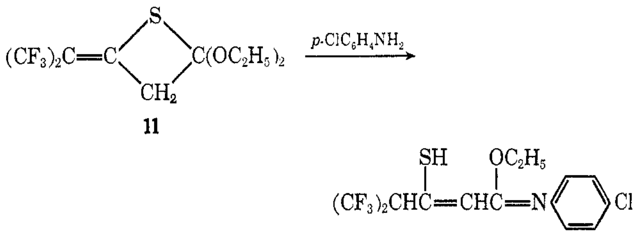




9

10

The adduct from ketene acetal also reacts with *p*-chloroaniline. The ^{19}F nmr of **11** again has two quadruplets with the components of the low-field one split to apparent triplets. The ^1H nmr for **12** has singlets at 6.25 (=CH) and 14.95 (hydrogen-bonded SH). Further data appear in the Experimental Section.

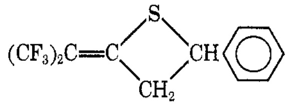


11

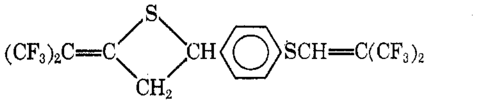
12

With *cis*-1,2-dimethoxyethylene (Table II, no. 16), stereospecific cycloaddition takes place as judged from the nmr spectrum in $CDCl_3$ which shows a doublet ($J = 5.2$ Hz) at 5.52 ppm for Hα to S and a broad multiplet at 5.20 from splitting by F for the other ring proton. *trans*-1,2-Dimethoxyethylene caused dimerization of the thioketene and did not form a cycloadduct.

Styrene gave the normal product **13** with the usual nmr pattern and in addition a 1:2 adduct (**14**). The $(CF_3)_2C{=}CH{-}S{-}$ group, encountered frequently in the chemistry of the thioketene, shows a diagnostic quadruplet ($J = 1.4$ Hz) for H at about 7.4 ppm in the nmr spectrum.



13



14

Unsaturates containing a double bond that can shift, including dimethylketene, undergo an "ene" reaction

---

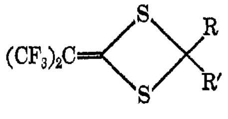
[30] L. C. Case, *Nature*, **183**, 675 (1959); W. E. Erner, *J. Org. Chem.*, **29**, 2091 (1964).

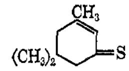
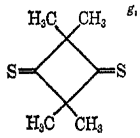
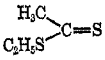
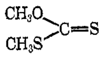
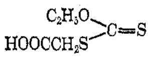
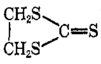
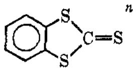
[31] W. J. Middleton, *ibid.*, **30**, 1395 (1965).

[32] A. Ohno, Y. Ohnishi, and G. Tsuchihashi, *J. Amer. Chem. Soc.*, **91**, 5038 (1969), and references therein.

TABLE I

2,2-SUBSTITUTED 4-[2,2,2-TRIFLUORO-1-(TRIFLUOROMETHYL)ETHYLIDENE]-1,3-DITHIETANES[a,b]

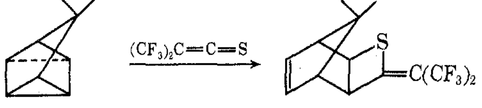


No.	Reactant, RR′C=S	Product mp or bp (mm), °C	Recrystn solvent	Yield, %
1	$(C_6H_5)_2C=S$[c]	59-59.5	CH_3OH	77
2	$[p\text{-}(CH_3)_2NC_6H_4]_2C=S$[d]	137-138	Cyclohexane	73
3	$(CF_3)_2C=S$[e]	126-127 $n^{25}D$ 1.3669		53
4	 [f]	77 (0.3) $n^{25}D$ 1.4848		74
5	 [g,h]	255	C_6H_6	82
6	 $(H_3C)(C_2H_5S)C=S$[i]	44 (0.2) $n^{25}D$ 1.4819		95
7	$(CH_3O)_2C=S$[j]	50-51	Hexane	73
8	$(C_6H_5O)_2C=S$[k]	42-42.5	CH_3OH	78
9	 $(CH_3O)(CH_3S)C=S$[l]	Liquid, dec $n^{25}D$ 1.4869		High
10	 $(C_2H_5O)(HOOCCH_2S)C=S$[m]	88.3-90	Cyclohexane	50
11	 [d]	85.5-86.5	CH_3OH	87
12	 [n]	Solid, dec		96
13	$C_6H_5N=C=S$[d]	46-47	CH_3OH	49
14	$p\text{-}ClC_6H_4N=C=S$[o]	48.5-49	CH_3OH	54
15	$p\text{-}O_2NC_6H_4N=C=S$[d]	62.5-63	CH_3OH	37
16	$m\text{-}O_2NC_6H_4N=C=S$[d]	53-53.5	CH_3OH	51
17	$p\text{-}C_6H_5N=NC_6H_4N=C=S$[p]	118-119	C_2H_5OH	71
18	$3,4,5\text{-}(CH_3O)_3C_6H_2N=C=S$[q]	89.7-90.5	Hexane	73
19	$p\text{-}S=C=NC_6H_4N=C=S$[r]	158.2-158.4	CCl_4	45
20	1-Naphthyl-N=C=S[d]	128.5-128.7	CH_2Cl_2-EtOH	79

[a] Disclosed in part in M. S. Raasch, U. S. Patents 3,336,334, 3,337,586, 3,355,446 (1967). [b] Ed. note: Satisfactory analytical data (±0.35%) for C, H, and S were reported for all compounds except no. 9 and 12 which were not analyzed and no. 6 (Calcd: C, 30.57. Found: C, 31.11) and no. 7 (Calcd: H, 2.01. Found: H, 2.45). [c] B. F. Gofton and E. A. Braude in "Organic Syntheses," Coll. Vol. IV, N. Rabjohn, Ed., Wiley, New York, N. Y., 1963, pp 927-928. [d] Distillation Products Industries, Rochester, N. Y. [e] Reference 28. [f] D. E. Winkler and S. A. Ballard, U. S. Patent 2,437,985 (1948). [g] R. D. Lipscomb, U. S. Patent 3,297,765 (1967); joint experiment with Dr. Lipscomb. [h] Reference 14. [i] C. S. Marvel, P. deRadzitsky, and J. J. Brader, *J. Amer. Chem. Soc.*, **77**, 5997 (1955). [j] M. Delepine, *Bull. Soc. Chim. Fr.*, [4] **7**, 409, 727 (1910). [k] H. Eckenroth and K. Kock, *Ber.*, **27**, 1369 (1894). [l] I. B. Douglas and W. J. Evers, *J. Org. Chem.*, **29**, 419 (1964). [m] E. Biilmann, *Justus Liebigs Ann. Chem.*, **339**, 355 (1905). [n] R. Huisgen and V. Weberndörfer, *Experientia*, **17**, 566 (1961). [o] G. M. Dyson *in* "Organic Syntheses," Coll. Vol. I, 2nd ed, H. Gilman and A. H. Blatt, Ed., Wiley, New York, N. Y., 1941, p 165. [p] C. E. Bolser and E. B. Hartshorn, *J. Amer. Chem. Soc.*, **45**, 2349 (1923). [q] Prepared by Dr. J. C. Kauer of these laboratories by the method of ref *o;* mp 67-68° (hexane). [r] G. J. M. van der Kirk, C. W. Pluygers, and G. deVries, *Recl. Trav. Chim. Pays-Bas*, **74**, 1262 (1955).

with the thioketene instead of thietane formation. This will be discussed in a future publication.

Adducts with Quadricyclenes.—Polycyclic thietanes are obtained when the thioketene adds to quadricyclenes. As is the case with the addition of other unsaturates to quadricylene,[33] the reaction stereospecifically gives an adduct with the thietane ring in the *exo* position. The lack of splitting in the nmr spectrum for the bridgehead protons indicates *endo* protons at the thietane ring bridgeheads.[34]



R = H, Cl, CH_3COO

In the case of compounds with a substituent on the bridge, a configuration with the substituent *anti* to the thietane ring seems most likely for steric reasons. However, this was not established by nmr for these

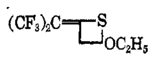
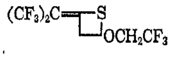
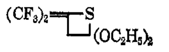
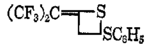
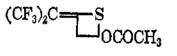
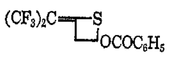
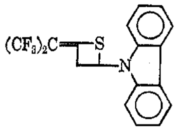
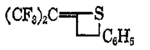
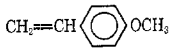
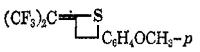
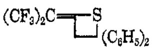
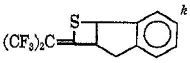
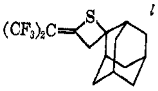
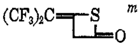
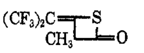
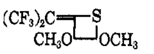
---

[33] C. D. Smith, *J. Amer. Chem. Soc.*, **88**, 4273 (1966).

[34] E. W. C. Wong and C. C. Lee, *Can. J. Chem.*, **42**, 1245 (1964), and sources cited in ref 33.

TABLE II

2-SUBSTITUTED 4-[2,2,2-TRIFLUORO-1-(TRIFLUOROMETHYL)ETHYLIDENE]THIETANES[n,o]

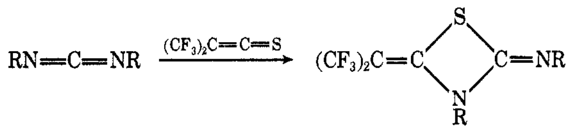
No.	Reactant	Reaction conditions	Product	Recrystn from, or $n^{25}\mathrm{D}$	Bp (mm) or mp, °C	Yield, %
1	$CH_2{=}CHOC_2H_5$[a]	10-25°		1.4173	70-72 (7)	90
2	$CH_2{=}CHOCH_2CF_3$[b]	10-25°		1.3893	79-82 (11)	80
3	$CH_2{=}C(OC_2H_5)_2$[c]	10-25°, pentane		1.4202	73-74 (1.65)	81
4	$CH_2{=}CHSC(CH_3)_3$[d]	10-25°		1.4583	114 (10)	61
5	$CH_2{=}CHSC_6H_5$[e]	10-25°		1.5198	72 (0.06)	81
6	$CH_2{=}CHOCOCH_3$[a]	100°, 15 hr		1.4180	93-96 (11)	25
7	$CH_2{=}CHOCOC_6H_5$[f]	100°, 16 hr		C_6H_{12}	102-102.6	46
8	N-Vinylcarbazole[f]	25°, CH_2Cl_2, 4 hr		C_2H_5OH	152-153	80
9	$CH_2{=}CHC_6H_5$[a]	100°, 15 hr		1.4946	67 (0.2)	26
10		10-25°		1.5060	98 (0.1) 23-24	69
11	$CH_2{=}C(C_6H_5)_2$[a]	100°, 15 hr		CH_3OH	59-59.1	64
12	Indene[a]	25°, 16 hr	 [k]	CH_3OH	134-137 (7) 76-77	53
13	2-Methyleneadamantane[g]	100°, 15 hr	 [l]	CH_3OH	78-79 (0.05) 39.5-40.5	40
14	$CH_2{=}C{=}O$[h]	0°, CH_2Cl_2, 15 hr	 [m]	1.4181	151-153	44
15	$CH_3CH{=}C{=}O$[i]	0-25°, Et_2O, 2 hr		1.4130	63-66 (29)	33
16	*cis*-$CH_3OCH{=}CHOCH_3$[j]	10-25°, C_6H_{12}		C_6H_{12}	104-105 (15) 42-43	94

