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Bis(trifluoromethyl)thioketene. 3. Further Cycloadditions

Maynard S. Raasch

Central Research and Development Department,[1] Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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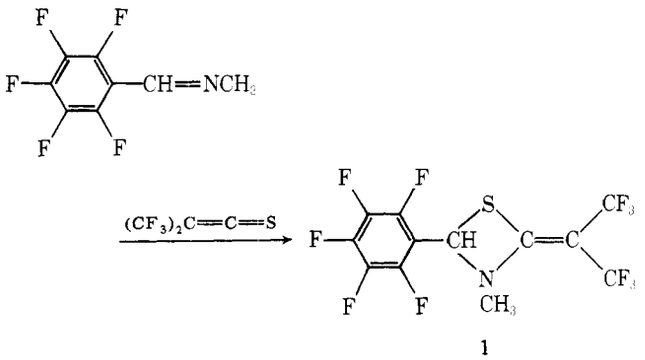
Bis(trifluoromethyl)thioketene cycloadds to Schiff bases to form thiazetidines and 1,3,5-dithiazines. Three moles of the thioketene adds to methyl isothiocyanate in a similar reaction. The thioketene adds to aryl azides to yield Δ^3-1,2,3,4-thiatriazolines which can be pyrolyzed to 2,1-benzisothiazoles. With phosphite esters, the thioketene forms phosphoranylidene-1,3-dithiolanes which hydrolyze to phosphonates. From certain methylbenzenes, substituted 1-phenethyl-3-hexafluoroisopropylidene-1,3-dithietanes are obtained. Novel heterocycles have been made by Diels–Alder reactions. Thiothiophthene forms adducts with 2 and 4 mol of the thioketene.

Previous articles have described the synthesis,[2a] cycloadditions,[2a] and acyclic derivatives[2b] of bis(trifluoromethyl)thioketene. The versatility of the thioketene as a reactant in a variety of cycloadditions is now further illustrated by its reaction with Schiff bases, aryl azides, phosphite esters, methylbenzenes, dienes, and thiothiophthene.

Cycloaddition to Schiff Bases. Both mono- and diadducts of bis(trifluoromethyl)thioketene with Schiff bases have been obtained. With *N*-(pentafluorobenzylidene)methylamine a 1,3-thiazetidine **1** is formed by a cycloaddition involving the thiocarbonyl group.

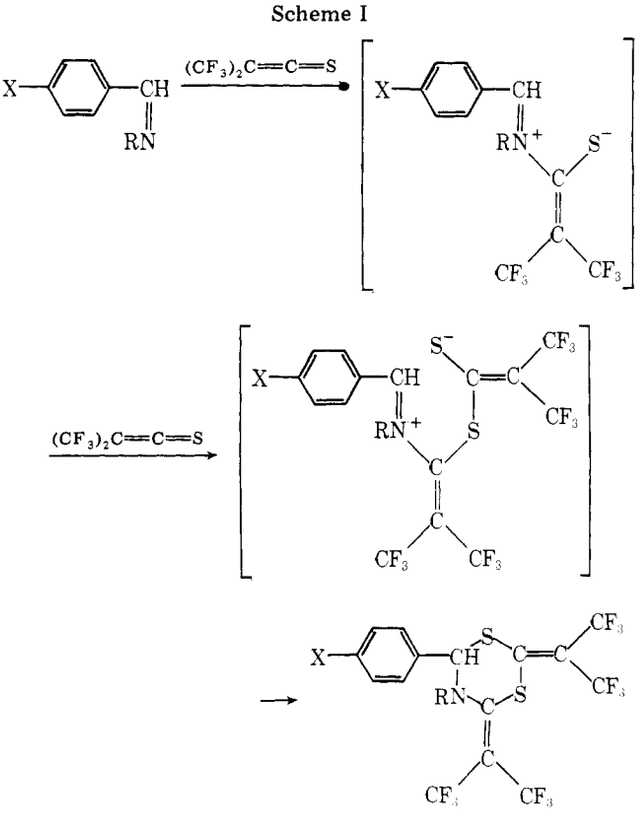


1

The structure was derived from IR and NMR data, with H–F and F–F couplings, as given in the Experimental Section. The mode of addition is analogous to the 1:1 reaction of the thioketene with carbodiimides to form 1,3-thiazetidines.[2a]

With ordinary arylideneamines, the reaction takes a different course and does not stop at the 1:1 stage even in the presence of excess Schiff base. Two molecules of the thioketene participate to form the 1,3,5-dithiazines **2** (Scheme I).

Scheme I



2a, X = H; R = CH_3
b, X = H; R = *i*-Pr
c, X = Cl; R = CH_3
d, X = O_2N; R = CH_3
e, X = CH_3O; R = *p*-$CH_3OC_6H_4$

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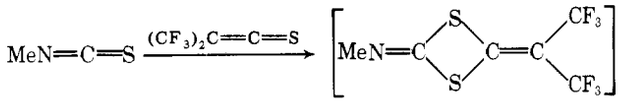
The mechanism is analogous to that proposed for the polymerization of the thioketene by Lewis bases,[2a] but here the process is terminated by cyclization.

Oxidation of **2a** with chromium trioxide in acetic acid yields $C_6H_5CON(CH_3)COCH(CF_3)_2$, prepared independently from *N*-methylbenzamide and $(CF_3)_2C{=}C{=}O$. This supports the sequence of atoms and substituents at positions 4, 5, and 6. The NMR analysis for **2a** is recorded in the Experimental Section.

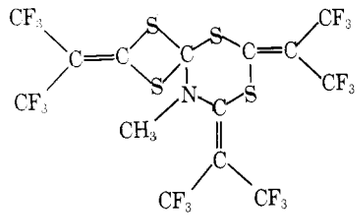
The asymmetric carbon atom in the 6 position is reflected in the ^1H NMR spectrum for **2b**, which shows a quartet for the methyl groups in $(CH_3)_2CH$ rather than a doublet.

In contrast to bis(trifluoromethyl)thioketene, hindered thioketenes are reported mainly to add to Schiff bases to form thiolactams by 2 + 2 cycloaddition of C=C to C=N.[10] In some cases, thiazetidine formation took place followed by cycloreversion to a thione and a ketenimine.

Addition to Methyl Isothiocyanate. Addition to aryl isothiocyanates to form 1,3-dithietanes was reported previously.[2a] With methyl isothiocyanate, three molecules of the thioketene add. The first step is probably analogous to the above reaction. The MeN=C double bond then functions as



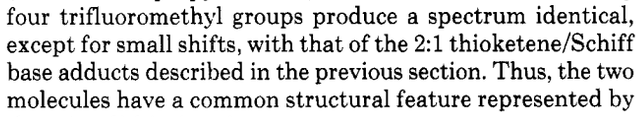
do the Schiff bases in the previous section because of the more basic nitrogen compared to ArN=C, and two more molecules of the thioketene add to form **3**.



3

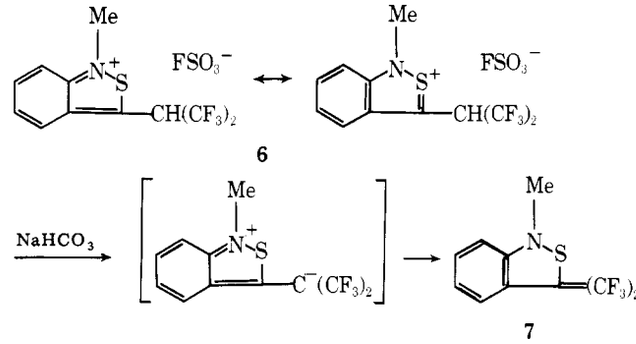
The $(CF_3)_2C{=}$ group on the left produces a singlet in the ^{19}F NMR spectrum as has been shown with many other 2-(hexafluoroisopropylidene)-1,3-dithietanes.[2a] The remaining four trifluoromethyl groups produce a spectrum identical, except for small shifts, with that of the 2:1 thioketene/Schiff base adducts described in the previous section. Thus, the two molecules have a common structural feature represented by the 1,3,5-dithiazine ring.

Addition to Aryl Azides. Aryl azides undergo 1,3-cycloaddition with bis(trifluoromethyl)thioketene to form yellow Δ^3-1,2,3,4-thiatriazolines **4a–e**. The ^{19}F NMR spectra show two quadruplets or an A_3B_3 pattern characteristic of $(CF_3)_2C{=}C$ attached to two different atoms, which indicates that addition to the thiocarbonyl group has occurred. The direction of addition is revealed by pyrolysis of the product to a 2,1-benzisothiazole, **5**. The 2,1-benzisothiazole structure



4a, X = H; Y = H
b, X = CH_3; Y = H
c, X = OMe; Y = H
d, X = Cl; Y = H
e, X = Cl; Y = Cl

Scheme II



6

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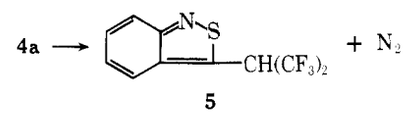
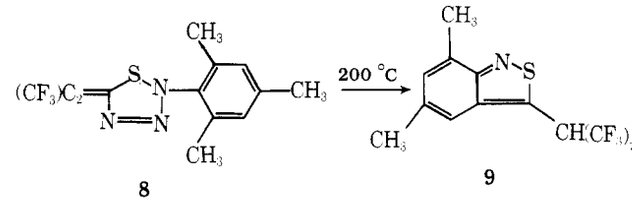


5

is supported by NMR data and reductive desulfuration with Raney nickel in ethanol to $2\text{-EtNHC}_6H_4CH_2CH(CF_3)_2$.[32] That the pyrolysis product was not 2-[2,2,2-trifluoro-1-(trifluoromethyl)ethyl]benzothiazole was demonstrated by the synthesis of this compound from 2-aminobenzenethiol and bis(trifluoromethyl)thioketene.

Methylation of **5** with methyl fluorosulfonate produces **6**. 2,1-Benzisothiazolium salts are known, but this one is converted to a substituted 1,3-dihydro-2,1-benzisothiazole (**7**) on treatment with base (Scheme II).

The pyrolysis was tried with a thiatriazoline (**8**) in which the ortho positions of the phenyl group were blocked by



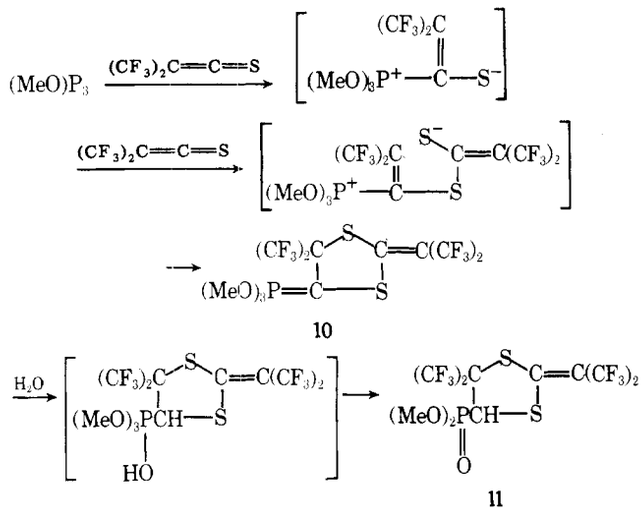
8 **9**

methyl groups. This, surprisingly, also gave a 2,1-benzisothiazole (**9**) with loss of the interfering methyl group. The loss of the methyl group is clearly shown by NMR. Since the yield was only 24%, the rest being tar, no clues to the mechanism were found.

