benzene (15 mL) in the presence of 1 (55.2 mg, 0.06 mmol) and (–)-DIPHOL (118.6 mg, 0.24 mmol) was carried out at 52 °C for 8 days under 500 psi of CO/H_2. NMR revealed complete conversion to **20b**: ($CDCl_3$) δ 1.5 ($(CH_3)_3C$, s), 2.0 (CH_2CH_2, m), 3.5 (>NCH_2, m), 4.1 (>NC**H**CHO, m), 9.52 (CHO, d, $J \simeq 2$ Hz). Oxidation by $KMnO_4/Me_2CO/MgSO_4$ yielded the corresponding acid (720 mg, 6 mmol): NMR ($CDCl_3$) δ 1.4 ($(CH_3)_3C$, s), 2.05 (CH_2CH_2, m), 3.4 (>NCH_2, m), 4.2 (>NC**H**COOH, m), 8.7 (COOH, br s). Esterification with ethereal diazomethane afforded the ester **21b** as a colorless, viscous oil: NMR ($CDCl_3$) δ 1.3 ($(CH_3)_3C$, s), 1.9 (CH_2CH_2, m), 3.65 (CH_3OCO, s), 4.2 (>NC**H**$COOCH_3$, m); yield 379.7 mg (56% from **19b**); $[\alpha]^{25}{}_D$ +0.19° (0.35% ee).

(*S*)-(–)-*N*-(*tert*-Butoxycarbonyl)proline ((*S*)-21b). (*S*)-Proline (1.15 g, 10 mmol) and triethylamine (2.1 mL, 15 mmol) were dissolved in dioxane (10 mL). Water (6 mL) and BOC-ON[20] (*t*-BuOCOONC(CN)Ph, 2.71 g, 11 mmol) were added, and after the mixture was stirred at 25 °C for 2.5 h, the homogeneous clear yellow solution was diluted with water (15 mL) and ethyl acetate (20 mL). The aqueous layer was separated, extracted with ethyl acetate (2 × 10 mL), and then acidified with 1 N HCl. The resulting emulsion was extracted with ethyl acetate (3 × 30 mL), dried ($MgSO_4$), and concentrated to afford a colorless oil which solidified on standing. (*tert*-Butoxycarbonyl)proline was obtained as a low-melting solid. Esterification with ethereal diazomethane followed by column chromatography on silica gel (10% acetone–hexane) gave (*S*)-**21b** as a colorless oil which was purified by distillation in a Kugelrohr oven (130 °C, 30 μm), $[\alpha]^{25}{}_D$ –54.54° (*c* 10.04, $CHCl_3$).

Hydroformylation of *N*-Allylacetamide (29). A mixture of **29** (5.0 mL) and **1** (99.6 mg) in benzene (10 mL) was hydroformylated under 500 psi of CO/H_2 (1:1) at 40 °C for 30 h. NMR and TLC analyses showed only a mixture of aldehydes. The crude mixture was fractionated at 0.1 mmHg. Two fractions were collected: I, bp 74–78 °C, 1.973 g (mainly starting material); II, bp 88–94 °C, 2.177 g. This fraction contained no starting material and consisted of **30** and **19a** in 54:46 ratio, respectively. Oxidation of this mixture with potassium permanganate–acetone yielded an acid which was esterified with diazomethane. The product, methyl 2-methyl-3-acetamidopropionate, was purified on a GLC column [10 ft × $^3/_8$ in. 20% Carbowax 20-M, Chromosorb W (60/80)] at 225 °C and was obtained as a colorless oil: NMR ($CDCl_3$) δ 1.15 (CH_3, d, J = 8 Hz), 1.92 ($COCH_3$, s), 2.7 (CH_2N<, m), 3.4 (CHCOOMe, m), 3.7 ($COOCH_3$, s), 5.9 (NH, br s).

Preparation of Catalyst 18. (+)-DIPHOL [$[\alpha]^{25}{}_D$ +66° (*c* 1.93, C_6H_6); 300 mg, 0.6 mmol] and $[Rh(CO)_2Cl]_2$ (108.8 mg, 0.28 mmol) were heated to reflux temperature in benzene under nitrogen for 5.5 h. The yellow precipitate was collected and dried to yield 342.2 mg (93%) of product, IR (KBr) 1975 (C=O) cm^{-1}. This complex (**17**; 100 mg, 0.15 mmol) was suspended in THF (10 mL) under nitrogen, and a phosphine ligand was added. The suspension was stirred and cooled to –78 °C whereupon a red coloration was observed. *n*-Butyllithium in hexane (120 μL, 0.3 mmol, 2.56 M) was added, and the reaction mixture was allowed to warm to 25 °C. After 3 h a red homogeneous solution was obtained. The solvent was removed in vacuo, and a dark red solid was obtained; IR (KBr) 1960 (C=O) cm^{-1}. The solid was dissolved in benzene (4 mL) under nitrogen. The resulting red solution was washed with water (4 × 5 mL) until the washings were neutral and then dried ($MgSO_4$). This solution was used directly as a catalyst for hydroformylation.

