remained at the end of the irradiation. GC analyses on appropriate fractions led to the estimates of thiol and disulfide yields given in Table III.

II. Mass Spectra Identification of Dichlorofluoromethyl Sulfides (Du Pont Model 21-490 Mass Spectrometer (70 eV) Interfaced to a Varian Model 144 Gas Chromatograph). A. Dichlorofluoromethyl Butyl Sulfides (28 and 29). These structures were assigned to the low yield products seen by GC (~2% each) from the reaction of dichlorofluoromethanesulfenyl chloride (**6**) and *n*-butane. Each pattern contained parent ions at *m/e* 190 (most intense parent ion), 192, and 194.

B. *Dichlorofluoromethyl* Cyclohexyl Sulfide (26). This structure was assigned to the low yield product from the reaction of dichlorofluoromethanesulfenyl chloride (**6**) and cyclohexane on the basis of the mass spectrogram which contains parent ions at *m/e* 216 (2.15%), 218 (1.54%), and 220 (0.24%).

III. Preparation of Starting Materials. A. Perfluoro-*tert*-butanesulfenyl Chloride (1). This material was obtained from Dr. D. C. England of this laboratory, who prepared it by chlorination of bis(perfluoro-*tert*-butyl) trisulfide.[19] It has also been prepared by chlorination of the mercury salt of perfluoro-*tert*-butanethiol.[12]

B. Heptafluoro-2-propanesulfenyl Chloride (2). A mixture of 75 g (0.186 M) of bis(heptafluoroisopropyl) disulfide[20] and 30 g (0.424 M) of chlorine contained in a 1-L Hastelloy-C lined autoclave was heated at 125 °C for 4 h and then at 150 °C for 4 h. Distillation of the resulting reaction mixture through a small spinning band still gave 45.1 g (51%) of heptafluoro-2-propanesulfenyl chloride (**2**) distilling at 53.5 °C, $n^{25}{}_D$ = 1.3244 (previously reported bp 54–55 °C[21]).

C. Heptafluoro-1-propanesulfenyl Chloride (3). A mixture of 131 g (0.325 M) of bis(heptafluoro-*n*-propyl) disulfide and 75 g (1.06 M) of chlorine was treated as described in the previous experiment. There was thus obtained 114 g (74%) of heptafluoro-1-propanesulfenyl chloride (**3**) distilling at 57 °C, $n^{25}{}_D$ 1.3210 (previously reported constants: bp 51–51.5 °C; $n^{23}{}_D$ 1.3239[22]).

D. 1,1,2,2-Tetrafluoroethanesulfenyl Chloride (4). This sulfenyl chloride was prepared by the chlorination of 1,1,2,2-tetrafluoroethanethiol as described previously.[23]

E. Chlorodifluoromethanesulfenyl Chloride (5). A mixture of 25 mL of liquid (at −76 °C) thiocarbonyl difluoride and 39 mL of liquid (at −76 °C) chlorine was loaded into a dry-ice cooled trap at atmospheric pressure under nitrogen and maintained at −76 °C for 2 days. The mixture was then allowed to reflux from a dry-ice cooled condenser for 0.5 h. After distillation of the excess volatiles, the residue was distilled through an 18 in. spinning-band still. There was thus obtained 30.8 g of chlorodifluoromethanesulfenyl chloride (**5**) distilling at 52 °C, $n^{26}{}_D$ 1.4099 (previously reported constants: bp 52 °C; $n^{19}{}_D$ 1.4195[24]).

F. Dichlorofluoromethanesulfenyl Chloride (6). This sulfenyl chloride was prepared by the reaction of trichloromethanesulfenyl chloride with mercuric fluoride as described previously.[25]

IV. ^{19}F NMR and Infrared Spectra. ^{19}F NMR spectra (56.4 MHz) were obtained from 10% solutions of the compounds in CCl_4 with Cl_3CF as external standard using a Varian A-56/60 spectrometer. The resonances are reported in parts per million measured from the resonance of Cl_3CF. The IR spectra reported were obtained from solutions of the compounds in CCl_4 with a Perkin-Elmer 21 (prism) spectrometer.

Registry No.—**8**, 68409-16-5; cyclohexane, 110-82-7; butane, 106-97-8; toluene, 108-88-3; bis(heptafluoroisopropyl) disulfide, 754-62-1; bis(heptafluoro-*n*-propyl) disulfide, 356-07-0; thiocarbonyl difluoride, 420-32-6.