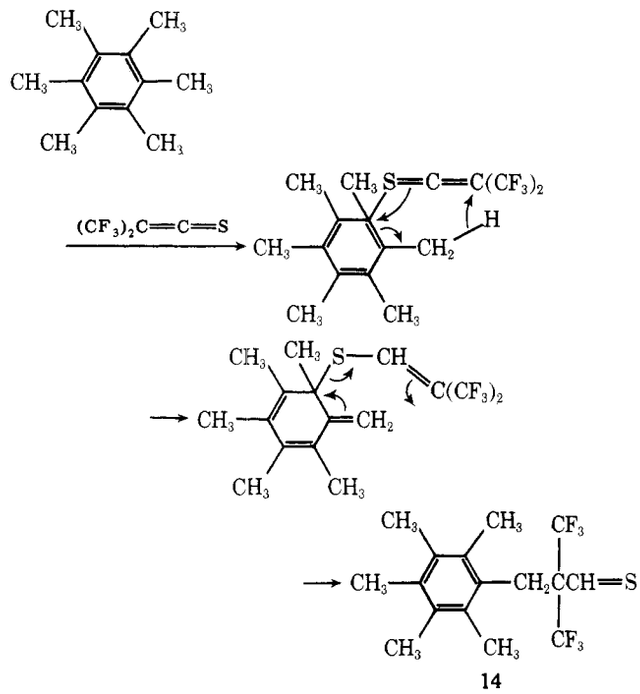
The formation of 1:1 $(CF_3)_2C{=}C{=}S$/azide adducts is accompanied by orange 2:1 adducts. These may also be formed by adding $(CF_3)_2C{=}C{=}S$ to the 1:1 adducts. The added molecule of $(CF_3)_2C{=}C{=}S$ produces a singlet in the NMR spectrum at a position for $(CF_3)_2$ attached to saturated carbon. The structure of the 2:1 adducts has not been established. In the mass spectrometer they break down to their components rather than providing definitive fragments.

Reaction with Phosphite Esters. Reaction of the thioketene with phosphite esters appeared to be a way to prepare a 1,4,2-dithiaphospholane, a ring system known only by a reference to it as an unstable intermediate in the reaction of chlorothioacetone with triethyl phosphite.[3] However, the cumulene structure of the thioketene made possible ring closure at a double bond, rather than at phosphorus, to form, with trimethyl phosphite, the water-sensitive phosphorus ylide **10** (Scheme III). Triphenyl phosphite also undergoes these reactions.

Scheme III



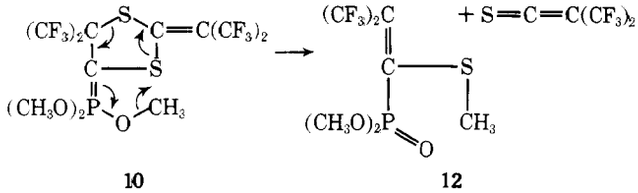
Scheme IV



When **10** is exposed to moist air, one methyl group is removed and there results the phosphonate **11** (Scheme III), which is relatively stable to hydrolysis. This may result from hydrolysis of a methoxy group followed by a proton shift from oxygen to carbon, or addition of water to P=C followed by loss of methanol. The ^1H NMR spectrum shows typical couplings of 19 Hz for HCP and 11 Hz for HCOP. Residence of the proton on carbon is further substantiated by the fact that the CF_3 groups in the 5 position now appear as a pair of quadruplets in the ^{19}F spectrum because one is cis and one is trans to the proton.

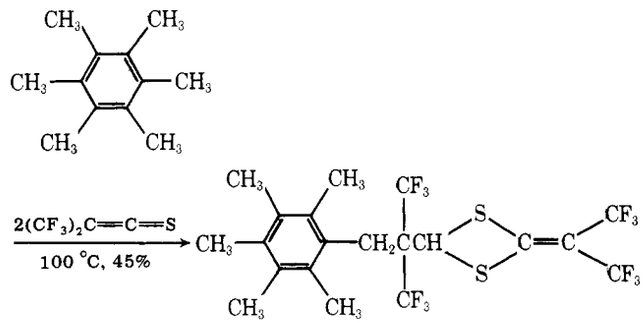
When **10** is subjected to vacuum distillation, it decomposes to **12**.

In contrast to the thioketene, hexafluorothioacetone and trimethyl phosphite form $(CF_3)_2C{=}P(OMe)_3$.[4] Thiofluorenone reacts in the same way,[4] while thiobenzophenone yields $(MeO)_3PS$, $Ph_2CHPO(OEt_2)$, $Ph_2CHSPO(OEt)_2$, and $Ph_2C{=}CPh_2$.[5] Thiocyclohexanone gives $(CH_2)_5C(SMe)PO(OMe)_2$ and $(CH_2)_5C(SH)PO(OMe)_2$.[6] Bis(trifluoromethyl)ketene and triethyl phosphite produce tetrakis(trifluoromethyl)allene.[7]



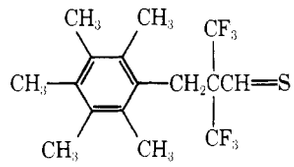
10 **12**

Addition to Methylbenzenes. Certain methylbenzenes add to the thioketene in an unusual reaction. With durene at 150 °C, a 54% yield of an analogous product was obtained, and with *p*-methylanisole at 150 °C the yield was 20%. Toluene and xylene were not reactive under these conditions.



13

The course of reaction might appear to be addition to C=C of the thioketene to form the intermediate thioaldehyde **14**,

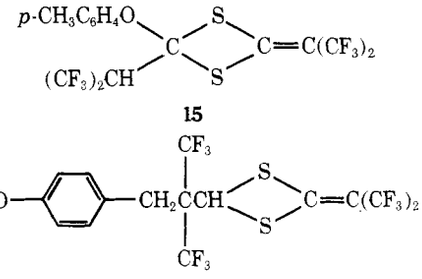


14

to which another molecule of the thioketene cycloadds to form the dithietane **13**. However, all other known reactions of the thioketene with organic compounds can be rationalized on the basis of addition to C=S. Hence, the following mechanism (Scheme IV) is proposed involving an initial ene reaction followed by rearrangement.[31] Ene reactions of the thioketene with aliphatic olefins have been amply demonstrated.[2b] Alkylbenzenes are known to undergo ene reactions with benzyne.[30]

A free-radical mechanism seems unlikely. The reaction proceeds just as well in the presence of the inhibitor 2,2-diphenyl-1-picrylhydrazyl, though the hydrazyl does not survive the heating period as such.

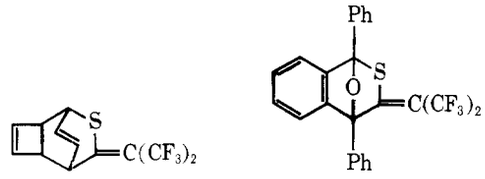
From the reaction of the thioketene with *p*-cresol at 100 °C, three compounds were isolated. The expected ester, $p\text{-}CH_3C_6H_4OCSCH(CF_3)_2$, was obtained in 35% yield. This added another mole of the thioketene to form the dithietane **15** (18%). Finally, a 1.7% yield of **16** was isolated, an analogue



15 **16**

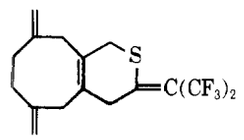
of the products obtained with the other methylbenzenes described above.

Diels–Alder Adducts. Diels–Alder adducts of the thioketene with 2,3-dimethylbutadiene[2a] and several cyclopentadienes[8,9] have been reported previously. The new heterocyclic ring systems **17**, **18**, and **19** have now been synthesized by reaction of the thioketene with cyclooctatetraene, 1,3-diphenylisobenzofuran, and 1,2,4,7-tetrakis(methylene)cyclooctane. Compound **17** represents the normal mode of Diels–Alder addition to cyclooctatetraene. Diels–Alder adducts have also been made from 6,6-diphenylfulvene, anthracene, pentamethyl-5-vinylcyclopentadiene, spiro[4.4]-nona-1,3-diene, butadiene, and 2,3-dichlorobutadiene. With 1,3-cyclohexadiene, both the Diels–Alder adduct **20** and the ene product **21** form.



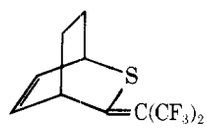
17

18

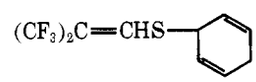


19

The cyclopentadiene adduct **22** has been progressively oxidized with *m*-chloroperbenzoic acid (Scheme V).



20, 54.5%



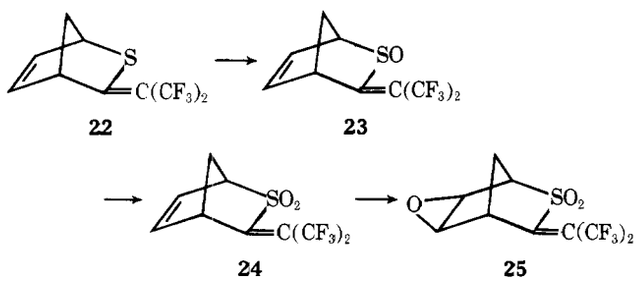
21, 45.5%

The sulfur atom does not interfere with catalytic hydrogenation. The cyclic double bond in **22** and the cyclobutene double bond in **17** have been reduced.