[a] Distillation Products Industries, Rochester, N. Y. [b] Air Reduction Co., Inc., Ohio Medical Products Division, Riverton, N. J. [c] S. M. McElvain and D. Kuniger in "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., Wiley, New York, N. Y., 1955, pp 506–508. [d] J. F. Arens and T. Doornbos, *Recl. Trav. Chim. Pays-Bas*, **75**, 481 (1956). [e] W. E. Parham, F. D. Blake, and D. R. Theissen, *J. Org. Chem.*, **27**, 2415 (1962). [f] Borden Chemical Co., Monomer Polymer Laboratories, Philadelphia, Pa. [g] P. von R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, **83**, 182 (1961); suggested by Dr. G. H. Berezin, Du Pont Co. [h] S. Andreades and H. D. Carlson, *Org. Syn.*, **45**, 50 (1965). [i] P. G. Blake and K. J. Hole, *J. Phys. Chem.*, **70**, 1464 (1966); A. D. Jenkins, *J. Chem. Soc.*, 2563 (1952). [j] B. R. O'Connor, *J. Org. Chem.*, **33**, 1991 (1968). [k] 2-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]indano[2,1-*b*]thietane. [l] 4′-[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]spiroadamantane[2,2′]thietane. [m] 3-Mercapto-5,5,5-trifluoro-4-(trifluoromethyl)-3-pentenoic acid β-thiolactone. [n] Disclosed in part in M. S. Raasch, U. S. Patent, 3,468,908 (1969). [o] Ed. note: Satisfactory analytical data (±0.35%) for C, H, and S were reported for all compounds except no. 2 (Calcd: C, 30.01; H, 1.57. Found: C, 30.74; H, 2.06), no. 7 (Calcd: C, 45.61. Found: C, 46.03), no. 8 (Calcd: C, 55.80; H, 2.86. Found: C, 55.47; H, 3.35), no. 10 (Calcd: C, 47.55; H, 46.98), no. 12 (Calcd: C, 50.31; H, 2.60. Found: C, 50.79; H, 2.99), no. 14 (Calcd: C, 30.51; H, 0.85. Found: C, 30.93; H, 1.45).

crystalline adducts as the bridge proton and the vinylene protons do not show the marked interaction that occurs in simple 7-substituted norbornenes with such a configuration.[35]

1,3-Thiazetidines.—The thioketene cycloadds to carbodiimides to form 1,3-thiazetidines, a little-known class of compounds.[36]

The reaction has been carried out with di-*p*-tolyl-, diisopropyl-, and dicyclohexylcarbodiimide. The products have spectral properties similar to those of the thietanes in that the ^{19}F nmr spectrum shows a pair of quadruplets and the ir has absorption at about 1628 cm^{-1} for the exocyclic double bond. Pyrolysis of the ditolyl compound at 240° caused splitting to *p*-tolyl isothiocyanate, a further proof of structure.

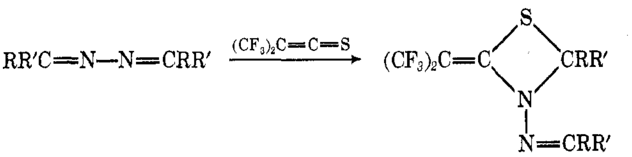


---

(35) E. I. Snyder and B. Franzus, *J. Amer. Chem. Soc.*, **86**, 1166 (1964).

(36) Many of the reports of 1,3-thiazetidines in the literature are incorrect. However, the reactions of thiocarbanilides with phosgene, thiophosgene, and diiodomethane do give 1,3-thiazetidines.

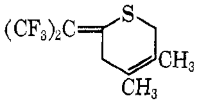
Less stable adducts were obtained from benzalazine and cyclohexanoneazine. The addition was reversed when the benzalazine adduct was heated at 120° with the formation of benzalazine and the thioketene dimer. The cyclohexanoneazine adduct was unstable at 25°.



The thioketene forms 2:1 adducts with Schiff bases. These will be discussed in a future article.

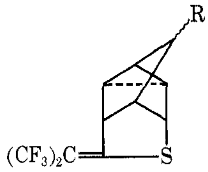
Diels-Alder Adducts.—The thiocarbonyl group of the thioketene readily acts as a dienophile, though the rate of reaction is not so great as for hexafluorothioacetone.[37] Differences in mode of reaction also occur. Whereas thietane formation takes place between the thioketene and styrene, hexafluorothioacetone undergoes a Diels-Alder reaction with styrene involving the vinyl group and a ring double bond. Other thiocarbonyl compounds have also been reported to form Diels-Alder adducts.[37-39]

Illustrative of the Diels-Alder reaction is the addition of the thioketene to 2,3-dimethylbutadiene to form **15**.

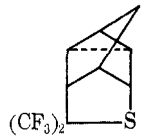


15

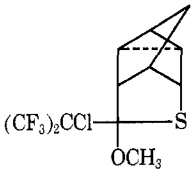
Addition to 2,5-Norbornadiene.—The addition of olefinic compounds across the 2,6-positions of norbornadiene[40-42] finds a counterpart in the chemistry of the thioketene as the thiocarbonyl group adds to these positions to form the structure **16**, a new polycyclic system. Apparently, thiocarbonyl compounds have not been added to norbornadiene previously, and the reaction has been extended by using hexafluorothioacetone to form **17**.



16a, R = H
b, R = $OC(CH_3)_3$
c, R = Cl



17



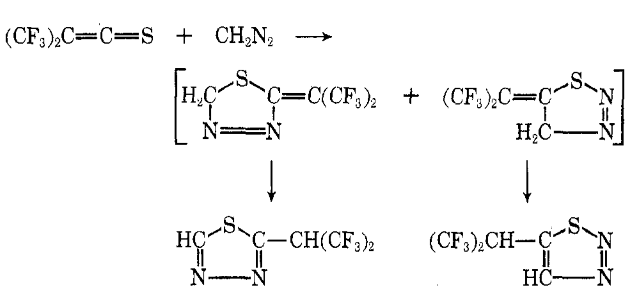
18

When a 7-monosubstituted norbornadiene is used, two stereoisomers are possible as products depending on whether the substituent is *syn* or *anti* to sulfur. The reaction proceeds with 7-*t*-butoxy- and 7-chloronorbornadiene but the stereochemistry has not been established. The chloro product consisted of isomers in a ratio of 65:35 by glpc.

Chlorine can be readily added to the double bond of **16a** by means of sulfuryl chloride. Treatment of the product with methanol displaces the reactive chlorine atom α to the sulfur atom with methoxyl to form **18**. Such additions and displacements would probably be operable with the other types of thioketene adducts also.

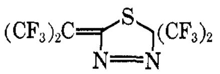
1,3-Dipolar Additions.—The thiocarbonyl group of bis(trifluoromethyl)thioketene participates in 1,3-dipolar additions[43] to form sulfur heterocycles containing other heteroatoms. Described here are 1,3 cycloadditions to diazomethane, benzonitrile oxide, and nitrones. Because of certain similarities, additions to hydrogen azide and aryl oximes are also included in this section.

A. Addition to Diazomethane.—Diazomethane adds to the thiocarbonyl group in both directions without loss of nitrogen. The presumed intermediate products then undergo a prototropic shift to form the more stable thiadiazoles (**19** and **20**) containing conjugated double bonds. The isomers were separated by glpc. The nmr spectra show the presence of $(CF_3)_2CH$, and, for **20**, coupling between the protons of the two CH groups.



19 59% **20** 41%

In the case of the reported addition of bis(trifluoromethyl)diazomethane to the thioketene to form **21**, such a prototropic shift cannot take place.[44]



21

Addition of diazomethane to the thioketene is similar to its reaction with aryl isothiocyanates to form 5-anilino-1,2,3-thiadiazoles,[45] but the reaction of diazo compounds with other thiocarbonyl compounds,[46a] including hexafluorothioacetone,[46b] is accompanied by loss of nitrogen.

B. Addition to Hydrogen Azide.—A solid, highly volatile 1,2,3,4-thiatriazole (22), the first aliphatic

22

---

[37] W. J. Middleton, *J. Org. Chem.*, **30**, 1390 (1965).

[38] A. Schönberg and B. König, *Chem. Ber.*, **101**, 725 (1968).

[39] K. Yamada, M. Yoshioka, and N. Sugiyama, *J. Org. Chem.*, **33**, 1240 (1968).

[40] E. F. Ullman, *Chem. Ind. (London)*, 1173 (1958).

[41] D. E. Applequist and D. C. England, U. S. Patent 2,940,984 (1960).

[42] R. C. Cookson, J. Dance, and J. Hudec, *J. Chem. Soc.*, 5416 (1964), and references therein.

[43] R. Huisgen, *Angew. Chem.*, **75**, 604, 742 (1963); *Angew. Chem., Int. Ed. Engl.*, **2**, 565, 633 (1963); *Helv. Chim. Acta*, **50**, 2421 (1967). R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964, pp 806–878.

[44] W. J. Middleton, *J. Org. Chem.*, **34**, 3201 (1969).

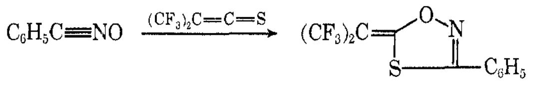
[45] H. von Pechmann and A. Nold, *Ber.*, **29**, 2588 (1896); M. Tisler, M. Hrovat, and N. Machiedo, *Croat. Chem. Acta*, **34**, 183 (1962).

[46] (a) A. Schönberg, B. König, and E. Singer, *ibid.*, **100**, 767 (1967); M. Sander, *Chem. Rev.*, **66**, 319 (1966). (b) W. J. Middleton and W. H. Sharkey, *J. Org. Chem.*, **30**, 1384 (1965).

derivative of this heterocycle to be stable at 25°,[47] is formed from the thioketene and hydrogen azide. The compound may result from the formation and cyclization of $(CF_3)_2CHC(=S)N_3$ rather than by direct cycloaddition. The compound decomposes with a puff at 100° with deposition of sulfur, and presumably with the formation of nitrogen and $(CF_3)_2CHCN$.

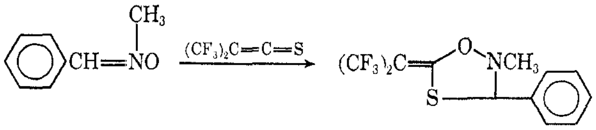
Aryl azides form 1:1 and 1:2 adducts with the thioketene. These will be reported in a future publication.

C. Addition to Benzonitrile Oxide.—A 1,4,2-oxathiazole results from reaction of the thioketene with benzonitrile oxide.

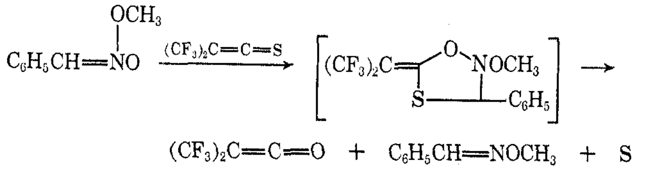


This addition is analogous to the trapping reaction used for dicyanothioketene and carbomethoxycyanothioketene.[8a] A number of aromatic thiocarbonyl compounds have also been added to nitrile oxides to form 1,4,2-oxathiazoles.[48] Carbon disulfide reacts with 2,4,6-trimethylbenzonitrile oxide in a more complex fashion but the initial product is thought to be a 1,4,2-oxathiazole.[49]

D. Addition to Nitrones.—What appears to be the first preparation of a 1,4,2-oxathiazolidine results from the addition of the thioketene to N-methyl-α-phenylnitrone. The ir spectrum has a band at 1618 cm^{-1} for the exocyclic C=C and the ^{19}F nmr spectrum shows an A_3B_3 pattern consistent with $(CF_3)_2C{=}C$ attached to O and to S. The compound decomposes in a few days at 25°.