General Procedure for Hydroesterification. The substrate was dissolved in 2-butanone, the solvent was flushed with nitrogen, and the catalyst was then added. The reaction mixture was placed in a high-pressure reactor. The unit was charged with carbon monoxide up to 1500 psi and maintained at 70 °C. The reaction mixture was stirred at this temperature for 1 or 2 days and then cooled to 0 °C. The pressure was slowly released, and the mixture was filtered. The filtrate was concentrated to dryness. When **3a** was the substrate, a semisolid was obtained which was directly analyzed by NMR. The isolation of the products was effected by chromatography on a silica gel column with acetone–petroleum ether as eluent (Table II).

Acknowledgment. This research was supported by the National Science Foundation (Grant CHE 77–08349).

Registry No. **1**, 17185-29-4; **2**, 13965-03-2; **3**, 2372-96-5; **3a**, 3485-84-5; **4**, 53531-15-0; **4a**, 73365-03-4; (*S*)-**6**, 73365-04-5; **7**, 39267-22-6; **8**, 108-30-5; **8a**, 85-44-9; (*R*)-**9**, 338-69-2; (*R*)-**9**·HCl, 16428-74-3; (*R*,*S*)-**9**, 302-72-7; (*S*)-**9**, 56-41-7; (*R*,*S*)-**10**, 73323-90-7; (*S*)-**10**, 73365-05-6; (*R*)-**10a**, 29588-83-8; (*S*)-**10a**, 4192-28-3; **11**, 107-95-9; **12**, 5724-76-5; (*R*)-**13**, 73323-91-8; (*S*)-**13**, 70058-19-4; (*R*,*S*)-**14**, 6168-72-5; (*S*)-**14**, 2749-11-3; **15a**, 73323-92-9; **15b**, 73323-93-0; **16**, 14523-22-9; **17**, 73333-86-5; **19a**, 23105-58-0; **19b**, 73286-71-2; **20a**, 73323-64-5; (*R*)-**20b**, 73365-02-3; **21a**, 27460-51-1; (*R*)-**21b**, 73323-65-6; (*S*)-**21b**, 59936-29-7; **22**, 7005-20-1; **23**, 65693-79-0; **24**, 24431-53-6; **25**, 73323-66-7; **26**, 5202-78-8; **27**, 73323-67-8; **28**, 73323-68-9; **29**, 692-33-1; **32**, 33745-25-4; **34**, 22156-23-6; α-methoxy-α-(trifluoromethyl)benzeneacetyl chloride, 20445-33-4; *N*-ethylphthalimide, 5022-29-7; *N*-acetylproline, 68-95-1; 1-*tert*-butyl (*R*)-1,2-pyrrolidinedicarboxylate, 37784-17-1; *t*-BOC-proline, 15761-39-4; methyl 2-methyl-3-acetamidopropionate, 73323-69-0; (+)-DIOP, 37002-48-5; (–)-DIOP, 32305-98-9; (–)-DIPHOL, 57221-96-2; (+)-DIPHOL, 73323-70-3; BPPM, 61478-28-2.

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Syntheses with Halogen Derivatives of Thiophene and Benzothiophene

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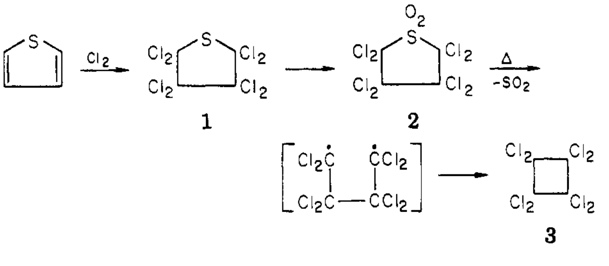
Pyrolysis of octachlorotetrahydrothiophene 1,1-dioxide provides a practical synthesis of octachlorocyclobutane. 1,2-Dichlorohexafluorotetrahydrothiophene 1,1-dioxide also yields a cyclobutane. Treatment of these sulfones with potassium hydroxide forms perhalogenated 3-butenesulfonates. From octachloro-2,3-dihydrobenzothiophene 1,1-dioxide, octachlorostyrene is produced by pyrolysis and hexachlorobenzothiophene 1,1-dioxide by treatment with sodium iodide. Hexachlorobenzothiophene has been prepared from octachloro-2,3-dihydrobenzothiophene and oxidized with chromium trioxide to a thiolactone (**17**). Hydrolysis of the latter gives a 2*H*-benzothiete (**18**). Oxidation of tetrachlorothiophene forms the thiolactone tetrachloro-2,3-dihydrothiophen-2-one (**19**). Octachlorodibenzothiophene can be made by direct chlorination.