Thiothiophthene Adducts. Thiothiophthene has attracted interest since its structure was elucidated by X rays in 1958.[11,28] Bis(trifluoromethyl)thioketene (2 mol) reacts with thiothiophthene (2,5-dimethyl[1,2]dithiolo[1,5-*b*][1,2]dithiol-7-S^{IV}, **26**) to form a product with the same orange color as thiothiophthene. The ^{19}F NMR spectrum shows a doublet for $(CF_3)_2CH$ and a singlet for $(CF_3)_2C{=}C<$. This indicates thiothiophthene is acylated by the thioketene to form the intermediate **27** in Scheme VI, and that the second molecule of the thioketene cycloadds to the introduced, reactive thiocarbonyl group to form the dithietane **28**. The trithiapentalene system is not as reactive as a free thione group.[12] The reaction is comparable to the thioacylation of indole with the thioketene.[2b]

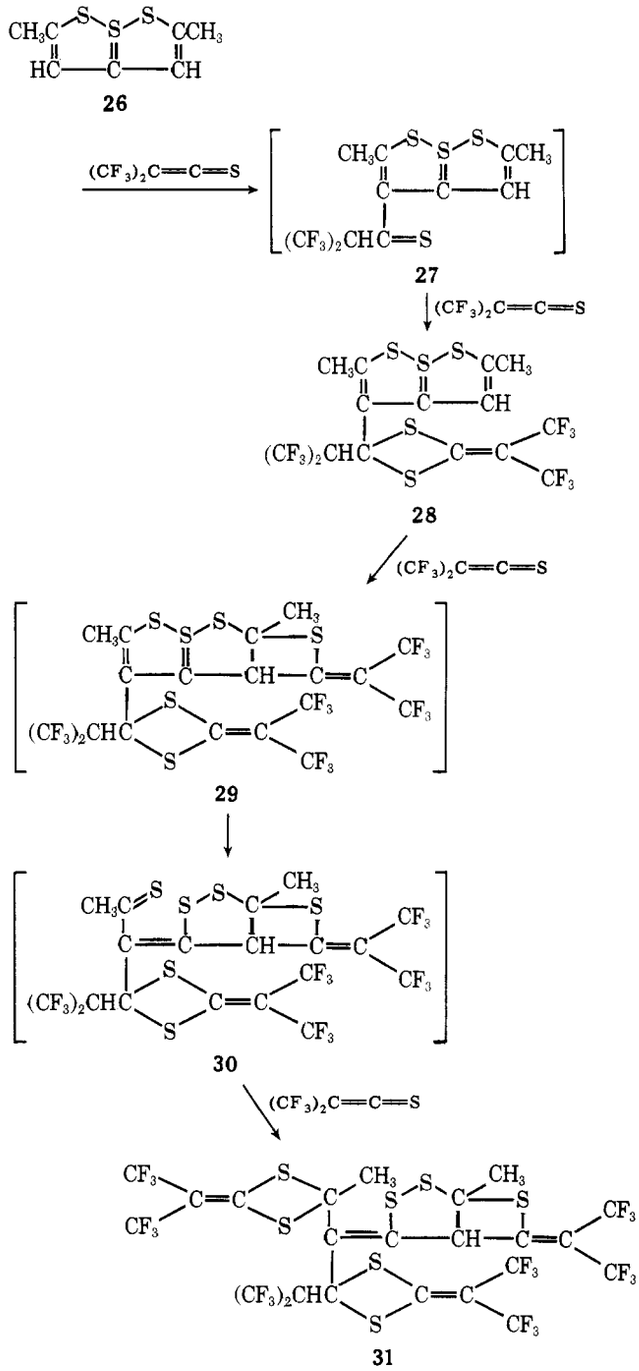
The compound **28** reacts with an additional 2 mol of the thioketene to form a white compound. The CH= absorption in the ^1H NMR spectrum is replaced by an upfield peak. This suggests thietane formation by cycloaddition of the thioketene to $-CH{=}C(CH_3)S-$ in the way the thioketene does to simple vinyl thioethers.[2a] Correlative to the shift of the proton peak is an A_3B_3 pattern at the proper shift for $(CF_3)_2C{=}$ in the ^{19}F spectrum. The addition would logically take place on the more electron-rich, less-hindered double bond not attached to the polyfluoro group to form the intermediate **29**. This cycloaddition disrupts the trithiapentalene system and bond rearrangement is postulated to take place to produce the intermediate conjugated thione **30**. The fourth molecule of the thioketene then reacts with the thiocarbonyl group of **30** to form another dithietane unit, which is indicated by an additional singlet at the proper shift in the ^{19}F NMR spectrum. A Raman spectrum band at 505 cm^{-1} is assigned to the disulfide link. Thus, **31** or its geometric isomer is proposed as the structure of the tetraadduct.

Scheme V



22 **23** **24** **25**

Scheme VI



26 **27** **28** **29** **30** **31**

Experimental Section

The ^1H NMR spectra were determined in Varian instruments using Me_4Si as internal reference. The ^{19}F NMR spectra were measured in a Varian A-56/60 instrument using CCl_2FCCl_2F as reference in a capillary placed in the sample tube. This standard is 3800 Hz (67.4 ppm) upfield from CCl_3F. The ^{13}C spectra, using Me_4Si as internal standard, and ^{31}P spectra, using H_3PO_4 in a capillary as reference, were taken on Bruker spectrometers. All downfield values are recorded as positive. A Perkin-Elmer Model 21 spectrometer was used for IR spectra. Raman spectra were taken on a Cary 81 laser spectrometer. Melting and boiling points are uncorrected.

For brevity, hexafluoroisopropylidene is used for $(CF_3)_2C=$ instead of the Chemical Abstracts name, 2,2,2-trifluoro-1-(trifluoromethyl)-ethylidene.

Addition to Schiff Bases. A. *N*-(Pentafluorobenzylidene)-methylamine. *N*-(Pentafluorobenzylidene)methylamine was prepared by stirring 6.5 g of pentafluorobenzaldehyde[13] with 10 mL of aqueous 40% methylamine solution for 16 h. A solid was filtered off and the liquid Schiff base in the filtrate was dissolved in dichloromethane, dried ($MgSO_4$), and distilled to give 2.98 g (43%); bp 55 °C (5 mm); $n^{25}D$ 1.4532; ^1H NMR ($CDCl_3$) 3.63 (s, CH_3), 8.41 ppm (m, CH).

Anal. Calcd for $C_8H_4F_5N$: C, 45.95; H, 1.93; N, 6.70. Found: C, 45.90; H, 2.30; N, 6.96.

To 1.05 g (0.005 mol) of the Schiff base in 10 mL of hexane was added 1.94 g (0.01 mol) of bis(trifluoromethyl)thioketene.[2a] The product precipitated and was filtered from the cooled mixture. Recrystallization from carbon tetrachloride–hexane gave 1.59 g (79%) of 2-(hexafluoroisopropylidene)-3-methyl-4-(pentafluorophenyl)-1,3-thiazetidine (**1**): mp 66.7–67.5 °C; IR 2967 (CH), 1631 (exocyclic C=C), 1515 cm^{-1} (aromatic C=C); ^1H NMR ($CDCl_3$) 2.82 (quadruplet, J = 2.6 Hz, CH_3), 6.21 ppm (s, broadened, CH); ^{19}F NMR 11.54 (quadruplet, J = 9.1 Hz, components split to doublets by CH, J = 1.2 Hz, with further splitting by CH_3, J = 0.5 Hz), 17.90 ppm (quadruplet, J = 9.1 Hz, components split to quadruplets by CH_3, J = 2.6 Hz, components split to doublets by CH, J = 1.3 Hz).

The two CF_3–CH_3 couplings, 0.5 and 2.6 Hz, support the structure given rather than the structure obtained by reverse addition. The two CF_3–CH couplings, 1.2 and 1.3 Hz, are consistent for a proton nearly symmetrically disposed with respect to the CF_3 groups.

Anal. Calcd for $C_{12}H_4F_{11}NS$: C, 35.74; H, 1.00; N, 3.48. Found: C, 35.97; H, 1.04; N, 3.51.

B. *N*-Benzylidenemethylamine. Bis(trifluoromethyl)thioketene (7.76 g, 0.04 mol) was slowly added to a stirred solution of 4.76 g (0.04 mol) of *N*-benzylidenemethylamine in 20 mL of petroleum ether cooled in ice. The product precipitated out and was filtered off (8.5 g). Recrystallization from carbon tetrachloride left 8.1 g (78%) of 2,4-bis(hexafluoroisopropylidene)-5,6-dihydro-5-methyl-6-phenyl-4*H*-1,3,5-dithiazine (**2a**): mp 162–162.8 °C; IR 3049 (=CH), 2941 (CH), 1575, 1548, 1502 cm^{-1} (C=C); ^1H NMR [$(CD_3)_2CO$] 2.65 (s, CH_3), 6.5 (s, CH), 7.1 ppm (Ph); ^{19}F NMR ($CDCl_3$) 9.30 (quadruplet, J = 8 Hz), 10.3 (quadruplet, J = 9 Hz), 11.4 and 13.5 ppm (ten-line patterns). Decoupling, which reduced the ten-line peaks to quadruplets, showed the 9.3-ppm peak to be coupled with 13.5 ppm and 10.3 ppm with 11.4 ppm. The latter two closely spaced peaks are assigned to $(CF_3)_2C=$ in the 2 position where the CF_3 groups are in a similar environment. The ten-line peaks result from F–F coupling (J = 4.5 Hz) between one CF_3 group in the 2 position with one in the 4 position. Coupling between CH_3 and one CF_3 is 1.3 Hz: ^{13}C NMR 40.7 (NCH_3), 70 (6-C in ring), 78, 93.9 [$(CF_3)_2C$], 116.4, 128.9 (CF_3), 152.4, 157.7 ppm (2- and 4-C in ring).

Anal. Calcd for $C_{16}H_9F_{12}NS_2$: C, 37.88; H, 1.79; S, 12.64. Found: C, 37.94; H, 1.90; S, 12.61.

C. *N*-Benzylideneisopropylamine. The adduct **2b** was prepared as above from *N*-benzylideneisopropylamine[14] in 52% yield: mp 138–139 °C; ^1H NMR ($CDCl_3$) 1.49 (d, J = 6.4 Hz, split to d's, J = 4.2 Hz, 2 CH_3), 4.38 (septuplet, CH), 5.93 (s, PhC**H**), 7.48 ppm (m, C_6H_5); ^{19}F NMR 10.13, 10.88 (quadruplets, 2 CF_3), 11.47, 14.94 ppm (m's, 2 CF_3).

Anal. Calcd for $C_{18}H_{13}F_{12}NS_2$: C, 40.47; H, 2.46; S, 11.98. Found: C, 40.35; H, 2.98; S, 12.00.

D. *N*-(4-Chlorobenzylidene)methylamine. The bis(trifluoromethyl)thioketene adduct **2c** of this Schiff base[15] was prepared as above in 60% yield: mp 143–144 °C; ^1H NMR (CCl_4) 3.03 (s, CH_3), 6.7 (s, CH), 7.65 ppm (4 H, aromatic).

Anal. Calcd for $C_{16}H_8ClF_{12}NS_2$: C, 35.47; H, 1.49; S, 11.84. Found: C, 35.10; H, 1.66; S, 11.80.

E. *N*-(4-Nitrobenzylidene)methylamine. Bis(trifluoromethyl)thioketene (3.88 g, 0.03 mol) was added to 1.64 g (0.01 mol) of *N*-(4-nitrobenzylidene)methylamine[16] in dichloromethane cooled in ice. The solvent was evaporated and the residue was recrystallized three times from carbon tetrachloride to give the adduct **2d**: mp 150–151 °C.

Anal. Calcd for $C_{16}H_8F_{12}N_2O_2S_2$: C, 34.80; H, 1.46; S, 11.61. Found: C, 34.88; H, 1.56; S, 11.63.

F. *N*-(4-Methoxybenzylidene)-4-methoxyaniline. To 2.41 g (0.01 mol) of the Schiff base[17] in 20 mL of dichloromethane was added 1.94 g (0.01 mol) of the thioketene. The solvent was removed and the crystals that slowly formed were washed with methanol to give 2.42 g of **2e**. Recrystallization from hexane left 1.94 g (62%): mp 122–123 °C; ^1H NMR ($CDCl_3$) 3.79 (s, CH_3), 3.82 (s, CH_3), 6.45 ppm (s, CH); ^{19}F NMR 8.50, 10.7 (quadruplets), 11.9, 13.1 ppm (m's).