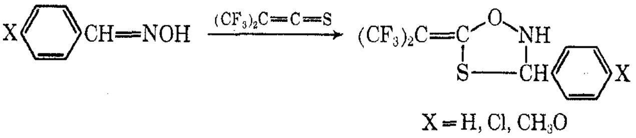
In the case of N-methoxy-α-phenylnitrone, the oxathiazolidine decomposed as formed according to the equation



All three products were identified. In effect, this is another exchange reaction in which the sulfur of the thioketene is exchanged for oxygen.

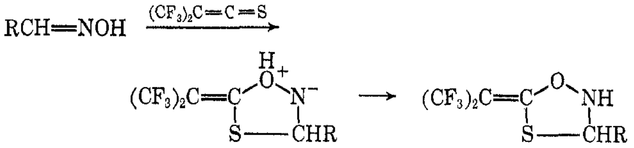
The addition of $C_6H_5N{=}C{=}S$ to nitrones is reported to occur across the N=C bond.[50]

E. Addition to Aryl Oximes.—Like nitrones, aryl oximes also form 1,4,2-oxathiazolidines with the thioketene. In this case they are unsubstituted on the nitrogen atom. These white, crystalline products precipitate out when the thioketene is added to a solution of the oxime in dichloromethane and petroleum ether at 10°. They may be filtered off and allowed to dry briefly, but after about 30 min at 25° the phenyl and *p*-chlorophenyl compounds go pffft and disappear in a cloud of vapor. The *p*-anisyl analog undergoes this change after about 5 min. The compounds can be stored at −80°.

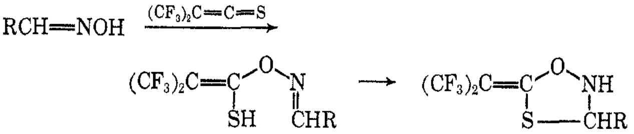


Though they are unstable, the phenyl and *p*-chlorophenyl compounds can be characterized by working rapidly. The ^{19}F nmr spectrum of the phenyl compound, for example, shows an A_3B_3 pattern comparable with that from the nitrone adducts. The ^1H nmr has a doublet ($J = 12$ Hz) at 6.05 ppm for CH and a doublet for NH ($J = 12$ Hz) at 6.53. When the solution is shaken with D_2O, the NH doublet disappears and the CH doublet is converted to a singlet. The ir spectrum shows bands at 3185 cm^{-1} for NH and 1621 for the exocyclic double bond.

Oximes can be alkylated on either nitrogen or oxygen but there is no physical evidence that they exist in part in the nitrone form. However, the reaction still could be represented as a 1,3 addition.[51]



Alternatively, the reaction course[52] might simply be



Decomposition of the phenyl derivative in dichloromethane gives benzonitrile and a compound, $C_{15}H_9F_{12}NOS$, whose structure is being investigated.

Experimental Section

The ^1H 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 from 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.

Tetraethyl 1,3-Dithietane-$\Delta^{2,\alpha:4,\alpha'}$-dimalonate[3] (1).—Into a 5-l., three-necked, round-bottomed flask, fitted with a mechanical stirrer and a large capacity reflux condenser, were placed 700 g (4.38 mol) of diethyl malonate and 1600 ml of tetrahydrofuran.

---

[47] K. A. Jensen and C. Pedersen, "Advances in Heterocyclic Chemistry," Vol. III, A. R. Katritsky, Ed., Academic Press, New York, N. Y., 1964, pp 263–284.

[48] R. Huisgen, W. Mack and E. Anneser, *Angew. Chem.*, **73**, 656 (1961).

[49] W. O. Foye and J. M. Kauffman, *J. Org. Chem.*, **31**, 2417 (1966).

[50] R. Huisgen, *Angew. Chem.*, **75**, 626 (1963); *Angew. Chem., Int. Ed. Engl.*, **2**, 588 (1963). R. Grashey, R. Huisgen, and H. Leitermann, *Tetrahedron Lett.*, No. 12, 9 (1960).

[51] In the addition of two molecules of dimethyl acetylenedicarboxylate to acetone oxime, N-alkenylation of the oxime with one molecule is proposed as the first step with 1,3 addition to the nitrone so formed as the second step: E. Winterfeldt and W. Krohn, *Angew. Chem.*, **79**, 722 (1967); *Angew. Chem., Int. Ed. Engl.*, **6**, 709 (1967).

[52] Proposed by one of the referees.

Sodium hydride (189 g of 55.6% in oil, 4.38 mol) was placed in a 500-ml erlenmeyer flask which was then connected to the large flask with Gooch tubing. During 1 hr, the sodium hydride was added to the tetrahydrofuran solution in portions and the Gooch tubing was clamped shut with a hemostat between additions. After all the sodium hydride was added, the condenser and Gooch tubing were removed and the flask was fitted with a thermometer and dropping funnel. Thiophosgene (252 g, 2.19 mol) dissolved in 200 ml of tetrahydrofuran was added through the dropping funnel during 75 min while the temperature of the reaction mixture was maintained at 18–22° with an ice bath. After all the thiophosgene had been added, the ice bath was removed and stirring was continued for 15 min. Then 1500 ml of distilled water was added and the product was filtered off on a suction funnel. The filter cake was washed with about 1 l. of ether, or until the yellow color was gone. The cake was then slurried with 1000 ml of water, refiltered, and washed with 4 to 6 l. of distilled water, or until no chloride ion was found in the rinse. The cake was rinsed with 200 ml of alcohol and then spread out to air dry. Final drying was done at 90° for 16 hr in a vacuum oven. The yield was 300–320 g (68–72.5%), mp 179–180°. Except for an off-white color, the compound is essentially pure and may be used without recrystallization for the reaction with SF_4. After recrystallization from dioxane, the compound melted at 180–181°: ir 1511 (C=C), 1672, 1689 cm^{-1} (C=O). Small amounts have been recrystallized from 70% nitric acid.

The tetramethyl ester[7b] can be prepared in the same way, but dimethyl sodiomalonate precipitates from tetrahydrofuran whereas the diethyl ester stays in solution.

2,4-Bis[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-dithietane (2).—Tetraethyl 1,3-diethietanedimalonate (150 g) was placed in a 1-l. "Hastelloy" C bomb which was then cooled in a Dry Ice–methanol bath and evacuated. The bomb was charged with 25 g of hydrogen fluoride and 310 g of water-white sulfur tetrafluoride. Heating was carried out at 125° for 2 hr, 150° for 2 hr, and 200° for 4 hr. The bomb was then allowed to cool overnight. The next morning it was vented, the valve was closed, and the bomb was cooled in a Dry Ice–methanol bath. Without prior evacuation, the bomb was charged with 85 g of HF and 310 g of SF_4 and heating was resumed, 150° for 2 hr and 200° for 4 hr. The bomb was cooled to 35–40°, vented, and unloaded into a polyethylene bottle. The product was carefully poured onto ice and the crystals containing tar were washed with water, 10% sodium carbonate solution, and water again. The crystals were steam distilled, filtered off, and placed on paper towels. Because of the volatility of the product, it was not allowed to air dry more than about 1 hr. The product was then dissolved in warm dichloromethane, dried with anhydrous magnesium sulfate, filtered warm, and crystallized by reducing in volume and cooling. The yield was 100–108 g (69–75%) in three crops: mp 84°; bp 170°; ir 1616 cm^{-1} (C=C); ^{19}F nmr (CCl_4) −8.30 ppm (s). While almost any organic solvent can be used for recrystallization, a solvent boiling higher than dichloromethane causes loss of product by volatilization when boiled. The SF_4 used should be pure, water-white. Otherwise, the preparation may fail. Chlorine is suspect as a deleterious impurity.

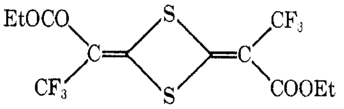
Anal. Calcd for $C_8H_{12}S_2$: C, 24.75; F, 58.74; S, 16.52. Found: C, 24.96; F, 58.28; S, 16.83.

Partial Fluorination of Tetraethyl 1,3-Dithietane-Δ$^{2,\alpha:4,\alpha'}$-dimalonate.—Preliminary experiments with the SF_4 treatment yielded partially fluorinated products from which three compounds were isolated and characterized. No attempt has been made to improve the yield of these.

Tetraethyl 1,3-dithietane-Δ$^{2\,\alpha:4,\alpha'}$-dimalonate (1, 50 g), 50 g of HF, and 150 g of SF_4 were heated in a 400-ml Hastelloy shaker tube for 2 hr each at 110, 125, 140, and 150°. The HF was allowed to evaporate from the product, water was cautiously added, and the mixture was made just basic with sodium hydroxide. The mixture was steam distilled and the oil that came over was collected with dichloromethane and dried ($MgSO_4$). The solid left after evaporation of the solvent was recrystallized from methanol to give 6.2 g which was sublimed at 100° to yield ethyl 3,3,3-trifluoro-2-{4-[2,2,2-trifluoro-1-(trifluoromethyl)ethyl)ethylidene]-1,3-dithietane-2-ylidene}propionate: mp 49–50°; ir 1577 (conjugated C=C), 1631 [$(CF_3)_2C$=C], 1685 cm^{-1} (C=O); ^{19}F nmr ($CDCl_3$) −8.72 [A_3B_3 pattern, $(CF_3)_2C$=], 9.60 ppm (s, CF_3).

Anal. Calcd for $C_{10}H_5F_9O_2S_2$: C, 30.62; H, 1.28; F, 43.69; S, 16.36. Found: C, 30.85; H, 1.28; F, 42.92; S, 16.20.

1 (20 g), 12 g of HF, and 60 g of SF_4 were heated to 140° in a 145-ml shaker tube. At this point, the reaction flashed to 181°. It was cooled to 140° and continued there for a total of 8 hr. The product was poured onto ice and the tarry precipitate was rinsed with water and ethanol. About 2 g of the tris(trifluoromethyl) compound described above was sublimed out. The residue was extracted with hot ethanol and the solution was decolorized and boiled down to give 5.1 g of crystals, mp 126–140°. Four recrystallizations from ethanol yielded 2.6 g of 2,4-bis[2,2,2-trifluoro-1-(ethoxycarbonyl)ethylidene]-1,3-dithietane: mp 153.5–154.5°; ir 1580 (C=C), 1701 cm^{-1} (C=O); ^{19}F nmr ($CDCl_3$) −8.81 ppm (s). The high melting point and single band in the ir are indicative of the *trans*, symmetrical structure.



Anal. Calcd for $C_{12}H_{10}F_6O_4S_2$: C, 36.36; H, 2.54; F, 28.77; S, 16.18. Found: C, 36.25; H, 2.66; F, 28.81; S, 16.05.

From the mother liquor was isolated 0.32 g of a compound, mp 97–98°, of the same composition but with stronger ir absorption, evidently the *cis* form: ^{19}F nmr ($CDCl_3$) −9.28 ppm (s).

Synthesis of 2 from Bis(trifluoromethyl)ketene.—Bis(trifluoromethyl)ketene (4.0 g, 0.025 mol) and 5.88 g (0.02 mol) of triphenylphosphine sulfide were heated in a Carius tube at 200° for 5 hr. The product was steam distilled to give 2.3 g (59%) of **2**, identified by melting point and mixture melting point. Perfluoroisobutylene and triphenylphosphine sulfide failed to react at 200°.