References and Notes

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(11) Perfluoro-*tert*-butanethiol was prepared by Knunyants et al. by acidification *of the mercury salt*.[12]

(12) B. L. Dyatkin, S. R. Sterlin, L. G. Zhuravkova, B. I. Martynov, E. I. Mysov, and I. L. Knunyants, *Tetrahedron*, **29**, 2759 (1973).

(13) This order presumably reflects the relative rates of the free-radical chain reaction consuming sulfenyl chloride and producing thiol compared with the rate of the ionic reaction between thiol and sulfenyl chloride producing disulfide (see Scheme I). The different solvent properties of the three hydrocarbons and differences in the temperatures at which the reactions were carried out no doubt also affect the relative yields of thiol and disulfide.

(14) The mercury salt of **9** has been reported by Knunyants et al.; apparently the thiol was not isolated.[12]

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(16) The two exceptions are the *n*-C_3F_7SCl reaction, in which the sulfide preference of the *n*-butyl radical appears to be essentially the same as that of benzyl radical, and the $(CF_3)_2CFSCl$ reaction, in which the ratios for the benzyl radical and the *n*-butyl radical are extremely small (0.04 and 0.09, respectively). Differences between these small ratios may not be significant.

(17) In a study of free-radical reactions of C_6F_5SCl with alkylbenzenes, overwhelming sulfide formation by the benzyl-type radicals was observed.[10]

(18) This is not the experiment tabulated in Table III. In other runs, including the one in Table III, the irradiation periods required for the loss of the characteristic yellow color were much shorter, suggesting that this can be a long chain reaction.

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Synthesis of Alkyl Trithioperesters (Alkyl Thiocarbonyl Disulfides)[1]

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The first synthesis of alkyl trithioperesters (RC(S)SSR′, alkyl thiocarbonyl disulfides) is described. *tert*-Butyl trithiophenylperacetate (**4**) was synthesized starting with benzyl chloride. The Grignard of benzyl chloride is treated with carbon disulfide and hydrolyzed to give dithiophenylacetic acid (**1**). The dithio acid **1** was stabilized by formation of the metal salt **2**, which was reacted with *tert*-butylsulfenyl iodide (**3**) to form the trithioperester **4**. Other trithioperesters, *tert*-butyl trithiophenylperformate (**5**) and *tert*-butyl trithioanisylperformate (**6**), were synthesized by the same general reaction differing only in how the dithio acid was obtained. Preliminary observations concerning the thermal decomposition of *tert*-butyl trithiophenylperacetate (**4**) are discussed.

Several examples of the thermal homolytic cleavage of simple S–S bonds have been reported.[2] However, some of these do not involve the simple cleavage of the S–S bond,[3] and the homolytic reactions which may involve a simple homolytic cleavage do not take place at a reasonable rate below 100 °C. The only thorough kinetic study of a simple S–S bond was

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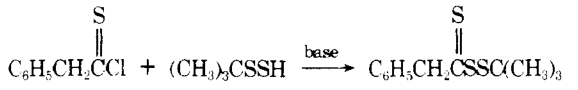
reported by Miyashita, Matsuda, and Iino[4] on organic sulfides. They observed (at temperatures between 196 and 217 °C) aryl disulfides underwent homolytic cleavage faster than alkyl disulfides, with di-*n*-butyl disulfide showing no decomposition under these conditions. It was also observed that all para substituents increased the rate of diphenyl disulfide decomposition. The activation energies obtained from the thermal decomposition of diaryl disulfides were 39.4 to 43.0 kcal/mol and were smaller than the bond energies of the S–S bond (60 ± 6 kcal/mol) calculated from thermochemical data.[5] In search for a class of compounds which might serve as a model for the simple investigation of the homolytic cleavage of the S–S bond, we have synthesized the first alkyl trithioperesters, RC(S)SSR′. Although compounds containing the trithiocarboxylate group have been synthesized, none have contained alkyl groups, and none have had their thermal stability investigated. Fischer and Gottfried[6] synthesized several compounds containing a trichloromethyl group and an ether, $ROC(S)SSCCl_3$; an amine, $R_2NC(S)SSCCl_3$; and an aryl group, $C_6H_5C(S)SSCCl_3$. Field and Buckman,[7] by another type of reaction, also prepared trithiocarbamates of the type $R_1R_2NC(S)SSR_3$, and more recently, Flamini, Furlani, and Piovesana[8] have prepared trithiocarboxylates, $RC(S)SS^-$, as ligands for nickel and zinc complexes without actually isolating the ligand.