Pyrolysis of Octahalotetrahydrothiophene 1,1-Dioxides. Octachlorocyclobutane has previously been made in 5% yield by treatment of octachloro-2-butene with aluminum chloride.[2] This preparation was the source of material for subsequent physical studies[3] on this interesting molecule, with its bent ring of four carbon atoms shielded by chlorine atoms. In 1976 a synthesis in 22% yield by heating $SnCl_2$ with CCl_4 at 140 °C in the presence of $BuEt_3NCl$ was reported.[4]

A synthesis has now been developed involving chlorination of thiophene to the known octachlorotetrahydrothiophene[5] (**1**) in 72% yield, oxidation of this with chromium trioxide in acetic acid to the 1,1-dioxide **2** in 97.5% yield, and pyrolysis of the dioxide in the liquid phase at 340–350 °C to octachlorocyclobutane (**3**) in 77.5% yield (eq 1).

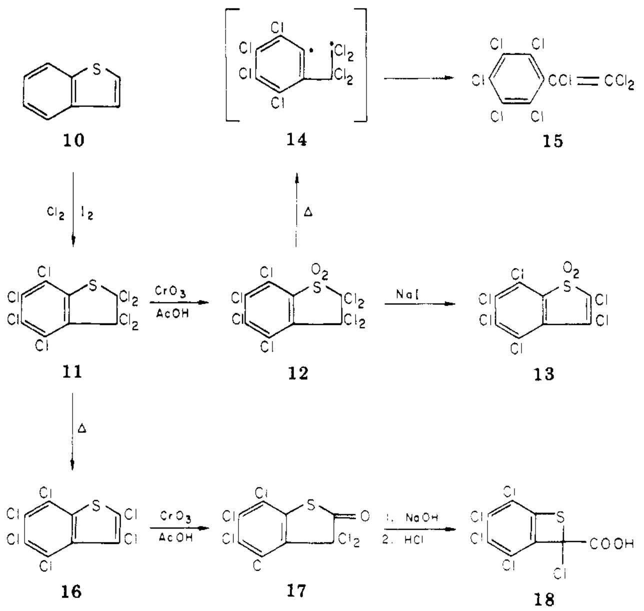


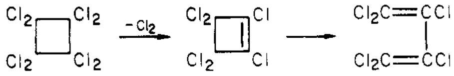
(1)

The pyrolysis has also been carried out in the gas phase at 452 °C and 0.05 mm, which indicates that the reaction is unimolecular and provides support for a diradical mechanism, which is usually proposed for the thermal decomposition of sulfones.[6] The composition of the liquid byproducts in the vacuum pyrolysis was determined by GLC. Thus, the identified products of the pyrolysis, besides sulfur dioxide, were established as 65.3% octachlorocyclobutane, 13.8% tetrachloroethylene, 0.70% hexachlorocyclobutene, and 12.3% hexachlorobutadiene. The high-yield ring closure of the somewhat stabilized but hindered diradical to form a strained ring rather than more tetrachloroethylene or rather than rearranging to octachloro-1-butene is noteworthy. Extended Hückel calculations[7] for total energy give values of −1175.16 eV for octachlorocyclobutane, −1175.50 eV for 2 $CCl_2{=}CCl_2$, and −1175.94 eV for $Cl_2C{=}CClCCl_2CCl_3$. This indicates that octachlorocyclobutane is less stable than 2 $CCl_2{=}CCl_2$ by 7.84 kcal and less stable than $Cl_2C{=}CClCCl_2CCl_3$ by 18.0 kcal. Thus, the course of the reaction appears to be kinetically rather than thermodynamically controlled. Pyrolysis of tetrahydrothiophene 1,1-dioxide and its alkyl derivative yield 2 mol of monoolefins.[8]

Separate vacuum pyrolysis of octachlorocyclobutane at 506 °C showed the pyrolysate to contain, besides chlorine, 1.20% hexachlorocyclobutene, 86% hexachlorobutadiene from ring opening of the hexachlorocyclobutene, and 0.3% tetrachloroethylene. The ring opening of hexachlorocyclobutene has been observed previously at 195 °C[2b] (eq 2). Hexachlorocyclobutene was not altered by the GLC conditions used.

Scheme I

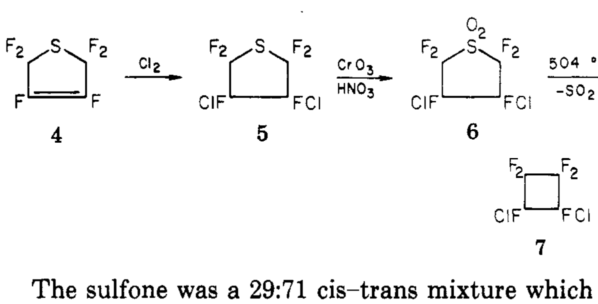




(2)

By differential scanning calorimetry, octachlorocyclobutane has an endotherm at 88 °C (4.01 kcal/mol), a melting point of 259 °C (1.52 kcal/mol), and a boiling point of 275 °C. X-ray powder diagrams taken below and above 88 °C show that the monoclinic[3] crystals change to another crystal form, probably of higher symmetry. The ^{13}C NMR spectrum of the solid was observed below and above the transition temperature. No line sharpening took place such as might result from molecular rotation, which occurs in crystals of various symmetrical molecules.[9]

A fluorinated tetrahydrothiophene dioxide has been similarly pyrolyzed in a platinum tube packed with quartz to the known[10] 1,2-dichlorotetrafluorocyclobutane (eq 3).