Anal. Calcd for $C_{23}H_{15}F_{12}NO_2S_2$: C, 43.88; H, 2.40; S, 10.19. Found: C, 44.12; H, 2.56; S, 10.16.

Oxidation of 2a. To 5.07 g (0.01 mol) of **2a** in 100 mL of acetic acid was added 7 g (0.07 mol) of chromium trioxide with stirring. After the mixture became cool, it was poured into 500 mL of water and the solid was filtered off and dried. The product (2.3 g) was recrystallized twice from hexane to leave 1.35 g (43%) of *N*-methyl-*N*-[3,3,3-trifluoro(2-trifluoromethyl)]propionylbenzamide: mp 56–57.2 °C; IR 3012 (=CH), 1712, 1695 (C=O), 1600, 1580, 1493 cm^{-1} (aromatic C=C); ^1H NMR ($CDCl_3$) 3.29 (s, CH_3), 5.46 [septet, $(CF_3)_2CH$], 7.66 ppm (m, C_6H_5); ^{19}F NMR 3.68 ppm (d, J = 7.5 Hz).

Anal. Calcd for $C_{12}H_9F_6NO_2$: C, 46.01; H, 2.90; N, 4.47. Found: C, 45.73; H, 2.94; N, 4.43.

The oxidation product was synthesized independently by passing $(CF_3)_2C=C=O^{18}$ into a solution of *N*-methylbenzamide in dichloromethane: mp 57–58 °C; ^1H NMR identical with above.

Addition to Methyl Isothiocyanate. Methyl isothiocyanate (1.46 g, 0.02 mol) and 3.88 g (0.02 mol) of bis(trifluoromethyl)thioketene were mixed and occasionally cooled in ice. After 30 min the product was recrystallized from carbon tetrachloride to give 2.25 g (52%) of **3**; mp 121.5–122.5 °C; IR 2994, 2941 (CH), 1629, 1592, 1560 (C=C), 1433 cm^{-1} (NCH_3); ^1H NMR (CCl_4) 3.23 ppm (s, CH_3); ^{19}F NMR 7.94 (quadruplet, J = 8.7 Hz, components split to quadruplets by CH_3, J = 1.2 Hz), 8.92 [s, $(CF_3)_2C=$], 9.79 (quadruplet, J = 9.3 Hz), 11.1, 12.5 ppm (ten-line patterns). Decoupling showed the 7.94-ppm peak to be coupled with 12.5 ppm and 9.79 ppm with 11.1 ppm.

Anal. Calcd for $C_{14}H_3F_{18}NS_4$: C, 25.66; H, 0.46; S, 19.58; mol wt. 655. Found: C, 25.64; H, 0.67; S, 19.60; mol wt (ebullioscopic), 655 (in acetone), 696 (in $ClCH_2CH_2Cl$).

Addition to Aryl Azides. A. Phenyl Azide. To 17.5 g (0.147 mol) of phenyl azide[19] in 100 mL of petroleum ether was added 28.5 g (0.147 mol) of bis(trifluoromethyl)thioketene. The solution was allowed to stand for 6 days and 13.1 g of yellow crystals was filtered off. Recrystallization from methanol left 12.2 g (26.5%) of yellow 5-(hexafluoroisopropylidene)-2-phenyl-Δ^3-1,2,3,4-thiatriazoline (**4a**): mp 125–125.5 °C; IR 3115, 3040 (=CH), 1667 (w), 1590, 1565, 1497 (C=C), 769–714 cm^{-1} (monosubstituted phenyl); ^1H NMR ($CDCl_3$) 7.73 ppm (s, C_6H_5); ^{19}F NMR 10.20, 11.08 ppm [quadruplets, $(CF_3)_2C=C<$].

Anal. Calcd for $C_{10}H_5F_6N_3S$: C, 38.34; H, 1.61; S, 10.24. Found: C, 38.71; H, 1.85; S, 10.54.

The petroleum ether filtrate was allowed to evaporate at room temperature. The crystalline residue was rinsed with cold methanol to give 10.5 g of orange crystals. Recrystallization from methanol left 8.1 g (22%): mp 80–81 °C; IR 3077 (=CH), 1634 (shoulder), 1587, 1572, 1493 cm^{-1} (C=C); ^1H NMR (CCl_4) 7.6–8.2 ppm (broad, split band, C_6H_5); ^{19}F NMR 0.21 (s, 2 CF_3), 9.54, 9.98 ppm (quadruplets, $(CF_3)_2C=C<$]. This compound is the thioketene/azide 2:1 adduct. It was also made by adding $(CF_3)_2C=C=S$ to the 1:1 adduct above in dichloromethane.

Anal. Calcd for $C_{14}H_5F_{12}N_3S_2$: C, 33.16; H, 0.99; S, 12.34. Found: C, 33.59; H, 1.31; S, 12.59.

B. Addition to *p*-Tolyl Azide.[20] The reaction was carried out with *p*-tolyl azide[17] as described for phenyl azide to give 35% of yellow **4b**: mp 124.5–125 °C; ^1H NMR ($CDCl_3$) 2.41 (s, CH_3), 7.57 ppm (AA'BB', *p*-C_6H_4); ^{19}F NMR 9.66, 10.57 ppm [quadruplets, $(CF_3)_2C=C$].

Anal. Calcd for $C_{11}H_7F_6N_3S$: C, 40.43; H, 2.16; N, 12.86; S, 9.80. Found: C, 40.48; H, 2.31; N, 12.70; S, 9.72.

The orange 2:1 adduct (6%) melted at 77.5–78.5 °C; ^1H NMR ($CDCl_3$) 2.45 (s, CH_3), 7.55 ppm (AA'BB', *p*-C_6H_4).

Anal. Calcd for $C_{15}H_7F_{12}N_3S_2$: C, 34.56; H, 1.35; S, 12.30. Found: C, 34.81; H, 1.51; S, 12.51.

C. 4-Methoxyphenyl Azide. To 5.47 g (0.03 mol) of 4-methoxyphenyl azide[21,22] in 15 mL of hexane was added 5.82 g (0.03 mol) of bis(trifluoromethyl)thioketene. After 16 h, 5.82 g (57%) of yellow **4c** was filtered off. Recrystallization from methanol left 4.53 g: mp

113–113.7 °C; ^{19}F NMR (CCl_4) 10.21, 10.92 ppm [A_3B_3, $(CF_3)_2C{=}C$].

Anal. Calcd for $C_{11}H_7F_6N_3OS$: C, 38.48; H, 2.06; S, 9.34. Found: C, 38.81; H, 2.15; S, 9.15.

Evaporation of the hexane filtrate gave 0.44 g (5.5%) of the orange 2:1 adduct. Recrystallization from methanol left 0.27 g: mp 117.5–118 °C; ^{1}H NMR (CCl_4) 3.80 (s, CH_3), 7.32 ppm (aromatic AA'BB' pattern); ^{19}F NMR 0.25 (s, 2 CF_3), 8.42, 8.63 ppm [quadruplets, $(CF_3)_2C{=}C<$].

Anal. Calcd for $C_{15}H_7F_{12}N_3OS_2$: C, 33.52; H, 1.31; S, 11.93. Found: C, 33.81; H, 1.47; S, 11.29.

D. 4-Chlorophenyl Azide. A solution of 4.61 g (0.03 mol) of 4-chlorophenylazide[21,22] and 5.82 g (0.03 mol) of bis(trifluoromethyl)-thioketene in 8 mL of hexane was allowed to stand for 4 days and then filtered to give 3.6 g of a mixture of the 1:1 and 2:1 adducts. Recrystallization from hexane gave 1.5 g (14.4%) of yellow **4d**: mp 119–119.5 °C; ^{19}F NMR ($CHCl_3$) 10.25, 10.57 ppm [quadruplets, $(CF_3)_2C{=}C<$].

Anal. Calcd for $C_{10}H_4ClF_6N_3S$: C, 34.54; H, 1.16; S, 9.22. Found: C, 34,56; H, 1.26; S, 8.93.

The original filtrate and the recrystallization filtrate were combined and allowed to evaporate. The recovered crystals were recrystallized from methanol to give 2.01 g (25%) of the orange 2:1 adduct: mp 102.5–103 °C; ^{19}F NMR (CCl_4) 0.39 (s, 2 CF_3), 9.52, 9.89 ppm [quadruplets, $(CF_3)_2{=}C<$].

Anal. Calcd for $C_{14}H_4ClF_{12}N_3S_2$: C, 31.06; H, 0.75; S, 11.85. Found: C, 30.93; H, 0.94; S, 11.15.

E. 3,4-Dichlorophenyl Azide. A solution of 0.03 mol each of 3,4-dichlorophenyl azide (mp 32 °C) and bis(trifluoromethyl)thioketene in 13 mL of hexane was filtered after 4 days to give 0.46 g (4%) of yellow **4e**: mp 116.5–117 °C from methanol; ^{19}F NMR ($CDCl_3$) 10.25 ppm [A_3B_3 pattern]. At 0 °C this became quadruplets at 10.76 and 11.65 ppm [$(CF_3)_2C{=}C<$].

Anal. Calcd for $C_{10}H_3Cl_2F_6N_3S$: C, 31.40; H, 0.79; S, 8.38. Found: C, 31.73; H, 1.00; S, 8.27.

The solvent from the original hexane filtrate was allowed to evaporate, the residue was stirred with cold methanol, and 2.48 g (29%) of the orange 2:1 adduct was filtered off. Recrystallization from methanol left 1.75 g (20%): mp 96.5–97 °C; ^{19}F NMR (CCl_4) 0.62 (s, 2 CF_3), 9.75, 10.07 ppm [A_3B_3, $(CF_3)_2C{=}C<$].

Anal. Calcd for $C_{14}H_3Cl_2F_{12}N_3S_2$: C, 29.18; H, 0.52; S, 11.13. Found: C, 29.27; H, 0.66; S, 11.14.

F. 2,4,6-Trimethylphenyl Azide. A solution of 1.61 g (0.01 mol) of 2,4,6-trimethylphenyl azide[23] in 5 mL of hexane and 1.94 g (0.01 mol) of bis(trifluoromethyl)thioketene deposited 1.44 g (41%) of yellow **8** after 1 day: mp 126.7–127.2 °C from methanol; ^{1}H NMR ($CDCl_3$) 2.03 (s, 2,6-Me_2), 2.28 (s, 4-Me), 6.93 ppm (s, 3,5-H_2); ^{19}F NMR 10.28, 10.78 ppm [quadruplets, $(CF_3)_2C{=}C<$].

Anal. Calcd for $C_{13}H_{11}F_6N_3S$: C, 43.94; H, 3.12; N, 11.83; S, 9.02. Found: C, 43.69; H, 3.03; N, 11.85; S, 9.40.