Results and Discussion

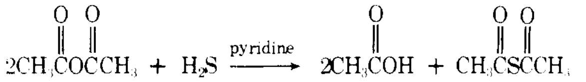
Since the oxygen analogue of *tert*-butyl trithiophenylperacetate (4) is usually synthesized by the Schotten–Baumen method, the first attempt to synthesize 4 was by the same method.



$$C_6H_5CH_2\overset{S}{\overset{\|}{C}}Cl + (CH_3)_3CSSH \xrightarrow{base} C_6H_5CH_2\overset{S}{\overset{\|}{C}}SSC(CH_3)_3$$

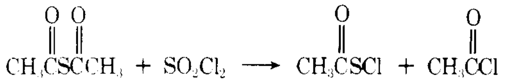
8 4

Hydrodisulfides were first synthesized by Bohme and Zinner[9] and although they did not synthesize *tert*-butyl hydrodisulfide, their procedure for the synthesis of alkyl hydrodisulfides was followed with the expectation that the results would be similar in this case. Diacetyl sulfide was prepared by bubbling a stream of dry H_2S through acetic anhydride with a catalytic amount of pyridine.



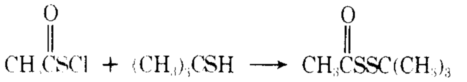
$$2CH_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3 + H_2S \xrightarrow{pyridine} 2CH_3\overset{O}{\overset{\|}{C}}OH + CH_3\overset{O}{\overset{\|}{C}}S\overset{O}{\overset{\|}{C}}CH_3$$

Addition of the sulfuryl chloride to diacetyl sulfide gave acetyl sulfurchloride [9]



$$CH_3\overset{O}{\overset{\|}{C}}S\overset{O}{\overset{\|}{C}}CH_3 + SO_2Cl_2 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}SCl + CH_3\overset{O}{\overset{\|}{C}}Cl$$

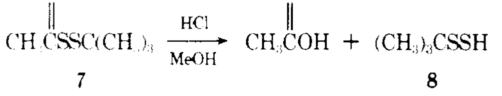
tert-Butyl mercaptan was reacted with acetyl sulfurchloride and gave *tert*-butyl acetyldisulfide,



$$CH_3\overset{O}{\overset{\|}{C}}SCl + (CH_3)_3CSH \longrightarrow CH_3\overset{O}{\overset{\|}{C}}SSC(CH_3)_3$$

7

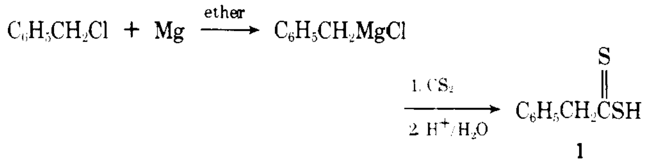
and subsequent hydrolysis of 7 with HCl gave the desired *tert*-butyl hydrodisulfide.



$$CH_3\overset{O}{\overset{\|}{C}}SSC(CH_3)_3 \xrightarrow[MeOH]{HCl} CH_3\overset{O}{\overset{\|}{C}}OH + (CH_3)_3CSSH$$

7 8

The procedure followed for the synthesis of dithiophenylacetic acid was that of A. Kjaer.[10]

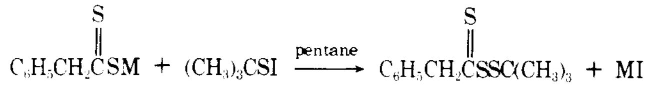


$$C_6H_5CH_2Cl + Mg \xrightarrow{ether} C_6H_5CH_2MgCl \xrightarrow[2.\ H^+/H_2O]{1.\ CS_2} C_6H_5CH_2\overset{S}{\overset{\|}{C}}SH$$

1

The syntheses of acid chlorides of dithio acids have been reported.[11] The preparation of phenylthioacetyl chloride was attempted with both thionyl chloride and oxalyl chloride, but a compound with the properties of an acid chloride was never isolated, therefore the last step of the Schotten–Baumen procedure was never attempted.