(3)

The sulfone was a 29:71 cis–trans mixture which was pyrolyzed at 504 °C in 62% yield to 1,2-dichlorotetrafluorocyclobutane of the same cis–trans composition. Other products of the pyrolysis were not determined.

Ring Opening of Octahalotetrahydrothiophene 1,1-Dioxides. Octachlorothiophene 1,1-dioxide is readily ring opened with alcoholic KOH at 23 °C to form potassium perchloro-3-butenesulfonate (**8**) (eq 4). 3,4-Dichlorohexafluorotetrahydrothiophene dioxide is similarly

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[1] Contribution No. 2756.

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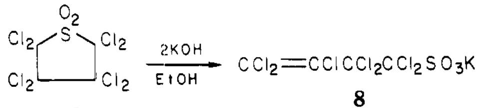

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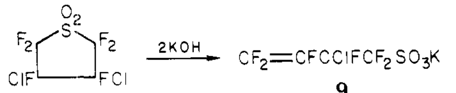


6 9 (5)

ring opened to **9** (eq 5). In contrast, ordinary sulfones are cleaved by alkali to form sulfinates by 1,2-elimination rather than sulfonates.[11]

Syntheses Based on Chlorinated Benzothiophene. Chlorination of benzo[*b*]thiophene (**10**) in the presence of 1 mol of iodine produced 2,2,3,3,4,5,6,7-octachloro-2,3-dihydrobenzo[*b*]thiophene (**11**) which underwent the transformations summarized in Scheme I involving three rearrangements.

Oxidation of octachloro-2,3-dihydrobenzothiophene (**11**) with chromium trioxide provided the 1,1-dioxide **12**. Unlike octachlorotetrahydrothiophene 1,1-dioxide, pyrolysis of **12** through the presumed diradical **14** did not result in ring closure to octachlorobenzocyclobutene but in rearrangement of the diradical to octachlorostyrene (**15**) in 84% yield. This reaction is mechanistically analogous to the pyrolysis of hexachlorobenzothiophene 1,1-dioxide (**13**) to hexachlorophenylacetylene,[12] of octachlorobenzocyclobutene to octachlorostyrene,[13] and of tetrachlorothiophene 1,1-dioxide to tetrachlorovinylacetylene.[14]

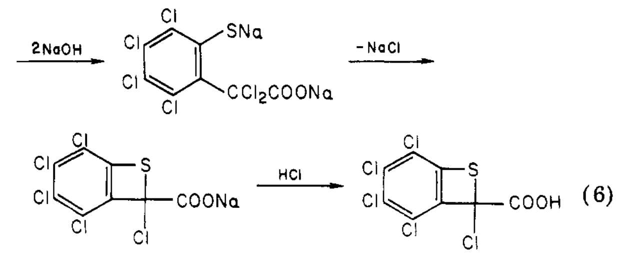
Pyrolysis of octachloro-2,3-dihydrobenzothiophene (**11**) at 240 °C or treatment with zinc gave hexachlorobenzothiophene (**16**) in 91–95% yield, thus providing a practical synthesis. This compound was made in 1908[15] and 1974,[12] in low, unspecified yield, by heating styrene dibromide, thionyl chloride, and sulfuryl chloride at 270 °C and was oxidized to the 1,1-dioxide (**13**). The latter was made in the present work by treating octachloro-2,3-dihydrobenzothiophene 1,1-dioxide (**12**) with sodium iodide.

Novel transformations are represented by the sequence **16** → **17** → **18**. While trifluoroperacetic acid oxidizes hexachlorobenzothiophene to the 1,1-dioxide,[12] chromium trioxide in acetic acid produced an oxidative rearrangement to form the thiolactone 3,3,4,5,6,7-hexachloro-2,3-dihydrobenzothiophen-2-one (**17**) in 29% yield. The mechanism may be related to that for the oxidation of $CCl_2=CCl_2$ to CCl_3COCl with peracids or nitric acid.[16]

Support for the structure of **17** lies in its transformation by sodium hydroxide (eq 6) to the 2*H*-benzothiete (7-thiabicyclo[4.2.0]octa-1,3,5-triene) **18** of which few examples are known.[17]

The procedure for oxidizing hexachlorobenzothiophene to a thiolactone (**17**) has been extended to tetrachlorothiophene. From the oxidation of this with chromium

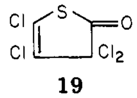
17



(6)

18

trioxide, the thiolactone **19** has been isolated in 16% yield. In comparison, oxidation of tetrachlorothiophene with nitric acid forms the thioanhydride **20**[18] and with 3-chloroperbenzoic acid the dioxide **21**.[14]



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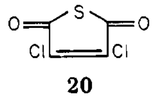

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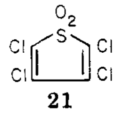

21

Octachlorodibenzothiophene. The two published syntheses of octachlorodibenzothiophene are (1) the chlorination of 4,4′-dichlorobiphenyl in the presence of sulfur and aluminum chloride (57%)[19] and (2) the irradiation of pentachlorobenzenesulfenyl chloride for 150 h (62%).[20] The compound can be made more simply in 84% yield by heating dibenzothiophene and chlorine in the presence of a catalytic amount of iodine in a pressure vessel at 100 °C. Octachlorodibenzothiophene was inert at 100 °C to chromium trioxide in acetic acid or in fuming nitric acid. Sulfone formation may be prevented by steric hindrance.