Thermal Decomposition of Thiatriazolines. A. 3-[2,2,2-Trifluoro-1-(trifluoromethyl)ethyl]-2,1-benzisothiazole (5). A test tube was placed in an oil bath heated to 210 °C and **4a** (7 g) was added to the tube in portions, each of which decomposed with a puff. The product was cooled and recrystallized from hexane to give 4.7 g (75%) of silky, white needles of the 2,1-benzisothiazole: mp 73.5–74.5 °C; IR 3077 (=CH), 2941 (CH), 742 cm^{-1} (ortho-substituted aromatic); ^{1}H NMR (CCl_4) 5.08 ppm [septuplet, J = 8 Hz, $(CF_3)_2CH$]; ^{19}F NMR 1.06 ppm (d).

Anal. Calcd for $C_{10}H_5F_6NS$: C, 42.11; H, 1.77; S, 11.25; mol wt, 285. Found: C, 42.52; H, 1.83; S, 11.29; mol wt, 285 (mass spectrum).

B. 5-Methyl-3-[2,2,2-trifluoro-1-(trifluoromethyl)ethyl]-2,1-benzisothiazole.[20] Pyrolysis of **4b** was carried out at 180 °C as described for the phenyl compound. The product (48%) melted at 89.5–91.5 °C; ^{1}H NMR ($CDCl_3$) 2.48 (s, CH_3), 4.99 [septuplet, $(CF_3)_2CH$], 7.26–7.85 ppm (3 H, aromatic).

Anal. Calcd for $C_{11}H_7F_6NS$: C, 44.14; H, 2.36; S, 10.71. Found: C, 44.54; H, 2.57; S, 10.39.

C. 5,7-Dimethyl-3-[2,2,2-trifluoro-1-(trifluoromethyl)ethyl]-2,1-benzoisothiazole. **8** (3.4 g) was decomposed at 200 °C as described above. The product was steam-distilled to give an oil which was collected with dichloromethane and dried ($MgSO_4$). Removal of the solvent left 1.6 g, mostly crystalline. Recrystallization from hexane left 0.72 g (24%) of the 2,1-benzoisothiazole **9**: mp 99–100 °C; IR 2924 (CH), 1634, 1541, 1517 cm^{-1} (C=C, C=N); ^{1}H NMR (CCl_4) 2.30 (s, Me), 2.55 (s, Me), 4.82 [septuplet, J = 8 Hz, $(CF_3)_2CH$], 6.94 (s, 6-H), 7.12 ppm (s, 4-H); ^{19}F NMR 1.08 ppm (d, J = 8 Hz).

Anal. Calcd for $C_{12}H_9F_6NS$: C, 46.01; H, 2.90; N, 4.47; S, 10.24. Found: C, 45.86; H, 2.72; N, 4.67; S, 10.60.

Desulfurization of 5. A mixture of 2.35 g of **5**, 85 mL of absolute alcohol, and 20 g of Raney nickel was refluxed for 15 h and then filtered. Hydrochloric acid (1 mL) was added and the solution was evaporated to a glass. The residue was taken up in 10% hydrochloric acid, filtered, and made alkaline with sodium carbonate. The product was extracted with ether which was dried ($MgSO_4$) and evaporated to leave 1.24 g of an oil. This was purified by GLC over silicone gum rubber SE-30 on Chromosorb WHP to yield a liquid fraction which is *N*-ethyl-2-[3,3,3-trifluoro-2-(trifluoromethyl)propyl]aniline: NMR ($CDCl_3$) 1.28 (t, CH_3), 2.95 [d, J = 6 Hz, CH_2 of $CH_2CH(CF_3)_2$], ~3.1 (NH band buried under other peaks, removed by D_2O), 3.15 (q, CH_2 of Et), 3.26 [septuplet, $CH(CF_3)_2$], 6.5–7.35 ppm (m, C_6H_4).

Anal. Calcd for $C_{12}H_{13}F_6N$: N, 4.91. Found: N, 5.07.

Methylation of 5. **5** was warmed briefly with a 10% excess of methyl fluorosulfonate[27] (toxic) until the solid melted. Reaction took place and the fluorosulfonate salt crystallized. The excess methyl fluorosulfonate was pumped off to leave a 100% yield of the 2,1-benzisothiazolium fluorosulfonate **6**: ^{19}F NMR (H_2O) 2.3 ppm [d, J = 8 Hz, $(CF_3)_2CH$].

Anal. Calcd for $C_{11}H_8F_7NO_3S_2$: C, 33.08; H 2.02; N, 3.51. Found: C, 33.07; H, 2.44; N, 3.58.

The above salt was treated with sodium bicarbonate solution. The solid so formed was filtered off, dried, and taken up in hexane. 3-(Hexafluoroisopropylidene)-1,3-dihydro-1-methyl-2,1-benzisothiazole (**7**) was crystallized from the filtered solution in 26% yield: mp 79–81 °C; IR 3077 (=CH), 2950, 2841 (CH), 1608, 1567, 1513, 1488 (C=C), 741 cm^{-1} (ortho-substituted aromatic and CF_3); ^{1}H NMR ($CDCl_3$) 3.30 (s, CH_3), 6.85–8.15 ppm (m's, C_6H_4); ^{19}F NMR 11.90, 13.90 ppm (quadruplets).

Anal. Calcd for $C_{11}H_7F_6NS$: C, 44.14; H, 2.36; N, 4.68. Found: C, 44.28; H, 2.52; N, 4.46.

2-[2,2,2-Trifluoro-1-(trifluoromethyl)ethyl]benzothiazole. To 1.25 g (0.01 mol) of 2-aminobenzenethiol[27] in 10 mL of dichloromethane was added 1.94 g (0.01 mol) of bis(trifluoromethyl)thioketene. The solvent was then removed and the residue was heated in a test tube with a flame for 5 min. The product boiled at 230 °C. The product was extracted with hexane, treated with decolorizing carbon, and crystallized from the hexane to give 1.12 g (39%) of the benzothiazole: mp 101–103 °C; IR 3067 (w, =CH), 2907 (CH), 1600, 1572, 1558, 1504 cm^{-1} (C=C, C=N); ^{1}H NMR (CCl_4) 5.00 ppm [septet, $(CF_3)_2CH$]; ^{19}F NMR 2.30 ppm (d, J = 6 Hz).

Anal. Calcd for $C_{10}H_5F_6NS$: C, 42.11; H, 1.77; S, 11.25. Found: C, 42.33; H, 1.80; S, 11.23.

Reaction with Phosphites. A. Trimethyl Phosphite. Trimethyl phosphite (1.24 g, 0.01 mol) in 5 mL of dichloromethane was stirred and cooled in ice while 2.91 g (0.015 mol) of bis(trifluoromethyl)-thioketene was added dropwise. The volatiles, including thioketene dimer, were pulled off under oil pump vacuum at 25 ° C for 15 h. This left 2.35 g (59%) of a pale yellow oil, 5,5-bis(trifluoromethyl)-2-(hexafluoroisopropylidene)-4-(trimethoxyphosphoranylidene)-1,3-dithiolane (**10**): ^{1}H NMR ($CDCl_3$) 3.81 ppm (d, J_{HCOP} = 11.3 Hz); ^{19}F NMR 0.89 [d, $J_{F\text{-}P}$ = 1.3 Hz, 5-$(CF_3)_2$], 9.68 ppm [m, 2-$(CF_3)_2C{=}$]; ^{31}P NMR 38.7 ppm (eight peaks, outer two peaks not discernible, J = 11 Hz).

Anal. Calcd for $C_{11}H_9F_{12}O_3PS_2$: C, 25.79; H, 1.77; F, 44.51. Found: C, 26.13; H, 2.08; F, 44.34.

Vacuum distillation of the product decomposed it to dimethyl 3,3,3-trifluoro-1-methylthio-2-(trifluoromethyl)-1-propenephosphonate (**12**): bp 77 °C (0.7 mm); n^{25}_D 1.4303; ^{1}H NMR ($CDCl_3$) 2.65 (s, CH_3), 3.90 ppm (d, J = 11.5 Hz, 2 CH_3O); ^{19}F NMR 7.35, 9.68 ppm (quadruplets); ^{31}P NMR 8.95 ppm (septuplet, J = 11 Hz); IR 1618 cm^{-1} (C=C).

Anal. Calcd for $C_7H_9F_6O_3PS$: C, 26.42; H, 2.85; S, 10.08. Found: C, 26.36; H, 2.90; S, 9.94.

In another run, 5.82 g (0.03 mol) of the thioketene was added to 3.72 g (0.03 mol) of trimethyl phosphite in 10 mL of pentane. The solvent was evaporated and the residue was allowed to stand in moist air. One methyl group was hydrolyzed off and the resulting product crystallized. Recrystallization from benzene gave 2.24 g (30%) of dimethyl 5,5-bis(trifluoromethyl)-2-(hexafluoroisopropylidene)-1,3-dithiolane-4-phosphonate (**11**): mp 100–101 °C; IR 2959, 2899 (CH), 1572 cm −1 (C=C); ^{1}H NMR ($CDCl_3$) 3.90 (d, J_{HCOP} = 11 Hz, 2 CH_3O), 4.70 ppm (d, J_{HCP} = 19 Hz, slowly removed by D_2O, CH); ^{31}P NMR 12.9 ppm (nine apparent peaks, d split to septuplets); ^{19}F NMR 1.67, 3.88 [quadruplets, 5-$(CF_3)_2$], 9.65 ppm [A_3B_3, 2-$(CF_3)_2C{=}$].

Anal. Calcd for $C_{10}H_7F_{12}O_3PS_2$: C, 24.10; H, 1.42; P, 6.20; S, 12.84. Found: C, 24.42; H, 1.66; P, 6.36; S, 12.67.

B. Triphenyl Phosphite. To 9.30 g (0.03 mol) of triphenyl phosphite was added 5.82 g (0.03 mol) of bis(trifluoromethyl)thioketene. The temperature was kept below 30 °C by cooling with ice. On standing in air, one phenyl group was hydrolyzed off and the resulting

product crystallized on scratching. The product was washed with cold hexane and recrystallized from hexane to give 5.8 g (62%) of diphenyl 5,5-bis(trifluoromethyl)-2-(hexafluoroisopropylidene)-1,3-dithiolane-4-phosphonate: mp 98–98.5 °C; IR 3067 (=CH), 1590, 1484 (aromatic C=C), 1565 cm −1 (exocyclic C=C); ^{1}H NMR (CCl_4) 4.78 ppm (d, J_{PCH} = 19 Hz); ^{19}F NMR 2.56, 4.47 [quadruplets, 5-$(CF_3)_2$], 9.95 ppm [A_3B_3, 2-$(CF_3)_2C$=].

Anal. Calcd for $C_{20}H_{11}F_{12}O_3PS_2$: C, 38.84; H, 1.81; F, 36.74; P, 5.03; S, 10.18. Found: C, 38.65; H, 1.78; F, 36.68; P, 4.87; S, 10.32.