The successful synthesis of *tert*-butyl perthiophenylperacetate (4) was realized by reacting metal salts, 2, of dithiophenylacetic acid with *tert*-butylsulfenyl iodide, 3.



$$C_6H_5CH_2\overset{S}{\overset{\|}{C}}SM + (CH_3)_3CSI \xrightarrow{pentane} C_6H_5CH_2\overset{S}{\overset{\|}{C}}SSC(CH_3)_3 + MI$$

2 3 4

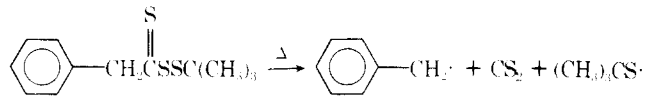
where M = Ag, Hg, and Pb.

This reaction is simple but heterogeneous; however, if this reaction is stirred well it is complete within 5 h giving good yields (>80%). The reaction was also carried out in other solvents (ether, carbon tetrachloride, tetrahydrofuran), but pentane proved preferable since the products are the cleanest.

Several dithio acid salts (Pb, Ag, Hg, and Zn) were used in the synthesis of 4, but the lead salt gave the best results, being both stable and reactive. The zinc was also very stable, but would not react with the sulfenyl iodide to give 4. The structure assigned compound 4 was in agreement with all the spectra and analysis. The electronic spectrum was consistent with literature examples[12] of compounds containing C=S absorptions.

Two other trithioperesters, *tert*-butyl trithiophenylperformate (5) and *tert*-butyl trithioanisylperformate 6, were synthesized by the same method, only differing in the manner the dithio acid was prepared. The three trithioperesters were all reasonably stable compounds, when pure, except for being sensitive to strong light. The thermal behavior of the benzyl compound, 4, differs from the behavior of the benzene derivatives 5 and 6. At 100 °C compound 4 decomposes at a rate similar to the perester analogue, *tert*-butyl phenylperacetate, while compounds 5 and 6 seem to be stable at this temperature.

Although it was originally hoped that trithioperesters, like 4, would thermally decompose by a mechanism similar to the oxygen analogue, preliminary work has indicated that it is not a simple homolytic cleavage of the S–S bond. The evidence that argued against a simple SS homolytic cleavage was the



4

following: no carbon disulfide was formed as a product in the thermal decomposition, although *tert*-butyl mercaptan was formed; radical scavengers such as galvinoxyl were not consumed during the thermal decomposition; and the rate of decomposition was dependent on the solvent polarity.

Work is currently in progress on the mechanism of the thermal decomposition of the benzyl type trithioperesters and on the generality of this synthetic method and will be reported on completion of the work.

Experimental Section

Melting points were determined using a Fisher-Johns block melting point apparatus and are uncorrected. All elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. The mass spectra were done by the High Resolution Mass Spectrometry Laboratory, Tallahassee, Fla.

Instruments. The nuclear magnetic resonance spectra were taken on Varian A-60 and Jeolco JM-4H-100 spectrometers. The chemical shift values were reported in ppm (δ) downfield from the internal standard tetramethylsilane (Me_4Si). Infrared spectra were recorded on a Perkin-Elmer Model 337. Spectra were calibrated with a polystyrene film and absorptions are reported in cm^{-1}. Ultraviolet and visible spectra were recorded on a Cary Model 14. Ethanol was used as a solvent and absorptions are reported in nanometers (nm).

Rate Measurements. The kinetics of the thermal decomposition of trithioperester **4** were studied directly in the probe of the Jeolco JM-4H-100. The temperature was regulated with a JES-VT-3 temperature controller and the temperature was controlled within ±0.5 °C during a kinetic run. The temperature of the run was calibrated before and after each run using ethylene glycol. The decomposition was followed by observing the disappearance of the methylene peak of **4** through three half-lives at δ 4.33. No other peaks appeared during the decomposition within 60 Hz of the methylene protons. The kinetic runs were analyzed in terms of first-order kinetics and gave excellent straight-line plots. The first-order rate constants were $4.3 \times 10^{-4}\ s^{-1}$ neat at 94 °C; $3.5 \times 10^{-4}\ s^{-1}$ in diphenylmethane at 97 °C; and $1.2 \times 10^{-4}\ s^{-1}$ in acetonitrile at 97 °C.

Materials. Most of the chemicals used were reagent grade and required no further purification. The following chemicals were purified as indicated: Fisher reagent grade acetonitrile was fractionally distilled over P_2O_5 through a 4 ft distillation column packed with glass beads. The fraction retained boiled between 81.6 and 81.9 °C at atmospheric pressure, and Karl Fisher titration showed less than 0.06% H_2O.