Reaction of 2-Diazo-1,1,1,3,3,3-hexafluoropropane with Carbon Disulfide.—2-Diazo-1,1,1,3,3,3-hexafluoropropane[23] (11 g, 0.062 mol) and 20 ml (0.33 mol) of carbon disulfide were heated in an 80-ml Hastelloy bomb at 175° for 12 hr. Distillation of the product gave 2.55 g (20%) of 3,5-bis[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,2,4-trithiolane (**5**): bp 91–93° (15 mm); n^{25}D 1.4519; ir 1553 cm^{-1}; ^{19}F nmr (neat) −7.60, −8.65 ppm (quadruplets).

Anal. Calcd for $C_8F_{12}S_3$: C, 22.86; F, 54.25; S, 22.90. Found: C, 22.57; F, 54.13; S, 23.34.

When the above reaction was run at 150° instead of 175°, a small amount of 3,6-bis[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-*s*-tetrathiane (**4**) was isolated, which indicates this is the precursor to the 1,2,4-trithiolane. 2-Diazo-1,1,1,3,3,3-hexafluoropropane (5 g, 0.028 mol) and 10 ml (0.16 mol) of carbon disulfide were heated at 150° for 8 hr. Distillation of the product gave 1.77 g, bp 90–109° (15 mm), in 2 cuts. Crystals separated from the higher cut. Filtration and crystallization twice from methanol yielded 150 mg of the *s*-tetrathiane, mp 44.3–44.5°. From the pot residue, 160 mg more was obtained (4.9% total yield): ir 1565 cm^{-1} (C=C, simple spectrum indicative of symmetrical molecule); ^{19}F nmr (CCl_4) −11.1 ppm (s, no impurities evident).

Anal. Calcd for $C_8F_{12}S_4$: C, 21.24; F, 50.41; S, 28.36. Found: C, 20.78; F, 49.29; S, 28.71.

Reaction of 3,3-Bis(trifluoromethyl)-3H-diazirine with Carbon Disulfide.—3,3-Bis(trifluoromethyl)-3H-diazirine[24] (5 g, 0.028 mol) and 15 ml of carbon disulfide were heated in an 80-ml Hastelloy bomb for 8 hr. Distillation of the product gave 2.17 g (37%) of **5**, bp 87–89° (13 mm), n^{25}D 1.4520. Analytical and spectral data agree with those above for **5**.

Conversion of the Cyclic Polysulfides to Bis(trifluoromethyl)thioketene Dimer (2).—Mixing **5** with a 1.2 mol equiv of triphenylphosphine produced an exothermic reaction. After the mixture was heated at 100°, it was steam distilled to give an 80% yield of **2** identified by melting point and mixture melting point. Similarly **4** was converted to **2**.

3,3-Bis(chlorodifluoromethyl)-3H-diazirine.—In a 500-ml flask fitted with magnetic stirrer and reflux condenser, 200 ml of 5.25% NaOCl (0.14 mol), 2 g of NaOH and 14 g (0.065 mol) of 1,3-dichloro-1,1,3,3-tetrafluoro-2,2-propanediamine[53] were stirred

---

[53] W. J. Middleton and C. J. Krespan, *J. Org. Chem.*, **30**, 1398 (1965).

at 25° for 20 hr. The temperature did not rise more than 1°. The flask was then connected to a Dry Ice trap and the product was pulled off under water vacuum. The product was dried ($MgSO_4$) and distilled using an oil bath to give 6.6 g (48%) of the diazirine: bp 57°; n^{25}_{D} 1.3363; ir 1640 cm^{-1} (N=N); uv max (isooctane) 293.5 mμ (ϵ 58), 303.5 (60); ^{19}F nmr (neat) −6.30 ppm (s).

Anal. Calcd for $C_3Cl_2F_4N_2$: Cl, 33.61; F, 36.02; N, 13.28. Found: Cl, 33.29; F, 35.60; N, 13.59.

When a few drops of the compound were heated over a flame in a small test tube, the compound exploded and broke the tube. When dropped onto a melting point block heated to 280°, the compound decomposed with a muted pop. This behavior is in contrast to that of 3,3-bis(trifluoromethyl)-3H-diazirine[54] which is reported to show no tendency to detonate. The above procedure is an adaptation of the one used to prepare the perfluoro analog.[24]

Decomposition of 3,3-Bis(chlorodifluoromethyl)-3H-diazirine.—3,3-Bis(chlorodifluoromethyl)-3H-diazirine (8 g) and 20 ml of carbon disulfide were heated at 175° for 10 hr in an 80-ml Hastelloy bomb. Distillation of the product gave 6.10 g, bp 36°, apparently an azeotrope of carbon disulfide and the fluoro olefin, 2.60 g, bp 36–46.5°, and the rest at 46.5°. Fluorine nmr of the 36°-cut showed only $CF_2=CClCF_2Cl$. Gas chromatography of this cut over 20% Kel-F ester on 60–80 mesh firebrick at 25° gave an area per cent of 36.6 for carbon disulfide (4.9 min retention time), 63.3 for the olefin (10.45 min), and 3 trace peaks of 0.03 or less. This indicated that the 36° cut contained about 56% of theory of the olefin. The cut was subjected to preparative scale gas chromatography under similar conditions to give an isolated yield of 2,3-dichloro-1,1,3,3-tetrafluoropropene[55] of 53%: bp 45°; n^{25}_{D} 1, 3450; ir 1743 cm^{-1} (C=C, gas phase); nmr −14.8 (d, J = 32 Hz, split to doublets, J = 8 Hz, CF_2Cl), 6 peaks at 9.5 to 11.1 and 5 at 11.8 to 12.5 ppm ($CF_2=$). The other distillation cuts were not examined.

Anal. Calcd for $C_3F_4Cl_2$: Cl, 38.77; F, 41.56. Found: Cl, 38.71; F, 41.58.

Bis(trifluoromethyl)thioketene (3).—The apparatus for cracking 2 consisted of a 0.5-in. platinum tube 24-in. long with the middle 12-in. packed with 3-mm sections of 6-mm quartz tubing. The ends of the tube were silver-soldered to stainless steel 18/9 spherical inner joints. Two porcelain-jacketed copper-Constantan thermocouples were taped to the tube with glass cloth electrical tape and the tube was mounted in a 12-in. flexible-band, ceramic-insulated heater. The tube was clamped at an angle of 30° with the horizontal to a ring stand. The lower end was connected by way of an external 18/9 spherical point to a glass trap cooled with liquid nitrogen and connected to an oil pump. The upper end of the pyrolysis tube was attached to an external 18/9 spherical joint on the side arm of a 100-ml distilling flask. The neck and side arm of the flask and the upper end of the pyrolysis tube were wrapped with heating tape to keep these parts above the melting point of the dimer. A Glas-Col heater was mounted beneath the flask. One thermocouple was attached to a Honeywell Pyr-O-Vane temperature controller with Powerstat and the other was connected to a potentiometer for checking the temperature.

The distilling flask was charged with 80 g of dimer 2, the pyrolysis tube was heated to 750°, and the pressure was reduced to *ca.* 1 mm with the oil pump. With the aid of the heater on the distilling flask, the dimer was sublimed through the pyrolysis tube during about 3 hr, or at such a rate that little dimer collected n the receiving trap. Nitrogen was then admitted and the trap was allowed to warm to room temperature. The trap contents were filtered or decanted from dimer if present and the mobile, reddish orange bis(trifluoromethyl)thioketene was then distilled: bp 52–53°; mp −55° (yellow solid); n^{25}_{D} 1.3495; d^{25}_{4} 1.462, dipole moment 1.95 D; ir and Raman 1783 cm^{-1} (5.61 μ); visible max (isooctane) 503 mμ (ϵ 8.5); uv max (isooctane) 239 mμ (ϵ 5590);[56] ^{19}F nmr (neat) −9.15 ppm (s). The still pot contained some dimer and a complex, liquid mixture. After correction was made for recovered dimer, the yield was 69–72%.

Anal. Calcd for C_4F_6S: C, 24.75; F, 58.74; S, 16.52. Found: C, 24.95; F, 58.65; S, 16.54.

In a single inhalation toxicity test, four rats were exposed to 5 ppm of the thioketene for 4 hr. No deaths occurred. The compound is thus less toxic than phosgene which kills at 5 ppm and is not comparable to the extemely toxic perfluoroisobutylene. The sample for this test was purified by glpc over 2.5% Kel-F ester on firebrick. The thioketene so obtained was less stable, but it is uncertain whether this was caused by introduction of a dimerization catalyst from the column, or removal of an inhibitor. The thioketene was restabilized by shaking with 1 drop of sulfuric acid and redistilling for the toxicity test.

Reaction of Bis(trifluoromethyl)thioketene with Sulfur.—Bis(trifluoromethyl)thioketene (23.3 g, 0.12 mol) and 4.23 g (0.13 mol) of sulfur were sealed in a glass tube and heated at 200° for 6 hr. The magenta liquid was decanted from 2.52 g of sulfur and distilled to give 18 g (71%) of a mixture, bp 83–111° (27 mm). Cuts, bp 90–100° (27 mm), were purified by glpc over 25% Dow-Corning FS 1265 on firebrick at 150°. The main fraction, 70–75% of the total product, was a magenta liquid: bp 191°; n^{25}_{D} 1.4570; ir 1577 cm^{-1} (C=C); visible max (isooctane) 528 mμ (ϵ 52.5); uv max (isooctane) 333 mμ (ϵ 12,000), 240 (10,880); ^{19}F nmr (neat) 1.63 (s, $2CF_3$), −7.75 ppm [A_3B_3 pattern, $(CF_3)_2C=$]. This compound is 6, 5,5-bis(trifluoromethyl)-2-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-dithiolane-4-thione.

Anal. Calcd for $C_8F_{12}S_3$: C, 22.86; S, 22.90. Found: C, 23.22; S, 23.05.

Distillation cuts boiling at 100–111° (27 mm) were chromatographed on the same column. Compound 5 came off later than 6 and was pale orange: n^{25}_{D} 1.4520; ir 1550 cm^{-1}; ^{19}F nmr (neat) −7.71, −8.60 ppm (quadruplets). These data and the elemental analysis are in agreement with those for the product (5) obtained from carbon disulfide and $(CF_3)_2C=N_2$.

Bis(trifluoromethyl)thioketene Tetramer (7).—Bis(trifluoromethyl)thioketene (15 g) and 6 g of selenium were sealed in a glass tube and heated at 200° for 5 hr. The solids were filtered from a purplish liquid mixture (*ca.* 3 g) and rinsed with a little dichloromethane. The solids were then extracted with acetone and the solution was boiled down to the crystallization point to give 4.5 g (30%) of tetramer, *trans*-2,2′-bis[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-5,5,5′,5′-tetrakis(trifluoromethyl)-$\Delta^{4,4'}$-bi-1,3-dithiolane: mp 130–130.6°; ir 1575 cm^{-1} [$(CF_3)_2C=C$]; Raman 1575 [$(CF_3)_2C=C$], 1520 cm^{-1} (central C=C); ^{19}F nmr ($CHCl_3$) −5.90 (s, $2CF_3$), −9.60 ppm [A_3B_3 pattern, $(CF_3)_2C=$]. The white color indicates absence of C=S.