Reaction with Methylbenzenes. A. Hexamethylbenzene. Hexamethylbenzene (4.87 g, 0.03 mol), 8 mL of benzene, and 6.40 g (0.033 mol) of bis(trifluoromethyl)thioketene were heated in a sealed glass tube at 100 °C for 15 h. The benzene was evaporated and the residue was heated at 100 °C and 1 mm to remove excess hexamethylbenzene by sublimation. The residue was recrystallized twice from methanol to give 4.04 g (45%) of 2-[1,1-bis(trifluoromethyl)-2-(pentamethylphenyl)ethyl]-4-(hexafluoroisopropylidene)-1,3-dithietane (**13**): mp 120–120.2 °C; ^{1}H NMR (CCl_4) 2.15 (s, 3,4,5-CH_3), 2.23 (s, 2,6-CH_3), 3.68 (s, CH_2), 4.98 ppm (broadened peak, CH); ^{19}F NMR 2.73 (s, 2 CF_3), 9.26 ppm [s, $(CF_3)_2C$=].

Anal. Calcd for $C_{20}H_{18}F_{12}S_2$: C, 43.63; H, 3.29; S, 11.65. Found: C, 44.00; H, 3.39; S, 11.56.

B. Durene. Durene (2.01 g, 0.015 mol) and 5.82 g (0.03 mol) of bis(trifluoromethyl)thioketene were sealed in a glass tube and heated at 150 °C for 6 h. The product crystallized on scratching and was allowed to stand in air for 3 days to permit durene and the thioketene dimer to sublime out. Recrystallization from methanol gave 4.24 g (54%) of 2-[1,1-bis(trifluoromethyl)-2-(2,4,5-trimethylphenyl)-ethyl]-4-(hexafluoroisopropylidene)-1,3-dithietane: mp 67–68 °C; IR 3012 (=CH), 2967, 2941, 2874 (CH), 1613 (exocyclic C=C), 1585, 1515 cm^{-1} (aromatic C=C); ^{1}H NMR (CCl_4) 2.20 (s, 4,5-CH_3), 2.30 (s, 2-CH_3), 3.58 (s, ch_2), 5.10 (s, CH), 6.31 (aromatic H), 6.60 ppm (aromatic H); ^{19}F NMR 2.39 (s, 2 CF_3), 9.57 ppm [s, $(CF_3)_2C$=].

Anal. Calcd for $C_{18}H_{14}F_{12}S_2$: C, 41.38; H, 2.70; S, 12.28. Found: C, 41.46; H, 2.92; S, 12.49.

C. *p*-Methylanisole. *p*-Methylanisole (4.88 g, 0.04 mol) and 7.76 g of bis(trifluoromethyl)thioketene were heated in a sealed glass tube at 150 °C for 8 h. The viscous product was distilled at 91–100 °C (0.05 mm). Seed crystals were obtained by cooling a portion in methanol in dry ice. The product was then seeded and the crystals were filtered from liquid. Recrystallization from methanol by cooling in dry ice gave 2.01 g (20%) in two crops of 2-[1,1-bis(trifluoromethyl)-2-(*p*-methoxyphenyl)ethyl]-4-(hexafluoroisopropylidene)-1,3-dithietane: mp 31.2–31.8 °C; IR 2950, 2849 (CH); 1613 (exocyclic C=C), 1515 (aromatic C=C), 1250 cm^{-1} (C=COC); ^{1}H NMR (CCl_4) 3.58 (s, CH_2), 3.78 (s, CH_3O), 5.13 (s, CH), 7.02 ppm (AA'BB', C_6H_4); ^{19}F NMR 2.54 (s, 2 CF_3), 9.72 ppm [$(CF_3)_2C$=].

Anal. Calcd for $C_{16}H_{10}F_{12}OS_2$: C, 37.65; H, 1.98; S, 12.57. Found: C, 37.99; H, 2.07; S, 12.73.

D. *p*-Cresol. Redistilled *p*-cresol (4.32 g, 0.04 mol) and 8.52 g (0.044 mol) of bis(trifluoromethyl)thioketene were heated in a sealed glass tube at 100 °C for 15 h. Combination of two runs and distillation gave a cut, bp 80–81 °C (7 mm), n^{25}_D 1.4444, 4.24 g (35%), which was *p*-tolyl 3,3,3-trifluoro-2-(trifluoromethyl)thiopropionate: ^{1}H NMR (neat) 1.78 (s, CH_3), 4.2 [septuplet, $(CF_3)_2CH$], 6.42 ppm (AA'BB', C_6H_4); ^{19}F NMR 1.29 ppm (d, J = 6 Hz).

Anal. Calcd for $C_{11}H_8F_6OS$: C, 43.71; H, 2.67; S, 10.61. Found: C, 43.87; H, 2.90; S, 10.59.

The distillation cut, bp 81–120 °C (7 mm), was partly crystalline. The crystals were filtered off and recrystallized from hexane to give 3.55 g (18%) of **15**: mp 76–77 °C; IR 3067 (=CH), 2944, 2941, 2882 (CH), 1623 (exocyclic C=C), 1511 (aromatic C=C), 842 cm^{-1} (*p*-aromatic); ^{1}H NMR (CCl_4) 2.31 (s, CH_3), 4.20 [septuplet, $(CF_3)_2CH$], 7.08 ppm (C_6H_4); ^{19}F NMR 6.27 [d, J = 7 Hz, $(CF_3)_2CH$], 8.87 ppm [s, $(CF_3)_2C$=].

Anal. Calcd for $C_{15}H_8F_{12}OS_2$: C, 36.29; H, 1.62; S, 12.91. Found: C, 36.84; H, 1.94; S, 12.58.

Finally, a dark distillation cut, bp 120–150 °C (7 mm), contained crystals which were filtered off and recrystallized from hexane to give 0.37 g (1.7%) of **16**: mp 102–104 °C; ^{1}H NMR (CCl_4) 3.6 (s, CH_2), 5.13 (s, CH), 5.64 (s, HO, exchanged with CF_3COOH), 6.9 ppm (AA'BB', C_6H_4); ^{19}F NMR 2.66 (s, 2 CF_3), 9.61 ppm [s, $(CF_3)_2C$=]. The compound dissolves in warm, dilute sodium hydroxide solution to give a surface active solution from which the compound can be reprecipitated with hydrochloric acid.

Anal. Calcd for $C_{15}H_8F_{12}OS_2$: C, 36.29; H, 1.62; S, 12.91. Found: C, 36.70; H, 1.68; S, 12.53.

Diels–Alder Reactions. A. Addition to Butadiene. Butadiene (10 g, 0.19 mol) was condensed into 50 mL of dichloromethane at −10 °C and 7.76 g of bis(trifluoromethyl)thioketene was added. The solution was allowed to stand 20 h at 0 °C while reaction slowly took place. Distillation gave 9.0 g (91%) of 6-(hexafluorisopropylidene)-5,6-dihydro-2*H*-thiopyran: bp 72–73 °C (8 mm); n^{25}_D 1.4439; IR 3077 cm^{-1} (=CH), 1642 (ring C=C), 1572 (exocyclic C=C); ^{1}H NMR (neat), 3.08, 3.17 (two peaks, 2 CH_2 groups), 6.06 ppm (center of nine peaks, CH=CH); ^{19}F NMR 9.79, 12.5 ppm (quadruplets).

Anal. Calcd for $C_8H_6F_6S$: C, 38.70; H, 2.44; S, 12.91. Found: C, 39.22; H, 2.71; S, 12.98.

B. Addition to 2,3-Dichlorobutadiene. 2,3-Dichlorobutadiene[24] (7.38 g, 0.06 mol) containing 100 ppm of phenothiazine and 11.64 g (0.06 mol) of bis(trifluoromethyl)thioketene were sealed in a glass tube and heated at 100 °C for 2 h. Distillation gave 13.7 g (72%) of 3,4-dichloro-6-(hexafluoroisopropylidene)-5,6-dihydro-2*H*-thiopyran: bp 64 °C (0.25 mm); n^{25}_D 1.4770; ^{1}H NMR (neat) 3.60 (s, CH_2S), 3.89 ppm (s, broader, CH_2); ^{19}F NMR 9.70, 12.60 ppm (quadruplets, former split to triplets).

Anal. Calcd for $C_8H_4Cl_2F_6S$: C, 30.30; H, 1.27; S, 10.11. Found: C, 30.69; H, 1.65; S, 10.23.

C. Addition to Pentamethyl-5-vinylcyclopentadiene. To 9.72 g (0.06 mol) of pentamethyl-5-vinylcyclopentadiene[25] was added 11.6 g (0.6 mol) of the thioketene in small portions with occasional cooling. Distillation gave 17.4 g (81%) of adducts: bp 76 °C (0.5 mm). These were isomers with the vinyl group syn and anti to the sulfur atom. Crystallization from methanol gave 8.5 g (36%) of a solid isomer of 3-(hexafluoroisopropylidene)-1,4,5,6,7-pentamethyl-7-vinyl-2-thiabicyclo[2,2.1]hept-5-ene:[6] mp 50–52 °C; IR 1656 (cyclic C=C), 1629 (vinyl C=C), 1563 cm^{-1} (exocyclic C=C); Raman 1665, 1637, 1567 cm^{-1}; ^{1}H NMR (CCl_4) 1.09 (s, 7-CH_3), 1.21 (1-CH_3), 4.85–6.85 ppm (m, CH_2=CH); ^{19}F NMR 9.65, 17.9 ppm (quadruplets, components of latter split to quadruplets, J = 2.6 Hz).

Anal. Calcd for $C_{16}H_{18}F_6S$: C, 53.93; H, 5.09; S, 9.00. Found: C, 53.77; H, 5.08; S, 9.12.

D. Addition to Spiro[4.4]nona-1,3-diene. To 6 g (0.05 mol) of spiro[4.4]nona-1,3-diene[26] in 15 mL of dichloromethane was added 9.7 (0.05 mol) of the thioketene in 10 mL of dichloromethane with cooling in ice. Distillation gave 12.8 g (83%) of 3-(hexafluoroisopropylidene)spiro(2-thiabicyclo[2.2.1]hept-5-ene-7,1′-cyclopentane): bp 65 °C (0.2 mm); n^{25}_D 1.4685; ^{1}H NMR (neat) 1.48 [s, $(CH_2)_4$], 3.84 (broadened peak, 1-H), 4.02 (m, 4-H), 6.02 (m, 5-H), 6.53 ppm (q, 6-H); ^{19}F NMR 8.13, 12.4 ppm (quadruplets).

Anal. Calcd for $C_{13}H_{12}F_6S$: C, 49.68; H, 3.85; S, 10.20. Found: C, 49.22; H, 3.68; S, 10.26.