Dithiophenylacetic Acid[10] (1). Benzyl chloride (200 g, 1.59 mol) was added to 24 g (1.65 mol) of magnesium turnings covered with 500 mL of anhydrous diethyl ether. The reaction was carried out in a 1-L three-neck flask equipped with a large surface condenser and drying tube and inlet and exit valves to maintain a positive pressure of nitrogen. The benzyl chloride was added at a sufficient rate to maintain a gentle reflux and upon completion of addition was refluxed for 3 h. The Grignard reagent was then siphoned, using a positive pressure of nitrogen, into a flask containing 195 g (2.43 mol) of dry carbon disulfide in either 200 mL of diethyl ether or tetrahydrofuran. The reaction mixture was kept at 0 °C throughout the addition of the Grignard reagent and after addition was stirred at room temperature for 12 h while under a positive pressure of nitrogen. It was found that if THF was used as a cosolvent with CS_2 the reaction of the Grignard proceeded more rapidly. After the mixture was poured onto 500 g of ice and water and the layers separated, the aqueous layer (red) was acidified with formic acid and extracted with several portions of ether. The ether portions were combined and dried over $MgSO_4$. Removal of the drying agent and evaporation of the ether gave 79.3 g (0.472 mol) of an orange oil **1** (30% yield). The oil solidifies in the freezer at 20 °C and if kept frozen is stable for a few months. The acid titrated to a sharp end point in 95% ethanol with NaOH ($pK_a = 4.15$): IR (neat) 3100–3040 (C–H aromatic), 2960 (C–H aliphatic), 2520 (S–H), 1600 and 1492 (C=C), 1445, 1425, 1220, 1160, 1080, 1020 (C=S), 910, 890, 860, 760, and 705 (C--H monosubstitution), 630 (C–S), 585 cm^{-1}; UV_{max} (EtOH) 300 nm (ϵ 8200), 340 (ϵ 1900); NMR (CCl_4) δ 7.40 (s, 5), 6.10 (s, 1), 4.25 (s, 2).

Lead Dithiophenylacetate (2). A saturated aqueous solution of lead acetate was added dropwise (60 mL) to a rapidly stirred solution of dithiophenylacetic acid (20.0 g, 0.159 mol) in 95% ethanol (200 mL) until no more precipitate formed. The brownish-yellow precipitate which formed was isolated by filtration and dried, giving 23.0 g (72%) of crude lead salt **2**, mp 145–155 °C (dec). The lead salt was recrystallized from benzene and gave gold flakes of **2**: mp 185 °C dec; NMR (Me_2SO-d_6) δ 4.05 (s, 2.00), 7.38 (m, 5.0); mass spectrum (70 eV) *m/e* (rel intensity) ion, 542 (0.1) parent ion, 375 (2.5) $C_6H_5CH_2C(S)SPb^{208}$, 374 (2) $C_6H_5CH_2C(S)SPb^{207}$, 373 (2) $C_6H_5CH_2C(S)SPb^{206}$, 167 (8) $C_6H_5CH_2C(S)S$, 135 (7) $C_6H_5CH_2C{=}S$, 134 (34) $C_6H_5CH{=}C{=}S$, 91 (100) $C_6H_5CH_2$.

Anal. Calcd for $C_{16}H_{14}S_4Pb$: C, 35.57; H, 2.61. Found: C, 35.47, H, 2.60.

The silver and mercury salts were also prepared in the same manner. The silver salt was a red-orange solid prepared in 86% yield with a melting point of 135 °C dec. The mercury salt was orange with a melting point of 106 °C dec. However, the lead salt proved the most stable and easiest to purify.

***tert*-Butylmercury Mercaptide.[13]** The reaction was carried out in a glove bag, in order to contain the vapors of *tert*-butyl mercaptan. Mercuric oxide (27.61 g, 0.209 mol) was added, in 1-g quantities, to a rapidly stirred solution of 18.9 g (0.209 mol) of *tert*-butyl mercaptan and 400 mL of 95% ethanol. The red color of HgO was immediately replaced by the white-tan color of the mercaptide. After the addition was complete, the mixture was stirred for 30 min and the mercaptide was removed by filtration. The mercaptide was then washed with 100 mL of 95% ethanol and dried in vacuum. It gave 43.4 g (0.104 mol) of a fluffy white solid (99% yield) with a melting point of 165 (sublimation).