Anal. Calcd for $C_{16}F_{24}S_4$: C, 24.75; S, 16.52; mol wt, 776. Found: C, 25.09; S, 16.72; mol wt, 791 (in $CHCl_3$ by vapor pressure osmometer).

Dithietanes.—Thiocarbonyl compounds no. 1, 2, 4, and 6–12 in Table I were dissolved in about 2 ml/g of dichloromethane and the solution was stirred and occasionally cooled with ice to maintain the temperature at 10–25° while an equivalent of bis(trifluoromethyl)thioketene was added. Reaction was rapid and completion was indicated by the disappearance of the color of the thioketene. No. 3 was used neat at 0° with a reaction time of 3 hr. No. 5 was sealed in a glass tube with 2 ml/g of hexane and 2 equiv of the thioketene and heated at 100° for 15 hr. No. 12–20 were sealed in glass tubes, neat if liquid or with dichloromethane if solid, together with 1 equiv of the thioketene, and heated at 100° for 15 hr. Solvent was removed from the products and they were then recrystallized or distilled as indicated in Table I. All the compounds are colorless, which shows absence of C=S in the structure. In accord with the assigned structure the ^{19}F nmr spectrum shows a singlet for $(CF_3)_2C=C$ attached to the two sulfur atoms. For the dithietane from $(CF_3)_2C=S$ (Table I, no. 3) this occurs at −7.15 ppm (neat). For the rest of the compounds, neat or in solution in $CDCl_3$ or CCl_4, the singlet falls in the range of −8.51 to −9.95 ppm. The C=C ir absorption for the compounds occurs around 1613–1637 cm^{-1}.

Reaction with *p*-Dialkylaminobenzaldehydes.—*p*-Dimethylaminobenzaldehyde (2.24 g, 0.015 mol) dissolved in 20 ml of dichloromethane was placed in a simple, magnetically stirred still whose outlet was connected to a trap containing 2.80 g (0.03 mol) of aniline in dichloromethane. To the still was added dropwise 5.82 g (0.03 mol) of bis(trifluoromethyl)thioketene. Bis(trifluoromethyl)ketene evolved and was captured by the aniline. After the end of the addition, the dichloromethane in the pot was distilled into the trap. The sparingly soluble 3,3,3-trifluoro-2-(trifluoromethyl)propionanilide isolated from the trap amounted to 2.32 g (57%). After recrystallization from benzene it had mp 170.5–171° which showed no depression with a sample

---

[54] D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Amer. Chem. Soc.*, **88**, 3617 (1966).

[55] W. T. Miller, U. S. Patent 2,733,277 (1956).

[56] "UV Atlas of Organic Compounds," Vol. I, Plenum Press, New York, N. Y., 1966, p B13/3.

prepared from $(CF_3)_2C{=}C{=}O$[22] and aniline (lit.[57] mp 168–169°).

The product in the still pot was recrystallized from hexane (decolorizing charcoal) to give 4.15 g (77%) of 2-(*p*-dimethylaminophenyl)-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-dithietane: mp 148–149°; ir 1600 cm^{-1} [$(CF_3)_2C{=}C$]; ^{19}F nmr (CCl_4) −9.95 ppm (s); ^1H nmr (CCl_4) 3.05 (s, $2CH_3$), 5.45 (s, CH), 7.09 ppm (center of aromatic A_2B_2 pattern).

Anal. Calcd for $C_{13}H_{11}F_6NS_2$: C, 43.44; H, 3.09; S, 17.85. Found: C, 43.75; H, 3.55; S, 17.95.

The diethylamino homolog was made in the same way in 28% yield: mp 81–82° from methanol; ^{19}F nmr (CCl_4) −10.10 ppm (s).

Anal. Calcd for $C_{15}H_{15}F_6NS_2$: C, 46.50; H, 3.90; S, 16.55. Found: C, 47.15; H, 3.97; S, 16.73.

Reaction with *p*-Dimethylaminocinnamaldehyde.—To 0.88 g (0.005 mol) of powdered *p*-dimethylaminocinnamaldehyde (Aldrich Chemical Co., recrystallized from methanol) suspended in 10 ml of hexane (which gives better results than dichloromethane) was added 1.94 g (0.01 mol) of bis(trifluoromethyl)thioketene. After 1 hr the solid was filtered off and recrystallized from methanol (decolorizing charcoal) to give 1.14 g (59%) of 2-(*p*-dimethylaminostyryl)-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-dithietane: mp 136–137°; ir 1613 (=CH), 1563, 1534, 1490 (C=C), 971 cm^{-1} (*trans* CH=CH); ^{19}F nmr (CCl_4) −10.10 ppm (s).

Anal. Calcd for $C_{15}H_{13}F_6NS_2$: C, 46.73; H, 3.40; N, 3.63. Found: C, 46.76; H, 3.42; N, 3.45.

Reaction with 4,4′-Bis(dimethylamino)benzophenone.—The reaction was carried out as with *p*-dimethylaminobenzaldehyde and gave a 64% yield of 2,2-bis(*p*-dimethylaminophenyl)-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-dithietane recrystallized from cyclohexane. After being recrystallized again from cyclohexane and from CCl_4, it melted at 135–136°, showed no depression in mixture melting point with dithietane no. 2, Table I, and had the same ^1H nmr as that product.

Anal. Calcd for $C_{21}H_{20}F_6N_2S_2$: C, 52.70; H, 4.21; S, 13.40. Found: C, 52.48; H, 4.22; S, 13.53.

Thietanes.—Conditions for preparing thietanes appear in Table II. A temperature of 10–25° indicates that the unsaturate was stirred and cooled in ice while 1 equiv of the thioketene was added dropwise. The reaction was complete at the end of the addition. Reactions at 100° were run in sealed glass tubes. The ^{19}F nmr spectra of the compounds in CCl_4, $CDCl_3$, or neat are similar and consist of two quadruplets, one at −7.7 to −9.7 ppm and the second at 1.2–1.6 ppm higher field. Components of the low field quadruplet are split to apparent triplets ($J = \sim 2.6$ Hz) for those thietanes containing a CH_2 group. For compounds no. 12 and 16, Table II, which contain a CH group adjacent to $(CF_3)_2C{=}C$, the low-field quadruplet components are split to doublets. Splitting in the high-field quadruplets is poorly defined or not evident. In the ^1H nmr spectrum, the CH_2 groups appear as broadened peaks with multiple splitting. Ir absorption for the exocyclic double bonds is at 1640–1670 cm^{-1}.

In the case of styrene (Table II, no. 9), which forms two products, the crude product from 7.76 g (0.04 mol) of the thioketene, 7.28 g (0.07 mol) of styrene, and 0.05 g of hydroquinone was diluted with methanol and 4.7 g of polymer was filtered off. The methanol was boiled from the filtrate and the residue was diluted with a small amount of petroleum ether. Crystals of the 2:1 thioketene:styrene adduct were filtered off and recrystallized from hexane to yield 2.54 g (26%) of 2-[2,2,2-trifluoromethyl)ethylidene]-4-{*p*-[3,3,3-trifluoro-2-(trifluoromethyl)propenylthio]phenyl}thietane (**14**): mp 75.5–76.5°; ir 3058 (=CH), 1621, 1577, 1481 (C=C), 853 cm^{-1} (*para*-disubstituted aromatic); ^{19}F nmr (CCl_4) −4.31, −7.00 [quadruplets, $(CF_3)_2C{=}CH{-}S{-}$], −10.8, −13.4 ppm (quadruplets); ^1H nmr (CCl_4) 2.00, 3.08, 3.57, 3.85 (AB pattern, latter 2 peaks split to doublets, CH_2), 4.44 (center of 2 doublets, thietane ring CH), 7.27 (4 aromatic H), 7.38 ppm [quadruplet for $(CF_3)_2C{=}CH$, $J = 1.6$ cps].

Anal. Calcd for $C_{16}H_8F_{12}S_2$: C, 39.02; H, 1.64; S, 13.03. Found: C, 39.20; H, 1.76; S, 12.94.

The 2-phenyl-4-[2,2,2-trifluoro-1-trifluoromethyl)ethylidene]thietane in the filtrate from the above 2:1 adduct was distilled as indicated in Table II: ir 1653 (exocyclic C=C), 1595, 1499 cm^{-1} (aromatic C=C); ^{19}F nmr (neat) −7.45, −8.80 ppm (quadruplets, $J = 7$ cps, split to triplets, $J = 2.6$ cps, the low field one more clearly so); ^1H nmr (neat) 3.40 (multiplet, CH_2), 4.20 (2 doublets, CH), 6.93 ppm (s, C_6H_5). The pot residue yielded 0.6 g more (6%) of the 2:1 adduct.

Supplemental evidence on the structure of the indene adduct (Table II, no. 12) was obtained by desulfurization. The adduct (4 g), 150 ml of absolute ethanol, and 20 g of Raney nickel were refluxed for 4 hr. The product was filtered and distilled to give 2.36 g (65%) of 2-[3,3,3-trifluoro-2-(trifluoromethyl)propenyl]indan: bp 92° (7 mm); mp 31–32° from methanol; ir 1675 cm^{-1} (linear C=C); ^{19}F nmr (neat) −2.14, −8.60 ppm (quadruplets); ^1H nmr (neat) 1.85–2.9 (multiplets, $2CH_2$), 3.12 (apparently a broad sextet and indicative of one proton split about equally by 5 protons, which would be consistent for the 2 proton of the indan nucleus in the proposed structure), 6.36 (d, =CH of substituent), 6.76 ppm (aromatic peak).

Anal. Calcd for $C_{13}H_{10}F_6$: C, 55.71; H, 3.60; F, 40.68. Found: C, 55.22; H, 3.83; F, 40.90.

2-(*p*-Methoxyphenyl)-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]thietane (Table II, no. 10) was converted to its 1,1-dioxide by heating 6.56 g (0.02 mol) in 25 ml of acetic acid with 6.2 ml (0.06 mol) of 30% hydrogen peroxide for 2 hr. Excess peroxide was destroyed by adding 5% Ru on C and the solvent was then evaporated from the filtered solution. Methanol was added to the cooled residue and the crystalline sulfone was filtered off and recrystallized from hexane to yield 4.7 g (72%), mp 97–97.5°.

Anal. Calcd for $C_{13}H_{10}F_6SO_3$: C, 43.33; H, 2.80; S, 8.90. Found: C, 43.29; H, 2.83; S, 9.03.

Synthesis of 10.—To 2.36 g (0.01 mol) of product no. 14, Table II, in 10 ml of dichloromethane was added 1.28 g of *p*-chloroaniline in 10 ml of dichloromethane. After 1 hr the solvent was evaporated and the residue was recrystallized from carbon tetrachloride to give 3.0 g (82%) of *p*-chloro-5,5,5-trifluoro-3-mercapto-4-(trifluoromethyl)-2-pentenanilide: mp 162.5–163°; ir 3226 (NH), 3040 (=CH), 1629, 1532 (*sec* amide), 1597, 1580, 1490 (C=C), 816 cm^{-1} (*para*-disubstituted aromatic band); ^1H nmr ($CDCl_3$) 3.72 [septuplet, $(CF_3)_2CH$], 6.31 (s, SH), 7.44 (s, =CH), 7.48 (A_2B_2 pattern, *p*-C_6H_4), 9.38 ppm (s, NH, removed by D_2O).

Anal. Calcd for $C_{12}H_8ClF_6NOS$: 39.63; H, 2.22; S, 8.82; mol wt, 364. Found: C, 39.49; H, 2.40; S, 8.66; mol wt, 389 (in $CHCl_3$ by vapor pressure osmometer).