E. Addition to 6,6-Diphenylfulvene. To 4.6 g (0.02 mol) of 6,6-diphenylfulvene[27] in 20 mL of hexane was added 3.88 g (0.02 mol) of the thioketene with occasional cooling. From the cooled mixture 7.18 g of product was filtered. Recrystallization from hexane left 6.22 g (73%) of 7-(diphenylmethylene)-3-(hexafluoroisopropylidene)-2-thiabicyclo[2.2.1]hept-5-ene: mp 118.3–119 °C; IR 3049 cm^{-1} (=CH), 1621 [$(CF_3)_2C$=C], 1577, 1502 (aromatic C=C); H NMR ($CDCl_3$) 4.80 (broad m, bridgehead protons), 6.27 and 6.65 (m and quartet, CH=CH), 7.1 ppm (m, 10 aromatic protons); ^{19}F NMR 8.70, 12.6 ppm (quadruplets).

Anal. Calcd for $C_{22}H_{14}F_6S$: C, 62.26; H, 3.33; S, 7.56. Found: C, 62.56; H, 3.36; S, 7.66.

F. Addition to 1,3-Cyclohexadiene. 1,3-Cyclohexadiene (17 g, 0.21 mol) in 50 mL of dichloromethane was stirred and cooled in ice while 38.8 g (0.2 mol) of bis(trifluoromethyl)thioketene was added during 1 h at 10–20 °C. Distillation gave 49.6 g (91%) of product: bp 45–47 °C (0.6 mm); ^{19}F NMR (neat) 3.41, 6.33 (quadruplets, J = 6.4 Hz, former split to doublets, J = 1.5 Hz), 9.55, 13.2 ppm (quadruplets, J = 9.7 Hz). The low-field pair of quadruplets represent the Diels–Alder adduct (**20**, 54.5%) and high-field pair the ene product (45.5%), 3-[3,3,3-trifluoro-1-(trifluoromethyl)propenylthio]-1,4-cyclohexadiene (**21**). The presence of the latter was confirmed in the ^{1}H NMR spectrum by a quadruplet at 7.34 ppm, J = 1.3 Hz, for $(CF_3)_2C$=CH.[2b] Preparative GLC over polyfluoroalkyl pyromellitate on Gas Chrom R at 150 °C gave 22 g (40%) of the Diels–Alder adduct, 3-(hexafluoroisopropylidene)-2-thiabicyclo[2.2.2]oct-5-ene[6] (**20**). To remove color, the compound in dichloromethane was slurried with neutral Woelm alumina and redistilled: bp 78 °C (5 mm); n^{25}_D 1.4589; ^{1}H NMR (neat) 1.2–2.2 (m, CH_2CH_2), 3.78, 4.30 (complex doublets, bridgehead protons), 6.12, 6.58 ppm (t's, J = 8 Hz, components of former split to doublets, CH=CH); ^{19}F NMR 9.65, 13.2 ppm [quadruplets, $(CF_3)_2C$=C<]. The ene product did not emerge from the column as it was converted to tar.

Anal. Calcd for $C_{10}H_8F_6S$: C, 43.79; H, 2.94; S, 11.66. Found: C, 43.73; H, 2.96; S, 11.99.

G. Addition to Anthracene. Anthracene (0.89 g, 0.005 mol) was dissolved in 60 mL of benzene, 0.97 g (0.005 mol) of the thioketene was added, and the solution was allowed to stand for 18 h. The reaction

was not complete and the solution was refluxed for 2 h, after which the benzene was evaporated off. The residue was taken up in ether, filtered from 0.27 g of anthracene, and the solution was evaporated to leave 1.1 g (59%) of 12-(hexafluoroisopropylidene)-11-thia-9,10-dihydro-9,10-ethanoanthracene: mp 118.5–119 °C from methanol; ^{1}H NMR ($CDCl_3$) 5.40, 6.05 ppm (singlets, bridgehead protons), 7.2 (m, 8 aromatic protons); ^{19}F NMR 9.79, 14.9 ppm (quadruplets).

Anal. Calcd for $C_{18}H_{10}F_6S$: C, 58.08; H, 2.71; S, 8.61. Found: 57.95; H, 2.97; S, 8.50.

H. Addition to Cyclooctatetraene. Cyclooctatetraene (3.12 g, 0.03 mol) and 5.82 g (0.03 mol) of the thioketene were sealed in a glass tube and heated at 100 °C for 16 h. Recrystallization of the product from methanol gave 7.0 g (78%) of 4-(hexafluoroisopropylidene)-3-thiatricyclo[4.2.2.0^{2,5}]deca-7,9-diene[6] (**17**) in three crops: mp 49–50 °C; IR 3067 (=CH), 2941 (CH), 1575 cm^{-1} (exocyclic C=C); ^{1}H NMR (CCl_4) 2.85, 3.20 (t's, six-membered ring bridgehead protons), 3.9, 4.4 (broad m's, saturated cyclobutene protons), 6.07 (sharp peak, cyclobutene CH=CH), superimposed on this is a broader absorption corresponding to another =CH, 6.43 ppm (t, =CH); ^{19}F NMR 10.3, 13.8 ppm (quadruplets).

Anal. Calcd for $C_{12}H_8F_6S$: C, 48.23; H, 2.70; S, 10.75. Found: C, 48.16; H, 298; S, 10.62.

I. Addition to 1,3-Diphenylisobenzofuran. A solution of 5.4 g (0.02 mol) of 1,3-diphenylisobenzofuran[27] in 35 mL of dichloromethane was stirred and cooled in ice and 4.27 g (0.022 mol) of the thioketene was added dropwise. The solvent was allowed to evaporate. The crystalline product was unstable to heat and was recrystallized cold by dissolving in 7 mL of dichloromethane, adding 75 mL of hexane, and concentrating the solution under reduced pressure. This gave 7.7 g (83%) of 3,4-dihydro-1,4-diphenyl-3-(hexafluoroisopropylidene)-1,4-epoxy-1*H*-[2]benzothiopyran (**18**). The compound is dissociated to its components by heat, but if placed in a hot bath, a melting point of 123 °C is obtained: IR 3067 (=CH), 1600 (exocyclic C=C), 1497 cm^{-1} (aromatic C=C); ^{19}F NMR (CCl_4) 6.84, 13.9 ppm (quadruplets).

Anal. Calcd for $C_{24}H_{14}F_6OS$: C, 62.07; H, 3.04; S, 6.90. Found: C, 62.42; H, 3.24; S, 6.81.

J. Addition to 1,2,4,7-Tetrakis(methylene)cyclooctane. To 2.4 g (0.0015 mol) of the tetraene[29] in 5 mL of dichloromethane was added 2.91 g (0.015 mol) of the thioketene. After 1 h the product was distilled to give 2.63 g of 6,9-bis(methylene)-3-(hexafluoroisopropylidene)-3,4,5,6,7,8,9,10-octahydro-1*H*-cycloocta[*c*]thiopyran (**19**): bp 88 °C (0.025 mm); n^{25}D 1.4975; IR 3125 (=CH), 2941, 2865 (CH), 1647 (CH_2=C), 1577 [$(CF_3)_2$C=C], 894 cm^{-1} (CH_2=C); Raman 1665, 1635, 1560 cm^{-1}; ^{1}H NMR (CCl_4) 2.19 (s, 7,8-CH_2), 3.07 (s, 2 CH_2), 3.16 (s, 2 CH_2), 4.71 ppm (2 CH_2=); ^{19}F NMR 10.3, 13.5 (quadruplets, J = 11 Hz).

Anal. Calcd for $C_{16}H_{16}F_6S$; c, 54.23; H, 4.55; S, 9.05. Found: C, 54.52; H, 4.82; S, 9.21.

Reduction of Diels–Alder Adducts. A. Cyclopentadiene Adduct. A solution of 30 g of 3-(hexafluoroisopropylidene)-2-thiabicyclo[2.2.1]hept-5-ene[8] (**22**) in 125 mL of ethanol containing 1.7 g of 5% palladium on carbon and 0.3 g of palladium black was subjected to hydrogenation at room temperature and 40 lb/in.^{2} hydrogen pressure. After 1 h the pressure drop had leveled off, and the solution was filtered and distilled to give 25.4 g (85%) of 3-(hexafluoroisopropylidene)-2-thiabicyclo[2.2.1]heptane:[6] bp 70 °C (5 mm); n^{25}D 1.4442; ^{1}H NMR (neat) 1.1–2.0 (m, 6 H), 3.52 (s, bridgehead in 1 position), 3.74 ppm (s, broader, bridgehead in 4 position); ^{19}F NMR 8.69, 11.5 ppm (quadruplets, J = 8.5 Hz, latter split to doublets, J = 2 Hz).

Anal. Calcd for $C_9H_8F_6S$: C, 41.23; H, 3.07; S, 12.23. Found: C, 41.61; H, 3.10; S, 12.39.

B. Reduction of Cyclooctatetraene Adduct. A solution of 25.6 g of **17** in 100 mL of alcohol containing 0.1 g of platinum oxide was hydrogenated at room temperature and 40 lb/in.^{2} for 1 h. The solution was filtered and distilled in a simple still at 120 °C (5 mm) to remove colloidal platinum. The white crystals (25.2 g) were recrystallized from methanol to give 23.5 g (91%) of 4-(hexafluoroisopropylidene)-3-thiatricyclo[4.2.2.0^{2,5}]deca-9-ene[6] in four crops: mp 46–46.5 °C; IR 3086 (=CH), 3003, 2874, 2857 (CH), 1631 (shoulder, ring C=C), 1577 cm^{-1} (exocyclic C=C); Raman 1575 (exocyclic C=C), 1635 cm^{-1} (ring C=C); ^{1}H NMR (CCl_4) 1–3.1 (m, 6 H), 3.82, 4.22 (2 m, bridgeheads), 6.35, 6.76 ppm (2 t, CH=CH), the sharp peak for the starting compound at 6.07 ppm, attributed to cyclobutene CH=CH, is gone; ^{19}F NMR 10.5, 14.0 ppm (quadruplets).

Anal. Calcd for $C_{12}H_{10}F_6S$: C, 48.00; H, 3.36; S, 10.68. Found: C, 48.22; H, 3.16; S, 10.88.

3-(Hexafluoroisopropylidene)-2-thiabicyclo[2.2.1]hept-5-ene 2-Oxide. To 26 g (0.1 mol) of 3-(hexafluoroisopropylidene)-2-thiabicyclo[2.2.1]hept-5-ene[8] (**22**) dissolved in 50 mL of dichloromethane was added at 15–20 °C 20.4 g (0.1 mol) of 85% *m*-chloroperbenzoic acid dissolved in 225 mL of dichloromethane. The solution was then washed with 5% sodium bicarbonate solution and dried (Na_2SO_4). The solvent was boiled off, finally under vacuum. The product was recrystallized from methanol by cooling in dry ice to give 10.26 g in two crops (38%) of the sulfoxide[9] **23**: mp 46–49 °C; IR 3077 (=CH), 2950 (CH), 1647 (exocyclic C=C), 1567 (ring C=C), 1042 cm^{-1} (SO); ^{1}H NMR (CCl_4) 2.65 (AB, bridge CH_2), 4.22, 4.32 (singlets, bridgeheads), 6.12 ppm (m, CH=CH); ^{19}F NMR 7.89, 9.70 ppm (quadruplets).