***tert*-Butylsulfenyl Iodide.[13] (3).** *tert*-Butylmercury mercaptide (11. 17 g, 0.03 mol) was added in 0.5-g quantities to a rapidly stirred solution of iodine (15.3 g, 0.06 mol) in 200 mL of pentane. It was found in later preparations that anhydrous diethyl ether could also be used as a solvent for this reaction. During the addition yellow mercuric iodide precipitated, and upon completion of the addition of the mercaptide, the purple color of the iodine solution was replaced by the red-orange color of *tert*-butylsulfenyl iodide. The mixture was gravity filtered, to remove the mercuric iodide, into a flask covered with aluminum foil to exclude light and cooled in an ice bath. *tert*-Butylsulfenyl iodide is unstable and must be used immediately after it is prepared.

***tert*-Butyl Trithiophenylperacetate (4).** Lead dithiophenylacetate (16.54 g, 0.03 mol) was added, all at once, to the covered flask containing the cooled *tert*-butylsulfenyl iodide in pentane. The resulting suspension was stirred rapidly until the red color of the sulfenyl iodide was replaced by the brilliant orange color of the trithioperester (4–5 h). If ether was used as a solvent the reaction only took 30 min. The yellow precipitate of lead iodide which formed during the reaction was removed by filtration, and the pentane was evaporated leaving a dark red oil. The oil was chromatographed with Florisil or a 60–40 mixture of Celite and powdered anhydrous $CaSO_4$ using pentane as the eluent. Removal of the pentane after chromatography gave 12.7 g (83%) of a bright orange oil. The trithioperester is mildly light sensitive and precautions to avoid direct light should be taken. When exposed to light the bright orange oil slowly changes to deep red. The silver and mercury salts were also used to prepare the trithioperester. Further purification of the oil was obtained by recrystallization from pentane at dry ice temperatures and gave orange crystals **4**: mp ~ 0 °C; UV_{max} (EtOH) 258 nm (ϵ 7.7×10^3), 315 (ϵ 1.1×10^4) ($\pi \rightarrow \pi^*$, C=S), 490 nm ($n \rightarrow \pi^*$, C=S); IR (neat) 3010 and 3005 (aromatic C–H), 2920 (aliphatic C–H), 1605, 1500, and 1475 (aromatic C=C), 1460, 1395, and 1370 (*tert*-butyl C–H), 1220, 1170, 1080, 1030, 980, 940, 902, 840, 800, 750, and 695 (aromatic C–H bend), 645, and 570 cm^{-1}; NMR (CCl_4) δ 1.23 (s, 9), 4.33 (s, 2), 7.12 (s, 5); mass spectrum (70 eV) *m/e* (rel intensity) ion, 256 (14) parent peak (also P + 1 at 257 and P + 2 at 258), 135 (44) $C_6H_5CH_2C{=}S$, 134 (84) $C_6H_5CH{=}C{=}S$, 102 (96) $C_6H_5CH{=}C$, 91 (34) $C_6H_5CH_2$, 57 (100) $(CH_3)_3C$.

Anal. Calcd for $C_{12}H_{16}S_3$: C, 56.20, H, 6.29; S, 37.51. Found: C, 56.13; H, 6.31; S, 37.76.

Lead Dithiobenzoate. Dithiobenzoic acid was prepared by the method of Becke and Hagen.[14] Powdered sulfur (8.9 g, 0.278 mol) was added to a solution of sodium (8.0 g, 0.348 mol) in methanol (150 mL). Benzyl chloride (17.0 g, 0.135 mol) was added to the stirred, cooled resulting mixture, and after a few minutes the solution turned dark purple. After solution was warmed at 60 °C for 1 h, the methanol was removed by evaporation, and 200 mL of water was added to the mixture. The mixture was extracted with several portions of ether, and the aqueous layer was acidified with concentrated hydrochloric acid. The acidified layer was extracted several times with ether, and the ether layers were combined and dried with $CaCl_2$. Evaporation of the ether left 19.3 g, 0.125 mol (93%), of a purple oil: IR (neat) 3155 and 3145 (aromatic C–H), 2975, 2920, and 2870 (aliphatic C–H), 2550 (S–H, broad), 1600, 1480, and 1490 (aromatic C=C), 1480, 1450, and 1440 cm^{-1}. Since dithiobenzoic acid is unstable and cannot be stored for any length of time, it was immediately converted to the lead salt. A saturated aqueous solution of lead acetate (50 mL) was added dropwise to a stirred ethanolic solution (200 mL) of dithiobenzoic acid (19.3 g, 0.125 mol), until no more red precipitate appeared. The mixture, after filtration and drying, gave 24.1 g, 0.469 mol (75%), of red solid with a mp of 130 °C dec.