Synthesis of 12.—On mixing 3.10 g (0.01 mol) of product no. 3, Table II, and 1.28 g (0.01 mol) of *p*-chloroaniline, the mixture became hot, liquified, and then crystallized. Recrystallization from ethanol gave 3.46 g (88%) of ethyl N-(*p*-chlorophenyl)-5,5,5-trifluoro-3-mercapto-4-(trifluoromethyl)-2-pentenimidate: mp 114–114.5°; ir 3067 (=CH), 3012, 2985, 2915 (C–H), 2558 (broad, hydrogen-bonded SH), 1645, 1575, 1560, 1499 (olefinic C=C, C=N, aromatic C=C), 831 cm^{-1} (*para*-disubstituted) aromatic; ^1H nmr (CCl_4) 1.46 (t, CH_3), 4.14 [quadruplet of ethyl CH_2 and septuplet of $(CF_3)_2CH$ superimposed], 7.20 (s, C_6H_4), 14.95 ppm (s, SH, removed by D_2O); ^{19}F nmr −2.62 ppm (d, $J = 8$ Hz).

Anal. Calcd for $C_{14}H_{12}F_6ClNOS$: C, 42.91; H, 3.09; S, 8.18. Found: C, 42.91; H, 3.24; S, 8.20.

Quadricyclene Adduct.[58]—To 7 g (0.076 mol) of quadricyclene (tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane)[59] in 10 ml of dichloromethane was added dropwise 15 g (0.077 mol) of bis(trifluoromethyl)thioketene. The temperature was kept at about 30° by cooling with ice. After the color of the thioketene had disappeared, the product was distilled to give 19.9 g (91%) of 4-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-3-thiatricyclo[4.2.1.0^{2,5}]non-7-ene: bp 93° (9 mm); $n^{25}{}_D$ 1.4655; ir 3077 (=CH), 2944, 2899 (saturated C–H), 1631 (exocyclic C=C), 1567 cm^{-1} (cyclic C=C); ^1H nmr (neat) 1.76 (center of AB pattern, bridge CH_2), 2.83 (s, 2 H, norbornene bridgeheads), 2.93 (s, H α to S), 3.33 [broad peak, H next to $(CF_3)_2C{=}C$ with splittings by F], 5.95 ppm (m, CH=CH); ^{19}F nmr (neat) −7.28, −9.30 ppm (quadruplets, components of latter split to doublets). A crude product prepared in CCl_4 had the same spectrum.

Anal. Calcd for $C_{11}H_8F_6S$: C, 46.15; H, 2.82; S, 11.20. Found: C, 46.51; H, 2.90; S, 11.42.

The compound did not isomerize when refluxed for 15 min at 226°.

---

(57) I. L. Knunyants, L. S. German, and B. L. Dyatkin, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 1353 (1956); *Bull. Acad. Sci. USSR*, Div. Chem. Sci., 1387 (1956).

(58) M. S. Raasch, U. S. Patent 3,406,184 (1968).

(59) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Amer. Chem. Soc.*, **83**, 4674 (1961).

7-Chloroquadricyclene Adduct.—The thioketene (8.73 g, 0.045 mol) was added to 7-chloroquadricyclene[60] (5.60 g, 0.045 mol) with occasional cooling. After the mixture had stood for 16 hr, it was scratched to induce crystallization and recrystallized from methanol to give 9.72 g (68%) of the 9-chloro derivative of the previous compound in four crops: mp 67–68°; ^{1}H nmr ($CDCl_3$) 3.25 (m, norbornene bridgehead protons plus H α to S), 3.67 (broad peak, H on the other thietane bridgehead with splittings by F), 4.95 (s, with evidence of splitting, bridge H), 6.20 ppm (m, CH═CH); ^{19}F nmr (CCl_4) −7.65, −9.80 (quadruplets, components of latter split to doublets).

Anal. Calcd for $C_{11}H_7ClF_6S$: C, 41.20; H, 2.20; S, 10.00. Found: C, 41.60; H, 2.36; S, 9.93.

7-Acetoxyquadricyclene Adduct.—To 5.60 g (0.037 mol) of 7-acetoxyquadricyclene[61] in 5 ml of dichloromethane was added 9.70 g (0.05 mol) of the thioketene with cooling. After 16 hr the mixture was cooled and 2.5 g of the thioketene dimer was filtered off. Distillation of the filtrate gave 8.85 g (66%) of the 9-acetoxy compound, bp 80–82° (0.12 mm), $n^{25}\mathrm{D}$ 1.4689. The product solidified in part and recrystallization from petroleum ether left 4.8 g: mp 44–45°; ^{1}H nmr ($CDCl_3$) 2.0 (s, CH_3), 3.25 (m, norbornene bridgehead protons plus H α to S), 3.58 (broad peak, H on the other thietane bridgehead, with splitting by F), 5.60 (s, broadened with indications of splitting, bridge H), 6.15 ppm (m, CH═CH); ^{19}F nmr (CCl_4) −7.75, −9.92 (quadruplets, components split to doublets).

Anal. Calcd for $C_{13}H_{10}F_6O_2S$: C, 45.34; H, 2.93; S, 9.31. Found: C, 45.31; H, 3.04 S, 9.30.

1,3-Thiazetidines. A. Di-*p*-tolylcarbodiimide Adduct.—To 6.66 g (0.03 mol) of di-*p*-tolylcarbodiimide in 25 ml of dichloromethane was added 6 g (0.03 mol) of bis(trifluoromethyl)thioketene. After 16 hr the solvent was allowed to evaporate and the residue was recrystallized from methanol to give 10.6 g (85%) of 3-*p*-tolyl-2-(*p*-tolylimino)-4-[2,2,2-trifluoro-1-(trifluoromethyl)-ethylidene]-1,3-thiazetidine: mp 83–84°; ir 1733 (C═N), 1629 (exocyclic C═C), 1603, 1511 (aromatic C═C), 820 cm^{-1} (*para*-disubstituted aromatic band); ^{19}F nmr ($CDCl_3$) −10.0, −14.1 ppm (quadruplets).

Anal. Calcd for $C_{19}H_{14}F_6N_2S$: C, 54.80; H, 3.39; S, 7.70; mol wt, 416. Found: C, 55.00; H, 3.42; S, 7.73; mol wt, 371 (ebullioscopic in 1,2-dichloroethane).

The above compound (5 g) was heated under reflux at 240° for 5 min. The product was steam distilled to give 2.2 g of *p*-tolyl isothiocyanate as an oil. Reaction of this with *p*-toluidine gave 4,4′-dimethylthiocarbanilide, identified by mp 178–180° and mixture melting point with an authentic sample.

B. Dicyclohexylcarbodiimide Adduct.—This thiazetidine was prepared and worked up in 92% yield as described for the *p*-tolyl analog: mp 56–56.5°; ir 1748 (C═N), 1626 cm^{-1} (C═C); ^{19}F nmr −10.9, 15.3 ppm (quadruplets, $J = 8$ Hz).

Anal. Calcd for $C_{17}H_{22}F_6N_2S$: C, 50.41; H, 5.54; S, 8.01; mol wt, 400. Found: C, 49.91; H, 5.28; S, 7.85; mol wt, 381, 369 (ebullioscopic in 1,2-dichloroethane).

C. Diisopropylcarbodiimide Adduct.—The thioketene was added directly to 1 equiv of the carbodiimide with cooling in ice. Distillation gave an 88% yield of the thiazetidine: bp 47–48° (0.15 mm); $n^{25}\mathrm{D}$ 1.4450; ^{1}H nmr (neat) 0.95 (d), 1.24 (d), 2.88, 3.79 ppm (centers of septuplets); ^{19}F nmr −9.80, −14.2 ppm (quadruplets).

Anal. Calcd for $C_{11}H_{14}F_6N_2S$: C, 41.25; H, 4.41; S, 10.01. Found: C, 41.42; H, 4.46; S, 10.50.

D. Benzalazine Adduct.—To 5.24 g (0.025 mol) of benzalazine in 50 ml of benzene was added 4.85 g (0.025 mol) of bis(trifluoromethyl)thioketene. After 16 hr, the solution was treated with decolorizing charcoal and the benzene was allowed to evaporate. The sticky mass of crystals remaining was washed with petroleum ether until free of benzalazine. The residual white crystals were recrystallized from methanol to give 1.6 g (19%) of 3-benzylideneamino-2-phenyl-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-thiazetidine: mp 136–138°; ir 3086, 3049 (═CH), 1653 (exocyclic C═C), 1610, 1567, 1504 (aromatic C═C), 785, 690 cm^{-1} (monosubstituted aromatic bands); ^{1}H nmr ($CDCl_3$) 6.37 (s, CH of thiazetidine ring), 7.2–7.7 ppm (m, C_6H_5 + C_6H_5CH═, this position for the CH is considered more likely for a 1,2 adduct than for a 1,4 adduct); ^{19}F nmr −12.1, −14.8 ppm (quadruplets, $J = 8$ Hz).

Anal. Calcd for $C_{18}H_{12}F_6N_2S$: C, 53.74; H, 3.01; S, 7.97; mol wt, 402. Found: C, 53.84; H, 3.05; S, 7.73; mol wt, 369 (ebullioscopic in 1,2-dichloroethane).

E. Cyclohexanoneazine Adduct.—Cyclohexanoneazine[62] (5.78 g, 0.03 mol) dissolved in 25 ml of petroleum ether was maintained at 10–15° while 8.0 g (0.04 mol) of bis(trifluoromethyl)thioketene was added. The solvent was allowed to evaporate and the residue was washed with cold methanol to leave 5.5 g of crystals of 3-cyclohexylideneamino-2-[2,2,2-trifluoro-1-(trifluoromethyl)-ethylidene]-1,3-thiaazaspiro[3.5]nonane. A small amount of this unstable compound could be recrystallized from nitromethane if done quickly, mp 99.5–100.5°, ir 1613 cm^{-1} (C═C).

Anal. Calcd for $C_{16}H_{20}F_6N_2S$: C, 49.72; H, 5.22; S, 8.30. Found: C, 49.65; H, 5.11; S, 8.29.

Addition to 2,3-Dimethylbutadiene.—Addition of 7.76 g (0.04 mol) of the thioketene to 3.61 g (0.044 mol) of 2,3-dimethylbutadiene with cooling in ice and distillation gave 9.3 g (84%) of 5,6-dihydro-3,4-dimethyl-6-[2,2,2-trifluoro-1-(trifluoromethyl) ethylidene]-2H-thiopyran (**15**): bp 96–98° (9 mm); $n^{25}\mathrm{D}$ 1.4503; ir 1570 (exocyclic C═C), 1376 cm^{-1} (C–CH_3); ^{1}H nmr (neat) 1.56 (s, 2CH_3), 3.05 ppm (s, broadened, 2CH_2); ^{19}F nmr −9.43, −13.0 ppm (quadruplets).

Anal. Calcd for $C_{10}H_{10}F_6S$: C, 43.47; H, 3.65; S, 11.60. Found: C, 43.69; H, 3.39; S, 11.28.