Anal. Calcd for C_9H_6OS: C, 39.14; H, 2.19; S, 11.61. Found: C, 39.31; H, 1.96; S, 11.58.

6-(Hexafluoroisopropylidene)-3,7-oxathiatricyclo[3.2.1.0^{2,4}]-octane 7,7-Dioxide. 3-Hexafluoroisopropylidene-2-thiabicyclo-[2.2.1]hept-5-ene 2,2-dioxide[8] (**24**, 21.4 g, 0.073 mol) was added to 16.4 g (0.081 mol) of 85% *m*-chloroperbenzoic acid in 150 mL of 1,2-dichloroethane and heated on a steam bath for 16 h. The solution was then washed with 5% aqueous sodium hydroxide, dried (Na_2SO_4), and evaporated. The residue was recrystallized from methanol to give 14.7 g (65%) of the epoxide **25**: mp 135–137 °C; IR 3086 (epoxide ring CH), 2994 (CH), 1675 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) 2.17 (m, CH_2), 3.6–4.1 ppm (m, 4 H).

Anal. Calcd for $C_9H_6F_6O_3S$: C, 35.07; H, 1.96; S, 10.40. Found: C, 35.23; H, 1.89; S, 10.33.

Addition to Thiothiophthene. To 2.82 g (0.015 mol) of thiothiophthen[28] (**26**) dissolved in 150 mL of dichloromethane was added 5.82 g (0.03 mol) of bis(trifluoromethyl)thioketene and the solution was allowed to stand for 20 h. Not all of the thiothiophthene had reacted and 1.94 g (0.01 mol) more of the thioketene was added. After 2 h the solvent was evaporated and the crystalline residue was washed with cold hexane to leave 5.6 g of product. Recrystallization from hexane left 5.0 g (58%) of deep orange **28**: mp 151–152 °C; IR 2985, 2857 (CH), 1613 [$(CF_3)_2$C=C], 1504 cm^{-1} (C=C); Raman, sample decomposed in laser beam; ^{1}H NMR (CCl_4) 2.77 (s, CH_3), 2.86 (s, CH_3), 4.48 [septuplet, $(CF_3)_2$CH], 7.3 ppm (s, =CH); ^{19}F NMR 4.49 [d, J = 7 Hz, $(CF_3)_2$CH], 9.84 ppm [s, $(CF_3)_2$C=].

Anal. Calcd for $C_{15}H_8F_{12}S_5$: C, 31.24; H, 1.40; S, 27.80. Found: C, 31.43; H, 1.50; S, 27.87.

To 1.15 g (0.002 mol) of the above compound in 10 mL of dichloromethane was added 1 g (0.0052 mol) of bis(trifluoromethyl)thioketene and the solution was allowed to stand for 16 h. Then 1 g more of the thioketene was added and the solution was let stand for 24 h. The solvent was evaporated and the residue was recrystallized from nitromethane to give 1.19 g (77%) of white **31**: mp 134–135 °C; IR 2994, 2941, (CH), 1603 [$(CF_3)_2$C=], 1558 cm^{-1} (C=C); Raman 1610 [$(CF_3)_2$C=C], 1565 (C=C), 505 cm^{-1} (S-S); ^{1}H NMR (CCl_4) 2.24 (s, CH_3), 2.55 (s, CH_3), 5.03 [septuplet, $CH(CF_3)_2$], 5.70 ppm (s, CH); ^{19}F NMR 3.03 [d, J = 6 Hz, $(CF_3)_2$CH], 9.73 [s, $(CF_3)_2$C=CS_2], 9.84 [s, $(CF_3)_3$C=CS_2], 9.66 ppm [A_3B_3, $(CF_3)_2$C=].

Anal. Calcd for $C_{23}H_8F_{24}S_7$: C, 28.63; H, 0.84; S, 23.27; mol wt, 965. Found: C, 28.80; H, 1.16; S, 23.28; mol wt, 970 (in $CHCl_3$ by vapor pressure osmometer).

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Registry No.—**1**, 66172-18-7; **2a**, 66172-19-8; **2b**, 66172-20-1; **2c**, 66172-21-2; **2d**, 66172-22-3; **2e**, 66172-23-4; **3**, 66172-24-5; **4a**, 66172-25-6; **4b**, 66172,26-7; **4c**, 66172-27-8; **4d**, 66172-28-9; **4e**, 66172-29-0; **5**, 66172-30-3; **6**, 66172-32-5; **7**, 66172-33-6; **8**, 66172-34-7; **9**, 66172-35-8; **10**, 66172-36-9; **11**, 66172-37-0; **12**, 66172-38-1; **13**, 66172-08-5; **15**, 66172-09-6; **16**, 66172-10-9; **17**, 24515-63-7; **18**, 24515-66-0; **19**, 66172-11-0; **20**, 35012-33-0; **21**, 66172-12-1; **22**, 35012,32-9; **23**, 35012-39-6; **24**, 35012-38-5; **25**, 66172-13-2; **26**, 2080-35-5; **28**, 66172-14-3; **31**, 66172-15-4; *N*-(pentafluorobenzylidene)methylamine, 62454-76-6; pentafluorobenzaldehyde, 653-37-2; methylamine, 74-89-5; bis(trifluoromethyl)thioketene, 7445-60-5; *N*-benzylidenemethylamine, 622-29-7; *N*-benzylideneisopropylamine, 6852-56-8; *N*-(4-chlorobenzylidene)methylamine, 13114-22-2; *N*-(4-nitrobenzylidene)methylamine, 877-80-5; *N*-(4-methoxybenzylidene)-4-methoxyaniline, 1749-08-2; *N*-methyl-*N*-[3,3,3-trifluoro(2-trifluoromethyl)]propionylbenzamide, 51254-13-8; $(CF_3)_2$C=C=O, 684-22-0; *N*-methylbenzamide, 613-93-4; methyl isothiocyanate, 556-61-6; phenyl azide, 622-37-7; *p*-tolyl azide, 2101-86-2; 4-

methoxyphenyl azide, 2101-87-3; 4-chlorophenyl azide, 3296-05-7; 3,4-dichlorophenyl azide, 66172-16-5; 2,4,6-trimethylphenyl azide, 14213-00-4; 5-methyl-3-[2,2,2-trifluoro-1-(trifluoromethyl)ethyl]-2,1-benzisothiazole, 66172-17-6; *N*-ethyl-2-[3,3,3-trifluoro-2-(trifluoromethyl)propyl]aniline, 66172-00-7; methyl fluorosulfonate, 421-20-5; 2-[2,2,2-trifluoro-1-(trifluoromethyl)ethyl]benzothiazole, 66172-01-8; 2-aminobenzenethiol, 137-07-5; trimethyl phosphite, 121-45-9; triphenyl phosphite, 101-02-0; diphenyl 5,5-bis(trifluoromethyl)-2-(hexafluoroisopropylidene)-1,3-dithiolane-4-phosphonate, 66172-02-9; hexamethylbenzene, 87-85-4; durene, 95-93-2; 2-[1,1-bis(trifluoromethyl)-2-(2,4,5-trimethylphenyl)ethyl]-4-(hexafluoroisopropylidene)-1,3-dithietane, 66172-03-0; *p*-methylanisole, 104-93-8; 2-[1,1-bis(trifluoromethyl)-2-(*p*-methoxyphenyl)ethyl]-4-(hexafluoroisopropylidene)-1,3-dithietane, 66172-04-1; *p*-cresol, 106-44-5; *p*-tolyl 3,3,3-trifluoro-2-(trifluoromethyl)thiopropionate, 66172-05-2; butadiene, 106-99-0; 6-(hexafluoroisopropylidene)-5,6-dihydro-2*H*-thiopyran, 24515-61-5; 2,3-dichlorobutadiene, 1653-19-6; 3,4-dichloro-6-(hexafluoroisopropylidene)-5,6-dihydro-2*H*-thiopyran, 66172-06-3; pentamethyl-5-vinylcyclopentadiene, 20145-47-5; 3-(hexafluoroisopropylidene)-1,4,5,6,7-pentamethyl-7-vinyl-2-thiabicyclo[2.2.1]hept-5-ene, 35012-44-3; spiro[4.4]nona-1,3-diene, 766-29-0; 3-(hexafluoroisopropylidene)spiro[2-thiabicyclo[2.2.1]hept-5-ene-7,1′-cyclopentene, 35012-45-4; 6,6-diphenylfulvene, 2175-90-8; 7-(diphenylmethylene)-3-(hexafluoroisopropylidene)-2-thiabicyclo[2.2.1]hept-5-ene, 24515-65-9; 1,3-cyclohexadiene, 592-57-4; anthracene, 120-12-7; 12-(hexafluoroisopropylidene)-11-thia-9,10-dihydro-9,10-ethanoanthracene, 24515-64-8; cyclooctatetraene, 629-20-9; 1,3-diphenylisobenzofuran, 5471-63-6; 1,2,4,7-tetrakis(methylene)cyclooctane, 35061-75-7; 3-(hexafluoroisopropylidene)-2-thiabicyclo[2.2.1]heptane, 35012-42-1; 4-(hexafluoroisopropylidene)-3-thiatricyclo-[4.2.2.0^{2,5}]deca-9-ene, 66172-07-4.

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Intramolecular Addition of Aryl Azides to the Azo Group. 2.[1] Synthesis and Properties of Benz[*cd*]indazole *N*-Arylimines

Piero Spagnolo,* Antonio Tundo, and Paolo Zanirato

Istituto di Chimica Organica dell'Università, Viale Risorgimento 4, 40136 Bologna, Italy

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Thermal and photochemical decomposition of 8-azido-1-arylazonaphthalenes results in intramolecular addition to the azo group to give previously unknown benz[*cd*]indazole *N*-arylimines in good yields by 1,5-cyclization. Only in one case 1,6-cyclization leading to a 2-arylnaphtho[1,8-*de*]triazine has also been observed. Chemical and spectroscopic properties of all *N*-imines are in accord with the proposed structures containing the stable 1,3-dipolar azimine system. Formation of products is discussed in terms of a possible concerted process not involving nitrene intermediates.

In a previous paper[1] we have reported what appears to be the first definite example of addition of aryl azides to the azo group leading to the formation of azimines, 1,3-dipolar valence tautomers of unknown triaziridines, presumably through the intermediacy of nitrenes. Photochemical decomposition of a number of 2-azido-2′-arylazobiphenyls (**1**, Ar = aryl) was in fact found to afford benzo[*c*]cinnoline *N*-arylimines (**2**) as major products as well as minor amounts of 4-arylazocarbazoles (**3**), 2-amino-2-arylazobiphenyls (**4**), and benzo[*c*]cinnoline (**5**).

These results prompted us to prepare a series of 1-azido-8-arylazonaphthalenes (**6**) and to investigate their thermal and photochemical decomposition in the hope that analogous intramolecular additions of the azido group (or nitrene) to the peri azo group would lead to the formation of 2-arylnaphtho[1,8-*de*]triazines (**7**) and/or benz[*cd*]indazole *N*-

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