***tert*-Butyl Trithiophenylperformate (5).** Lead dithiobenzoate (2.60 g, 0.00506 mol) was added to a freshly prepared solution of *tert*-butylsulfenyl iodide (1.87 g, 0.0494 mol, of *tert*-butyl mercury mercaptide, 2.48 g, 0.0195 mol, of iodine, and 250 mL of pentane) while the mixture was rapidly stirred. After 5 h of stirring the lead iodide was removed by filtration and pentane evaporated from the purple filtrate. Chromatography on Florisil, using pentane as the eluent, gave 1.90 g, 0.00784 mol (77%), of the trithioperester **5** as a dark purple oil: UV_{max} (EtOH) 230 nm (shoulder), 295 (ϵ 1×10^4) ($\pi \rightarrow \pi^*$, C=S), 530 (ϵ 1×10^2) ($n \rightarrow \pi^*$, C=S), 730 (ϵ 3.3×10^1); IR (neat) 3030 (C–H aromatic), 2940, 2900, 2870 and 2830 (C–H aliphatic), 1685, 1585, and 1470 (C=C aromatic), 1455, 1440, 1390, and 1360 (C–H *tert*-butyl), 1170, 1040, 880, 840, 760, and 680 cm^{-1} (C–H 5 adjacent aromatic H's); NMR (CCl_4) δ 1.32 (s, 9), 7.45 (m, 3), 8.00 (m, 2).

Anal. Calcd for $C_{11}H_{14}S_3$: C, 54.50; H 5.82; S, 39.68. Found: C, 54.32; H, 5.65.

Lead *p*-Methoxydithiobenzoate. *p*-Methoxydithiobenzoic acid was prepared by the method of Bruni.[15] Ammonium sulfide (dark), 25 mL, was added to a solution of *p*-anisaldehyde (13.6 g, 0.113 mol) in tetrahydrofuran. The mixture was heated at 70 °C in a flask equipped with a reflux condenser and stirred for 1.5 h, during which time the color changed from light brown to dark purple. The mixture was extracted with several portions of ether, and the aqueous layer was separated and acidified with concentrated hydrochloric acid. The acidified layer was extracted several times with ether, and the ether layers were combined and dried with $CaCl_2$. Evaporation of the ether gave 5.9 g, 0.0320 mol (28%), of the crude acid as a dark purple oil. Since the acid was unstable, it was converted into the lead salt immediately. A saturated aqueous solution of lead acetate was added dropwise (15 mL) to a stirred ethanolic solution (50 mL) of *p*-methoxydithiobenzoic acid (5.9 g, 0.0320 mol), until no more orange precipitate formed. The mixture after filtration and drying gave 2.38 g, 0.00417 mol (26%), of yellow-orange solid with a mp of 120 °C dec.

***tert*-Butyl Trithioanisylperformate (6).** Lead *p*-methoxydithiobenzoate (2.38 g, 0.00417 mol) was added to a freshly prepared solution of *tert*-butylsulfenyl iodide (1.4 g, 0.00383 mol, of *tert*-butyl mercury mercaptide, 1.92 g, 0.0151 mol, of iodine, and 250 mL of pentane) while the mixture was rapidly stirred. After 5 h of stirring the mixture in a covered flask the lead iodide was removed by filtration and the pentane evaporated from the purple solution. Chromatography on Florisil using pentane as an eluent gave 1.1 g, 0.0040 mol (49%), of a bright purple oil. Recrystallization of the oil in pentane at dry ice temperatures gave beautiful red-purple needles **6**: mp 32–35 °C; UV$_{max}$ (EtOH) 245 nm (ϵ 8.0 × 10^3), 341 (ϵ 2.2 × 10^4) ($\pi \rightarrow \pi$ C=S), 520 (ϵ 3.2 × 10^2) ($n \rightarrow \pi$, C=S), 720 (ϵ 2.1 × 10^3); IR (neat) 3030 (C–H aromatic), 2950 and 2870 (C–H aliphatic), 1600 and 1505 (C=C aromatic), 1390 and 1370 (C–H tert-butyl), 1310, 1245 (C–O–C), 1260, 1160, 1050, and 1030 (C–O–C), 940, 860, 840 (C–H, 2 adjacent aromatic H's), 758, 685 cm^{-1}; NMR (CCl_4) δ 1.31 (s, 9), 3.77 (s, 3), 6.78 (d, 2, J = 9 Hz), 8.05 (d, 2, J = 9 Hz); mass spectrum (70 eV) *m/e* (rel intensity) ion, 240 (7) parent ion, 183 (14) $CH_3OC_6H_4C(S)S$, 151 (100) $CH_3OC_6H_4C{=}S$, 107 (21) $CH_3OC_6H_4$, 92 (10) C_6H_4O, 76 (20) C_6H_4, 65 (4) C_5H_4, 57 (68) $C(CH_3)_3$, 41 (74) C_3H_5.