Experimental Section

The ^1H NMR spectra were determined with a Varian A-60 instrument using Me_4Si as internal standard. IR spectra (KBr wafer) were measured with a Perkin-Elmer Model 21 spectrometer. Thermal analyses were done in gold sample pans with a Du Pont Instruments 990 thermal analyzer coupled to a 910 differential scanning calorimeter module. Vacuum pyrolyses were carried out through a 0.5-in. platinum tube packed with 3-mm sections of 6-mm quartz tubing and heated with a 12-in. heater. The apparatus has been described.[21] GLC analyses of the pyrolysates from octachlorotetrahydrothiophene 1,1-dioxide and from octachlorocyclobutane were made by using 20% Triton X305 on Chromosorb W. Melting and boiling points are uncorrected.

Octachlorotetrahydrothiophene 1,1-Dioxide (2). Octachlorotetrahydrothiophene[4] (182 g, 0.5 mol) and 1000 mL of acetic acid were placed in a mechanically stirred 2-L, three-necked flask and heated on a steam bath. Chromium trioxide (250 g, 2.5 mol) was added in portions over 40 min. When the temperature reached 115–118 °C, addition was stopped until the temperature began to subside. Heating was continued for 2.5 h at the end of the addition. The solution was then poured into 1500 mL of ice and water, and the product was filtered off and washed by repeated slurrying with water and filtering until the green color was gone. The sulfone **2** was air-dried; 193 g (97.5%). The crude product is suitable for pyrolysis. Material for characterization was recrystallized from ethanol: dec 318 °C; IR 1387, 1175 (SO_2), 776 cm^{-1} (CCl).

Anal. Calcd for $C_4Cl_8O_2S$: C, 12.14; Cl, 71.67. Found: C, 12.01; Cl, 71.87.

Octachlorocyclobutane (3). A 300-mL, single-necked, round-bottomed flask was fitted with a $^3/_4$-in. uncooled column to serve as condenser and half-immersed in a Wood metal bath

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maintained at 340–350 °C. Octachlorotetrahydrothiophene 1,1-dioxide (200 g) was added through the condenser in portions during 35 min. The first portions were allowed to heat for about 5 min to generate some liquid octachlorocyclobutane before proceeding. Heating was continued for 15 min after all was added. Some reflux took place during the cracking because of the formation of hexachlorobutadiene. The product was recrystallized from dichloromethane to give 130 g (77.5%) of octachlorocyclobutane (3) in four crops: mp 259 °C; bp 275 °C by differential scanning calorimetry. Removal of solvent and hexachlorobutadiene from the mother liquor and washing the residue with methanol left 15 g of solid which was mostly the sulfone. The sulfone is very soluble in dichloromethane.

Anal. Calcd for C_4Cl_8: C, 14.48; Cl, 85.52. Found: C, 14.77; Cl, 85.22.

3,4-Dichlorohexafluorotetrahydrothiophene (5). Hexafluoro-2,5-dihydrothiophene[22] (4; 29.1 g, 0.15 mol) was placed in a side-arm flask with a dry ice condenser. Chlorine was passed in slowly while the flask was irradiated with a sun lamp until chlorine dripped permanently from the condenser. Distillation gave 1.41 g, bp 72–105 °C, and 30.8 g (77%), bp 105–109 °C, of a partly solid mixture of cis and trans isomers of the adduct 5. The solid melted at 33 °C.

Anal. Calcd for $C_4Cl_2F_6S$: Cl, 26.76. Found: Cl, 26.56.

3,4-Dichlorohexafluorotetrahydrothiophene 1,1-Dioxide (6). A mixture of 26.5 g (0.1 mol) of 3,4-dichlorohexafluorotetrahydrothiophene (5), 100 mL of 90% nitric acid, and 40 g (0.4 mol) of chromium trioxide[23] was stirred and heated on a steam bath under reflux for 3.5 h. The cooled mixture was poured onto 300 g of ice, and the volatile product was filtered off, liquefied with 2 mL of pentane, and dried ($MgSO_4$). Distillation gave 20 g (67%) of the sulfone 6: bp 140 °C; mp 46–47 °C. The product gave no indication of separation into isomers by GLC over 20% Triton X305 on Chromosorb W. However, ^{19}F NMR showed the product to be a 28:72 cis–trans mixture.[24]

Anal. Calcd for $C_4Cl_2F_6O_2S$: C, 16.18; Cl, 23.87. Found: C, 16.54; Cl, 24.23.