Norbornadiene Adduct.—2,5-Norbornadiene (3.68 g, 0.04 mol) and 7.76 g (0.04 mol) of bis(trifluoromethyl)thioketene were sealed in a glass tube and heated at 100° for 16 hr. The red liquid obtained was distilled at 106–110° (10 mm) and then crystallized in part. The crystals were filtered off and recrystallized from methanol to give 3.73 g (33%) of hexahydro-2-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-3,5,6-metheno-2H-cyclopenta[*b*]thiophene[58] (**16a**) in 3 crops: mp 53–53.5°; ir 1608 cm^{-1} (C═C); ^{1}H nmr (CCl_4) 1.25 to 1.75 (m, 3 cyclopropane H), 1.85 (s, CH_2, 2.39 (broadened peak, 1 H), 3.37 (m, 1 H), 3.52 ppm (quartet, 1 H); ^{19}F nmr −9.31, −11.9 ppm (quadruplets). The nmr shows absence of ═CH.

Anal. Calcd for $C_{11}H_8F_6S$: C, 46.15; H, 2.82; S, 11.20. Found: C, 46.43; H, 3.14; S, 10.99.

The foreshot from the distillation contained a small amount of an unsaturated purple thione. Although not obtained analytically pure by glpc, nmr and ir indicated that the compound was the result of the addition of the C═C bond of the thioketene across the 2,3 positions of norbornadiene.

Norbornadiene Adduct Sulfone.—The above compound (2.86 g, 0.01 mol) was heated at 100° for 4 hr with 20 ml of acetic acid and 3 ml of 30% hydrogen peroxide. Water (20 ml) was then slowly added and crystals separated. After cooling, the crystals were filtered off (3.02 g, 95%) and recrystallized from methanol containing a little water to give 2.93 g of the 1,1-dioxide, mp 124.5–125°; ir 1669 cm^{-1} (C═C).

Anal. Calcd for $C_{11}H_8F_6O_2S$: C, 41.52; H, 2.53; S, 10.08. Found: C, 41.54; H, 2.74; S, 10.01.

7-*t*-Butoxynorbornadiene Adduct.—7-*t*-Butoxy-2,5-norbornadiene[63] (13.02 g, 0.08 mol) and 15.52 g (0.08 mol) of the thioketene were heated in a sealed glass tube at 100° for 15 hr. The mixture was cooled, 5 ml of dichloromethane was added, and 6.9 g of the thioketene dimer was filtered off. The filtrate was distilled at 70° (0.05 mm) and the crystals in the distillate were rinsed with methanol cooled in Dry Ice. Recrystallization from methanol left 4.48 g (16%) of 4-*t*-butoxyhexahydro-2-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-3,5,6-metheno-2H-cyclopenta[*b*]thiophene (**16b**) in three crops, all melting at 72–73°: ^{1}H nmr (CCl_4) 1.2 [s, $(CH_3)_3$], 1.55 (m, 3 H), 2.20, 3.35 (broadened peaks, each 1 H), 4.02 ppm (m, 2 H); ^{19}F nmr −9.15, −11.9 ppm (quadruplets, components of latter split to doublets).

Anal. Calcd for $C_{15}H_{16}F_6OS$: C, 50.26; H, 4.50; S, 8.95. Found: C, 50.66; H, 4.60; S, 8.82.

Removal of methanol from the original rinse left 2.35 g of liquid which may have contained some of the other stereoisomer.

7-Chloronorbornadiene Adduct.—7-Chloro-2,5-norbornadiene (9 g, 0.07 mol) and 27 g of the thioketene were sealed in a glass tube and heated at 100° for 15 hr. The thioketene dimer (9 gm) was filtered off and rinsed with dichloromethane. Distillation of the filtrate gave 9.37 g (41%) of the 4-chloro compound (**16c**): bp 68–69° (0.15 mm); $n^{25}\mathrm{D}$ 1.4872; ^{1}H nmr (neat) 1.9 (m, 3 H),

---

(60) P. R. Story and S. R. Fahrenholtz, *J. Amer. Chem. Soc.*, **86**, 527 (1964).

(61) H. G. Richey, Jr., and N. C. Buckley, *ibid.*, **85**, 3057 (1963).

(62) A. N. Kost and I. I. Grandburg, *Zh. Obshch. Khim.*, **25**, 1719 (1955); *J. Gen. Chem. USSR*, **25**, 1673 (1955).

(63) Frinton Laboratories, South Vineland, N. J.

2.61 (s, 1 H), 3.5–4.4 ppm (m, 3 H); ^{19}F nmr −8.65, −10.4 ppm (quadruplets). The spectra do not show clear evidence of two isomers, but glpc over fluorosilicone on firebrick demonstrated a purity of 99.5% and an isomer ratio of 35:65 with retention times of 6.9 and 8.5 min.

Anal. Calcd for $C_{11}H_7ClF_6S$: C, 41.20; H, 2.20; S, 10.00. Found: C, 41.38; H, 2.37; S, 10.29.

Norbornadiene–Hexafluoroacetone Adduct (17).—A 200-ml flask with a thermometer in a side arm was equipped with a magnetic stirrer and a dropping funnel cooled with Dry Ice. The flask was cooled with an ice–salt bath and charged with 12 g (0.13 mol) of norbornadiene and 50 ml of dichloromethane. Through the dropping funnel was added in rapid drops 23 g (0.13 mol) of hexafluorothioacetone[28] in 50 ml of dichloromethane while the temperature in the flask was maintained at 8–10°. The thioketone was almost immediately decolorized. Distillation gave 8.7 g (25%) of 2,2-bis(trifluoromethyl)hexahydro-3,5,6-metheno-2H-cyclopenta[*b*]thiophene (**17**): bp 60° (1.5 mm); n^{25}D 1.4405; ^{1}H nmr (neat) 1.57 (m, 3 H), 1.80 (s, CH_2), 2.8 (m, H), 3.35 ppm (s, broad, 1 H); ^{19}F nmr −3.58, +2.62 ppm (quadruplets, J = 11 Hz).

Anal. Calcd for $C_{10}H_8F_6S$: C, 43.80; H, 2.94; S, 11.69. Found: C, 44.21; H, 3.26; S, 11.73.

Chlorination of 16a.—**16a** (1 g, 0.035 mol) and 0.47 g (0.0035 mol) of sulfuryl chloride formed a clear solution when mixed. Sulfur dioxide was evolved and the product crystallized on scratching. This was 2-chloro-6-[1-chloro-2,2,2-trifluoro-1-(trifluoromethyl)ethyl]hexahydro-3,5,6-metheno-2H-cyclopenta[*b*]-thiophene. The compound is sensitive to moisture. Warming with methanol caused replacement of Cl α to S with CH_3O. Cooling the methanol in Dry Ice caused 0.88 g (72%) of 2-methoxy compound (**18**) to crystallize out: mp 44.7–45.5°; ir no C=C; ^{1}H nmr (CCl_4) 1.48, 1.58 (2 peaks, 1st broadened, 2nd a triplet, 5 H), 2.43, 2.61 (broad peaks, each 1 H), 3.16 (1 H), 3.50 ppm (s, CH_3).

Anal. Calcd for $C_{12}H_{11}ClF_6OS$: C, 40.86; H, 3.14; Cl, 10.05. Found: C, 40.97; H, 3.21; Cl, 10.21.

Addition to Diazomethane.—A solution of 1.8 g (0.043 mol) of diazomethane[64] in 150 ml of ether was cooled in ice and 9.7 (0.05 mol) of bis(trifluoromethyl)thioketene was added dropwise with stirring. After all had been added, the ether was boiled off, the residue was cooled, and some of the thioketene dimer was filtered off and rinsed with dichloromethane. Distillation of the filtrate and rinse gave 8.0 g (79%) of two isomers, bp 65–67° (10 mm), n^{25}D 1.4000. The isomers were revealed by the ^{19}F nmr spectrum which showed a doublet at +1.06 ppm (59%) and another at 0 ppm (41%), both arising from $(CF_3)_2CH$. Separation was accomplished by glpc over 20% DC-200 silicone oil on Chromosorb P at 125°. Isomer **19** came at 11.7 min and **20** at 14.2 min. Compound **19** is 2-[2,2,2-trifluoro-1-(trifluoromethyl)-ethyl]-1,3,4-thiadiazole: n^{25}D 1.4004; ir 3115 (=CH), 1626, 1490 cm^{-1}; ^{1}H nmr (neat) 5.3 septuplet, $(CF_3)_2CH$], 8.8 ppm (s, no splitting, ring proton); ^{19}F nmr +1.03 ppm (d). Compound **20** is 5-[2,2,2-trifluoro-1-(trifluoromethyl)ethyl]-1,2,3-thiadiazole: n^{25}D 1.4002; ^{1}H nmr (neat) 5.4 ppm [septuplet, $(CF_3)_2CH$]; ir 3096 (=CH), 1458 cm^{-1}; ^{1}H nmr (neat) 5.4 [septuplet, $(CF_3)_2CH$], 9.7 ppm (d, J = 1 Hz, ring proton, shows CH–C=CH structure in this isomer); ^{19}F nmr −0.05 ppm (d).

Anal. Calcd for $C_5H_2F_6N_2S$: C, 25.43; H, 0.85; S, 13.57. Found for **19**: C, 25.53; H, 0.80; S, 13.87. Found for **20**: C, 25.71; H, 0.78; S, 13.73.

Hydrogen Azide Adduct.—To a mixture of 3.9 g (0.06 mol) of sodium azide, 4 ml of water, and 25 ml of dichloromethane was added 3 g (0.03 mol) of sulfuric acid with magnetic stirring at 10° or less. Sodium sulfate (6 g) was added for drying, and 19 ml (0.045 mol) of solution was decanted. To this was added 5.82 g (0.03 mol) of the thioketene with stirring and occasional cooling to keep the temperature at 20–30°. The solvent was allowed to evaporate at 25° to give 7.1 g (100%) of 5-[2,2,2-trifluoro-1-(trifluoromethyl)ethyl]-1,2,3,4-triazole (**22**). This very volatile solid was recrystallized from pentane: mp 60.5–61°; ir double bonds not evident, no evidence of azide; ^{1}H nmr (CCl_4) 5.32 ppm (septuplet); ^{19}F nmr −1.26 ppm (d).

Anal. Calcd for $C_4HF_6H_3S$: C, 20.26; H, 0.43; S, 13.53. Found: 20.58; H, 0.59; S, 13.43.

Benzonitrile Oxide Adduct.—To benzonitrile oxide in ether, prepared from 6.8 g (0.044 mol) of benzoyl chloride oxime[65] was added 8.5 g (0.044 mol) of the thioketene with cooling in ice. Evaporation of the ether gave 10.75 g of crystals which were recrystallized from methanol to give 9.3 g (68%) of 3-phenyl-5-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,4,2-oxathiazole in two crops: mp 98–99°; ir 3106, 3049 (=CH), 1618 (exocyclic C=C) 1587, 1548, 1497 (C=N and aromatic C=C), 770–715 cm^{-1} (monosubstituted aromatic); ^{1}H nmr (CCl_4) 7.5 ppm (m, C_6H_5); ^{19}F nmr −9.6 ppm (A_3B_3 pattern).

Anal. Calcd for $C_{11}H_5F_6NOS$: C, 42.18; H, 1.61; S, 10.24. Found: C, 42.51; H, 1.88; S, 10.34.

N-Methyl-α-phenylnitrone Adduct.—To 4.05 g (0.03 mol) of N-methyl-α-phenylnitrone[66] dissolved in 15 ml of dichloromethane and cooled in ice was added 5.82 g (0.03 mol) of the thioketene with stirring. The solvent was allowed to evaporate and the residue (9.7 g) was recrystallized from hexane to give 8.85 g (90%) of 2-methyl-3-phenyl-5-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,4,2-oxathiazolidine: mp 49.5–5.5; ir 1613 (exocyclic C=C), 1497 cm^{-1} (aromatic C=C); ^{1}H nmr (CCl_4) 2.95 (s, CH_3), 5.83 (s, CH), 7.60 ppm (s, C_6H_5); ^{19}F nmr −10.7 ppm (A_3B_3 pattern). Had the unlikely reverse addition across the thiocarbonyl group taken place, the ^{19}F nmr would show two well-separated quadruplets, and the CH would reveal coupling with F.