Anal. Calcd for $C_{12}H_{16}OS_3$: C, 52.90; H 5.92; S, 35.31. Found: C, 52.72; H, 5.96; S, 35.31.

***tert*-Butyl Acetyl Disulfide (7).** Diacetyl was prepared as described by Bohme, Goulbeaud, and Stackel.[16] The faint pink liquid, obtained in 53% yield, was purified by several vacuum distillations and the cut retained at 56 °C (12 mm of Hg) had properties of the compound previously reported. Acetylsulfur chloride[16] was prepared as described by Bohme et al. and gave 4.78 g (0.0423 mol) (99%) of an orange liquid with the same properties of the compound previously reported.

In the type of synthesis first described by Bohme and Zinner[9] *tert*-butyl mercaptan (4.4 g, 0.0488 mol) was added to a solution of acetyl sulfurchloride (4.78 g, 0.0423 mol) in 50 mL of anhydrous either, while the mixture was cooled in an ice bath. As the mercaptan was added an exothermic reaction changed the orange color of the original solution to a light yellow. After the addition of mercaptan was complete, the reaction mixture was kept in an ice bath for 1 h and then left at room temperature for 2 h. Aspiration of the reaction mixture produced a light yellow oil, which upon vacuum distillation gave 3.0 g, 0.0183 mol (44%), of a colorless liquid, **7**: bp 115–125 °C (9 mm); IR (neat) 2970 to 2860 (C–H aliphatic), 1740 (C=O), 1710 (C=O), 1470, 1460, 1395, and 1370 (C-H *tert*-butyl) 1220, 1150, 1101, 940, 590 (C–S) cm^{-1}; NMR (CCl_4) δ 1.33 (s, 9), 2.47 (s, 3).

***tert*-Butyl Hydrodisulfide (8).** Dilute hydrochloric acid (6 N) was added dropwise to a rapidly stirred solution of *tert*-butyl acetyldisulfide (3.0 g, 0.0183 mol) in 20 mL of methanol, which had been saturated with nitrogen. The reaction was run under nitrogen, and after the addition of 4 mL of hydrochloric acid a colorless oil started to form. To prevent two layers from forming 10 mL of methanol was added and the reaction mixture was stirred for 2 h before adding more HCl. The remainder of the HCl (6 mL) was added and the solution was stirred for 6 h. Water (100 mL) was added to the reaction mixture and the organic layer that formed was extracted several times with ether, separated, and dried with $CaCl_2$. Evaporation of the ether and vacuum distillation of the remaining oil (40 °C, 120 mm) gave 1.3 g, 0.0107 mol (58%), of a colorless, unpleasant smelling oil **8**: IR (neat) 2970–2780 (C–H aliphatic), 2480 (S–H), 1470, 1450, 1380, and 1370 (C–H *tert*-butyl), 1210, 1160, 1140, 930, 570 (C–S) cm^{-1}; NMR (CCl_4) δ 1.38 (s, 9), 1.43 (s, 1).

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Registry No.—**1**, 5873-91-6; **2** lead salt, 68409-47-2; **2** silver salt, 68409-48-3; **2** mercury salt, 68409-49-4; **3**, 25558-08-1; **4**, 68409-50-7; **5**, 59937-89-2; **6**, 68409-51-8; **7**, 31172-01-7; **8**, 68409-52-9; benzyl chloride, 100-44-7; *tert*-butylmercury mercaptide 3374-16-1; lead dithiobenzoate, 2909-55-9; dithiobenzoic acid, 121-68-6; lead *p*-methoxydithiobenzoate, 20704-52-3; *p*-methoxydithiobenzoic acid, 2168-77-6; carbon disulfide, 75-15-0; mercuric oxide, 21908-53-2; *tert*-butyl mercaptan, 75-66-1; acetyl sulfurchloride, 6405-82-9.

References and Notes

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