Pyrolysis of 3,4-Dichlorohexafluorotetrahydrothiophene 1,1-Dioxide (6). The sulfone (10 g) was distilled during 30 min through a platinum tube packed with sections of quartz tubing and heated to 504 °C with a 12-in. heater. The product was collected in a dry ice trap. Distillation gave, besides sulfur dioxide, 4.2 g of 1,2-dichlorohexafluorocyclobutane[10] (7): bp 58 °C; n^{25}_{D} 1.3318. The pot residue (1.09 g) contained 83% of the cyclobutane and 12% of the sulfone, as determined by GLC over 20% Triton X305 on Chromosorb W. With correction for this, a 62% yield is accounted for. The product was a 29:71 cis–trans mixture as measured by ^{19}F NMR.[24]

Potassium Heptachloro-3-butenesulfonate Hydrate (8). To 99 g (0.25 mol) of octachlorotetrahydrothiophene 1,1-dioxide (2) dissolved in 1100 mL of ethanol was added with stirring 34.5 g (0.52 mol) of 85% potassium hydroxide in 200 mL of ethanol at 20–30 °C. The mixture was stirred for 1 h and then filtered. The solid was slurried with acetone to dissolve the product away from potassium chloride. The original filtrate was evaporated, and the residue was dissolved in acetone. The combined acetone solutions were filtered and concentrated to give 96 g (89%) of the sulfonate 8 in two crops. Each crop was washed with ethanol rather than acetone as the compound is less soluble in ethanol: NMR [$(CD_3)_2CO$] 2.98 ppm (s, H_2O of crystallization); IR 3623, 3497, 1618 (H_2O), 1538 ($CCl_2{=}CCl$), 1252, 1071 cm^{-1} (SO_2O). The salt can also be recrystallized from water.

Anal. Calcd for $C_4Cl_7KO_3S\cdot H_2O$: C, 11.09; H, 0.47; Cl, 57.26. Found: C, 11.36; H, 0.70; Cl, 57.18; Cl^-, negative.

Pyrolysis of the salt gives perchlorobutadiene.

Potassium 2-Chloro-1,1,2,3,4,4-hexafluoro-3-butene-1-sulfonate (9). To 40 g (0.135 mol) of 3,4-dichloro-2,2,3,4,5,5-hexafluorothiophene 1,1-dioxide (6) dissolved in 80 mL of tetrahydrofuran was added 17.8 g (0.27 mol) of potassium hydroxide in 35 mL of water with stirring at 20–25 °C. The mixture was stirred for 16 h, and the solvent was then removed under reduced pressure. The product was dissolved in acetone and filtered from potassium chloride. The acetone was evaporated, and the residue was dissolved in a minimum amount of *tert*-butyl alcohol. This solution was filtered from additional potassium chloride, and benzene was added to the filtrate to precipitate the crystalline potassium sulfonate 9: 35.5 g (83%); IR 1795 cm^{-1} ($CF_2{=}CF$). The compound can also be recrystallized from dioxane but then contains dioxane of crystallization.

Anal. Calcd for $C_4F_6ClKO_3S$: C, 15.17; Cl, 11.20; F, 36.00. Found: C, 15.34; Cl, 10.81; F, 35.08.

2,2,3,3,4,5,6,7-Octachloro-2,3-dihydrobenzothiophene (11). Benzothiophene (55.3 g, 97%, 0.4 mol), 300 mL of chloroform, and 102 g (0.4 mol) of iodine were placed in a 1-L, three-necked flask fitted with a mechanical stirrer, thermometer, and gas inlet and outlet tubes. Chlorine was passed in at 5–10 °C for 8 h. The mixture became dark and was allowed to stand for 16 h without cooling. The iodine trichloride was filtered off and rinsed with carbon tetrachloride. Nitrogen was passed through the filtrate to remove hydrogen chloride, and the filtrate was washed first with 10% sodium carbonate solution (foaming) and then with sodium thiosulfate solution. The solution was dried ($MgSO_4$, decolorizing charcoal), and the solvent was removed. Acetone was added, the mixture was cooled, and the product was filtered off and washed with cold acetone; yield 114 g. The product was recystallized twice from ethyl acetate, after filtering off 0.9 g of an impurity, to give 96 g (58%) of 11: mp 117–118 °C; dec 226 °C.

Anal. Calcd for C_8Cl_8S: C, 23.33; Cl, 68.88. Found: C, 23.34; Cl, 68.81.

Octachloro-2,3-dihydrobenzothiophene 1,1-Dioxide (12). Octachloro-2,3-dihydrobenzothiophene (11; 41.2 g, 0.1 mol) and 200 mL of acetic acid were mechanically stirred and heated on a steam bath. Chromium trioxide (50 g, 0.5 mol) was added in portions. Heating was continued for 1 h, and the mixture was the poured into water and ice. The product was filtered off and air-dried; yield 42 g (94%). Recrystallization from 1-propanol left 38.4 g (86%) of 12: mp 152–153 °C; dec 230 °C; IR 1529 (aromatic C=C), 1376, 1179 cm^{-1} (SO_2).