Anal. Calcd for $C_{12}H_9F_6NOS$: C, 43.76; H, 2.76; S, 9.73. Found: C, 43.70; H, 2.64; S, 9.68.

Reaction with N-Methoxy-α-phenylnitrone.—To 5.3 g (0.035 mol) of N-methoxy-α-phenylnitrone[67] in 10 ml of dichloromethane was added 6.8 g (0.035 mol) of the thioketene while cooling in ice to keep at 20°. During the addition the solution became cloudy as sulfur began to separate and gas was evolved. This gas was identified as $(CF_3)_2C{=}C{=}O$ by passing it into a solution of aniline in dichloromethane to form $(CF_3)_2CHCONHC_6H_5$, mp 171–172°, identical with an authentic sample. At the end of the reaction, 0.3 g of gummy sulfur was removed from the solution. The dichloromethane was boiled off and from the cooled residue 0.15 g of sulfur crystallized out. The liquid residue was distilled to give 2.33 g (49%) of O-methylbenzaldoxime, bp 79–82° (15 mm), n^{25}D 1.5410, identified by comparison of its nmr spectrum with that of an authentic sample prepared from methoxyamine and benzaldehyde.

Benzaldoxime Adduct.—A solution of 3.63 g (0.03 mol) of *syn*-benzaldoxime in 6 ml of dichloromethane and 24 ml of petroleum ether was cooled in ice and 5.82 g of the thioketene was added with stirring. The white, beautifully crystalline 3-phenyl-5-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,4,2-oxathiazolidine separated and was filtered off and rinsed with petroleum ether to yield 7.4 g (78%). If the compound is allowed to stand at 25° for about 30 min, it starts to turn yellow and suddenly disappears in a cloud of smoke with a hissing sound. It can be stored at −80° and showed ir 3185 (NH), 1621 (exocyclic C=C), 1587, 1499 (aromatic C=C), 770–715 cm^{-1} (monosubstituted aromatic).

Anal. Calcd for $C_{11}H_7F_6NOS$: C, 41.90; H, 2.24; S, 10.17. Found: C, 42.15; H, 2.33; S, 10.20.

By working rapidly, the nmr spectra in $CDCl_3$ were obtained: 6.05 (d, CH, J = 12 Hz), 6.53 (d, NH, J = 12 Hz), 7.48 ppm (s, C_6H_5) (when the solution was shaken with D_2O, the NH doublet disappeared and the CH doublet was converted to a singlet); ^{19}F nmr −10.4 ppm (A_3B_3 pattern as in the nitrone adducts).

***p*-Chlorobenzaldoxime Adduct.**—To 1.56 g (0.01 mol) of *syn*-*p*-chlorobenzaldoxime[68] in 15 ml of cold dichloromethane was added 1.94 g (0.01) of the thioketene. Petroleum ether (3.5 ml) was added and the solution was cooled in Dry Ice. The 3-*p*-chlorophenyl derivative was filtered off and washed with petroleum ether to yield 1.6 g (31%). It had about the same instability as the phenyl compound and a closely similar ^{1}H nmr spectrum.

Anal. Calcd for $C_{11}H_6ClF_6NOS$: S, 9.17. Found: S, 8.84.

Anisaldoxime Adduct.—The reaction was carried out as described for benzaldoxime. The 3-*p*-anisyl compound was much less stable and existed at 25° for only 5 min before suddenly decomposing.

---

[64] J. A. Moore and D. E. Reed, *Org. Syn.*, **41**, 16 (1961).

[65] G. W. Perold, A. P. Steyn, and F. V. K. von Reiche, *J. Amer. Chem. Soc.*, **79**, 462 (1957).

[66] O. L. Brady, F. P. Dunn, and R. F. Goldstein, *J. Chem. Soc.*, 2390 (1926).

[67] F. Arndt and J. D. Rose, *ibid.*, 6 (1935).

[68] H. Erdmann and E. Schwechtern, *Justus Liebigs Ann. Chem.*, **260**, 63 (1890).

Registry No.—Table I—1, 14970-97-9; 2, 14970-98-0; 3, 14971-00-7; 4, 24515-92-0; 5, 24515-93-3; 6, 18795-65-8; 7, 18795-63-6; 8, 18795-64-7; 9, 24515-97-7; 10, 18795-66-9; 11, 18795-62-5; 12, 24516-00-5; 13, 18174-52-2; 14, 18174-53-3; 15, 24516-03-8; 16, 24516-04-9; 17, 18174-54-4; 18, 19323-42-3; 19, 24514-62-3; 20, 18174-55-5; Table II—1, 23592-26-9; 2, 23592-27-0; 3, 23592-28-1; 4, 23592-30-5; 5, 23592-38-3; 6, 23592-31-6; 7, 23592-32-7; 8, 24514-71-4; 9, 23592-33-8; 10, 23592-34-9; 11, 23592-35-0; 12, 24514-75-8; 13, 23592-40-7; 14, 23592-36-1; 15, 23592-37-2; 16, 24514-79-2; **1**, 7555-16-0; **2**, 7445-61-6; ethyl 3,3,3-trifluoro-2-{4-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-dithietane-2-ylidene}propionate, 24515-27-3; 2,4-bis[2,2,2-trifluoro-1-(ethoxycarbonyl)ethylidene]-1,3-dithietane, 24515-15-9; **3**, 7445-60-5; **4**, 7555-17-1; **5**, 7592-88-3; 3,3-bis(chlorodifluoromethyl)-3H-diazirine, 24515-31-9; **6**, 24515-32-0; **7**, 24553-67-1; 2-(*p*-dimethylaminophenyl)-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-dithietane, 15008-38-5; 2-(*p*-diethylaminophenyl)-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-dithietane, 14970-99-1; 2-(*p*-dimethylaminostyryl)-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-dithietane, 24515-35-3; **14**, 24515-36-4; 2-[3,3,3-trifluoro-2-(trifluoromethyl)propenyl]indan, 24515-37-5; 2-(*p*-methoxyphenyl)-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]thietane 1,1,-dioxide, 23592-41-8; quadricyclene adduct with bis(trifluoromethyl)thioketene, 19438-57-4; 7-chloroquadricyclene adduct with bis(trifluoromethyl)thioketene, 24515-17-1; 7-acetoxyquadricyclene adduct with bis(trifluoromethyl)thioketene, 24515-18-2; 3-*p*-tolyl-2-(*p*-tolylimino)-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-thiazetidine, 24515-56-8; dicyclohexylcarbodiimide adduct with bis(trifluoromethyl)thioketene, 24515-57-9; diisopropylcarbodiimide adduct with bis(trifluoromethyl)thioketene, 24515-58-0; 3-benzylideneamino-2-phenyl-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-thiazetidine, 24515-59-1; 3-cyclohexylideneamino-2-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-thiaazaspiro[3.5]nonane, 24515-60-4; **15**, 7527-44-8; **16a**, 20877-47-8; **16a** dioxide, 20877-48-9; **16b**, 19441-45-3; **16c**, 20877-50-3; **17**, 24515-71-7; **18**, 24515-72-8; **19**, 24515-73-9; **20**, 24515-74-0; **22**, 24515-76-2; 3-phenyl-5-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,4,2-oxathiazole, 24515-77-3; 2-methyl-3-phenyl-5-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,4,2-oxathiazolidine, 24515-78-4; 3-phenyl-5-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,4,2-oxathiazolidine, 24515-80-8; 3-*p*-chlorophenyl-5-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,4,2-oxathiazolidine, 24515-81-9.

Acknowledgment.—The author is indebted to Drs. J. E. Carnahan, C. G. Krespan, B. C. McKusick, and W. A. Sheppard for helpful discussions; to Drs. H. Foster and G. S. Reddy, Mr. C. B. Matthews, and Mrs. Jean L. Read for nmr consultations; and to Misses Carol J. Hermann, Naomi E. Schlichter, and Ellen Wallace for ir and uv spectra interpretations.

Small Charged Rings. XII.[1] Aziridinium Ring Opening by Carboxylic Acids[2]

NELSON J. LEONARD AND DANIEL B. DIXON

Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois 61801

Received March 23, 1970

Polycyclic aziridinium salts have been found to react with carboxylic acids at elevated temperatures to give compounds possessing amine salt and ester functionality. The monocyclic aziridinium salt 5-azoniadispiro[4.0.5.1]dodecane perchlorate (**1**) was found to rearrange thermally before carboxylic acid addition occurred. The bicyclic aziridinium salt, 1,6-dimethyl-1-azoniabicyclo[4.1.0]heptane perchlorate (**4**), reacted with carboxylic acids, probably *via* a β-amino tertiary carbonium ion intermediate, to form an ammonium ester (**5**). The tri- and tetracyclic aziridinium salts, 1-azoniatricyclo[4.4.1.$0^{1,6}$]undecane perchlorate (**6**) and 1-azoniatetracyclo[7.3.2.$0^{1,13}$.$0^{5,13}$]tetradecane perchlorate (**8**), reacted "abnormally" at the aziridinium methylene to give ammonium esters of primary alcohols, *e.g.*, 6-acetoxymethyl-1-azabicyclo[4.4.0]decane perchlorate (**7a**) and 13-acetoxymethyl-1-azatricyclo[7.3.1.$0^{5,13}$]tridecane perchlorate (**9a**), respectively. The position of carboxylic acid reaction with the aziridinium ring was determined by following the nmr chemical shift of the methylene protons from the original aziridinium ring to the ammonium ester product, and then to the corresponding free amine ester.

Discovery of the reaction of diazomethane with ternary iminium perchlorates and fluoroborates to form aziridinium salts has made a variety of substituted aziridinium salts readily available and has permitted investigation of their chemistry.[3] Previous papers in the series have described the reaction of 1,1,2,2-tetrasubstituted aziridinium salts. The aziridinium salts have been found to undergo ring opening by solvolysis-type reaction at the more substituted ring carbon;[3b] nucleophilic displacement at the less hindered, less substituted ring carbon;[3b] thermal rearrangement;[3b] and ring opening and expansion *via* cycloaddition of aldehydes,[4] ketones,[5] nitriles,[6] and nitrones.[7] The solvolytic ring opening, ring expansion, and thermal

---

[1] For the preceding article in this series, see N. J. Leonard and D. A. Durand, *J. Org. Chem.*, **33**, 1322 (1968).

[2] We are pleased to acknowledge the support of the National Science Foundation by Research Grant GP-8407X.

[3] For pertinent references and general summaries of work in this field, see (a) N. J. Leonard, *Rec. Chem. Progr.*, **26**, 211 (1965), and (b) D. R. Crist and N. J. Leonard, *Angew. Chem.*, **81**, 953 (1969); *Angew Chem., Int. Ed. Engl.*, **8**, 962 (1969).

[4] N. J. Leonard, E. F. Kiefer, and L. E. Brady, *J. Org. Chem.*, **28**, 2850 (1963).

[5] N. J. Leonard, J. V. Paukstelis, and L. E. Brady, *ibid.*, **29**, 3383 (1964).

[6] N. J. Leonard and L. E. Brady, *ibid.*, **30**, 817 (1965).

[7] N. J. Leonard, D. A. Durand, and F. Uchimaru, *ibid.*, **32**, 3607 (1967).