Anal. Calcd for $C_8Cl_8O_2S$: C, 21.65; Cl, 63.91. Found: C, 21.63; Cl, 63.82.

Pyrolysis of Octachloro-2,3-dihydrobenzothiophene 1,1-Dioxide. Five grams of octachloro-2,3-dihydrobenzothiophene 1,1-dioxide (12) was heated in a test tube in a Wood metal bath at 300 °C for 0.5 h. Sulfur dioxide was evolved, and 4.25 g of product was left. This was recrystallized from ethanol to give 3.91 g (91%) of octachlorostyrene[13] (15) in two crops: mp 95–96 °C; IR 1623, 1541 cm^{-1} (C=C).

Hexachlorobenzothiophene (16). Octachloro-2,3-dihydrobenzothiophene (11; 41.2 g, 0.1 mol) was placed in a 29 × 200 mm test tube and heated with a free flame. At 240 °C chlorine was evolved, and heating was continued until the internal temperature was 400 °C. The product (33.7 g) was recrystallized from benzene to give 31 g (91%) of hexachlorobenzothiophene (16), mp 158–159 °C (lit.[15] mp 158 °C).

Octachloro-2,3-dihydrobenzothiophene (11; 8.24 g, 0.02 mol) was dissolved in 100 mL of dioxane and heated and stirred on a steam bath while 2 g (0.03 mol) of zinc dust was added in portions. The reaction was vigorous after an induction period. After the reaction subsided, the solution was filtered and boiled down to crystallization. The mixture was cooled, 20 mL of the methanol was added, and the product was filtered off and washed with methanol to give 6.48 g (95%) of hexachlorobenzothiophene (16): mp 156–157.5 °C; mp 157–158 °C after recrystallization from benzene.

Hexachlorobenzothiophene 1,1-Dioxide (13). To 8.88 g (0.02 mol) of octachloro-2,3-dihydrobenzothiophene 1,1-dioxide (12) dissolved in 50 mL of acetone was added 9 g (0.06 mol) of sodium iodide dissolved in 25 mL of acetone, and the mixture was refluxed for 16 h. The acetone was evaporated, and the residue was washed first with sodium thiosulfate solution to remove iodine and then with water. The product (6.92 g) was recrystallized from ethyl acetate to leave 5.97 g (80%) of 13: mp 167–168 °C (lit.[12] mp

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(22) Krespan, C. G. U.S. Patent 3069431, 1962; *Chem. Abstr.* **1963**, *58* 10173*h*.

(23) This reagent (CrO_3 + 90% HNO_3) has been used to oxidize fluorinated 1,3-dithietanes and 1,4-dithiane. Carboni, R. A.; Kauer, J. C. U.S. Patent 3058993, 1962; *Chem. Abstr.* **1963**, *58*, 5696*e*.

(24) The NMR analysis followed that used for 1,2-dibromohexafluorocyclobutane by: Cullen, W. R; Singh, P. *Can. J. Chem.* **1963**, *41*, 2397–9.

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166–167 °C); IR 1580, 1529 (aromatic C=C), 1339, 1167 cm^{-1} (SO$_2$).

3,3,4,5,6,7-Hexachloro-2,3-dihydrobenzothiophen-2-one (17). Hexachlorobenzothiophene (**16**; 10.23 g, 0.03 mol) was suspended in 100 mL of acetic acid and stirred and heated on a steam bath. Chromium trioxide (15 g, 0.15 mol) was added in portions, and heating was continued for 40 min. The mixture was then poured into ice and water. The product was filtered off and recrystallized from acetone to give 3.11 g (29%) of the thiolactone **17**: mp 144.8–145 °C; IR 1745 (C=O), 1558 cm^{-1} (conjugated C=C). The mass spectrum showed the following peaks of sequential decomposition: *m/e* 354 (parent), 319 (–Cl), 291 (–CO), 256 (–Cl), 221 (–Cl), 151 (–Cl).

Anal. Calcd for C_8Cl_6OS: C, 26.02; Cl, 59.60; S, 8.98. Found: C, 27.09; Cl, 59.42; S, 8.90.

Hydrolysis of 17. 3,3,4,5,6,7-Hexachloro-2,3-dihydrobenzothiophen-2-one (**17**; 3.41 g, 0.01 mol) and a solution of 0.88 g (0.022 mol) of sodium hydroxide in 25 mL of water were heated on a steam bath. The lactone soon dissolved, and, on cooling the solution, the sodium salt of the product crystallized out. It was dissolved by adding water, and the free acid was precipitated with hydrochloric acid. The product was filtered off, air-dried, and recystallized from carbon tetrachloride to give 2.25 g (66.5%) in two crops of 2,3,4,5,8-pentachloro-7-thiabicyclo[4.2.0]-1,3,5-octatriene-8-carboxylic acid (**18**): mp 183–184 °C; NMR (CDCl$_3$) 9.60 ppm (s); IR 3333–2500, 1730 (C=O, typical of COOH), 1475 cm^{-1} (aromatic C=C). The mass spectrum showed peaks at *m/e* 336 (parent, strong), 301 (–Cl), 291 (–COOH), and 654 (weak, anhydride).

Anal. Calcd for $C_8HCl_5O_2S$: C, 28.39; H, 0.30; Cl, 52.38. Found: C, 28.43; H, 0.46; Cl, 52.36.

3,3,4,5-Tetrachloro-2,3-dihydrothiophen-2-one (19). A solution of 22.2 g (0.1 mol) of tetrachlorothiophene[14] in 120 mL of acetic acid was warmed and stirred on a steam bath. The heat was removed, and 20 g (0.2 mol) of chromium trioxide was added in portions. The reaction was vigorous. The solution was cooled and poured into 600 mL of ice and water. The oil was separated, and the aqueous layer was extracted once with ether. The combined oil and ether extract were dried (MgSO$_4$) and distilled to give 11.6 g of product: bp 75–77 °C (1.8 mm); $n^{25}{}_D$ 1.5913–1.5918. The product was purified by GLC over 25% fluoroalkyl pyromellitate on Gas Chrom R. Tetrachlorothiophene came off at 18.4 min and the product (3.86 g, 16%) at 35 min. The product (**19**) was redistilled: bp 75 °C (2.2 mm); $n^{25}{}_D$ 1.5920; IR 1733 (C=O), 1608 cm^{-1} (C=C).

Anal. Calcd for C_4Cl_4OS: C, 20.19; Cl, 59.61; S, 13.48. Found: C, 20.51; Cl, 59.81; S, 13.57.

Octachlorodibenzothiophene. Dibenzothiophene (9.2 g, 0.05 mol), 150 mL of carbon tetrachloride, 1 g of iodine, and 32 g (0.9 mol) of chlorine were charged into a 360-mL Hastelloy C shaker tube and heated 4 h at 100 °C. The octachlorobenzothiophene (20.3 g, 88%) was filtered off. Recrystallization from xylene left 19.3 g (84%) of product, mp 304–307.5 °C (lit.[20] mp 302 °C).

Anal. Calcd for $C_{12}Cl_8S$: Cl, 61.69. Found: Cl, 61.46.

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Registry No. 1, 18043-32-8; **2**, 73308-46-0; **3**, 7294-43-1; **4**, 380-40-5; *cis*-**5**, 73308-47-1; *trans*-**5**, 73308-48-2; *cis*-**6**, 73308-49-3; *trans*-**6**, 73308-50-6; *cis*-**7**, 3934-26-7; *trans*-**7**, 3832-15-3; **8**, 73308-51-7; **9**, 73308-52-8; **10**, 11095-43-5; **11**, 73308-53-9; **12**, 73308-54-0; **13**, 54087-31-9; **15**, 29082-74-4; **16**, 54087-24-0; **17**, 73308-55-1; **18**, 73308-56-2; **19**, 73308-57-3; tetrachlorothiophene, 6012-97-1; dibenzothiophene, 132-65-0; octachlorodibenzothiophene, 7683-05-8; hexachlorocyclobutene, 6130-82-1; hexachlorobutadiene, 87-68-3.

Quinone Chemistry. Reaction of 2,3-Dichloro-1,4-naphthoquinone with *o*-Aminophenols under Various Conditions

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The reaction of 2,3-dichloro-1,4-naphthoquinone (**1**) and *o*-aminophenols (**2**) under various reaction conditions was reinvestigated. Despite earlier literature, **1** and **2a** in alcohol react to give a mixture of 6-chloro-12a-hydroxy-5*H*-benzo[*c*]phenoxazin-5-one (**4a**), 6-chloro-12a-alkoxy-5*H*-benzo[*c*]phenoxazin-5-one (**5**), 6-chloro-5*H*-benzo[*a*]phenoxazin-5-one (**7a**), 2-amino-3*H*-phenoxazin-3-one (**8**) and triphenodioxazine (**9a**). Contradictory to earlier findings, **1** and **2a** in MeOH/KOH afford **7a** but the highest yield of the compound is achieved by using EtOH or MeOH and anhydrous potassium acetate. A probable mechanism for the formation of all reaction products is presented and detailed spectroscopic data of all compounds are given.

Most of the reported methods for the synthesis of phenoxazones[1–9] from quinones and *o*-aminophenols involve the initial attack of the amino group of the *o*-aminophenol on the quinone substituent (OH, OCH$_3$, halogen, etc.) and subsequent ring closure. An *o*-aminophenol exchange reaction or a rearrangement leads finally to the phenoxazone system.

Van Allan and co-workers have reported that 2,3-dichloro-1,4-naphthoquinone (**1**) reacts with *o*-aminophenol (**2a**) in ethanol to give 6-chloro-5-hydroxybenzo[*a*]phenoxazine (A) (47%),[10] and in methanol they described 2-chloro-3-(2-hydroxyanilino)-1,4-naphthoquinone (**3a**)[11] as the main reaction product (93%). They have assigned the structure of these compounds by elemental analysis and infrared spectra. From our experience[1–8] in phenoxazone

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