INTERACTION OF THIETES WITH ELECTRON-DEFICIENT MOLECULES

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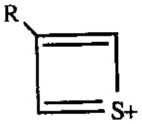
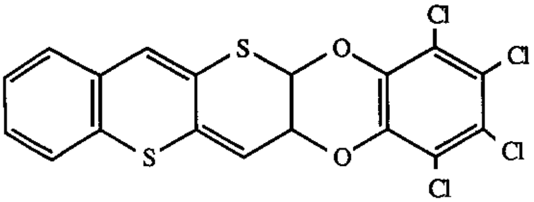
Abstract - Thietes (thiacyclobutenes) give substituted 1,4-benzodioxanes when treated with the o-quinones, o-chloranil and o-bromanil, but dehydrogenation occurs with the p-quinone, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), as indicated by the formation of the hydroquinone in good yield. Colored solutions are formed when thietes are mixed with the electron acceptors DDQ, tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ). The stoichiometry of the charge transfer complexes appears to be 1:1 (donor:acceptor) according to Job plots. Formation constants do not vary greatly from complex to complex. Blue-black solids have been obtained from thietes and TCNQ. The material obtained from 2H-thiete is electrically conducting - a semiconductor - but that from 3-phenyl-2H-thiete is an insulator. Several of the isolated charge-transfer complexes give satisfactory elemental analyses for 1:1 complexes and most of them give broad electron spin resonance spectra.

The powerful electron acceptors, tetracyanoquinodimethane (TCNQ), tetracyanoethylene (TCNE) and high potential quinones such as 2,3-dichloro-4, 5-dicyano-p-benzoquinone (DDQ), form electron donor-electron acceptor complexes with a variety of donor compounds.[1] Special interest has been aroused in sulfur-containing donors such as tetrathiafulvalene (TTF) because of the formation of highly electrically conducting complexes with TCNQ.[2,3] Thietes (thiacyclobutenes) embody a novel ring system with constraint of the α,β-unsaturated sulfide chromophore, and their interaction with electron acceptors would be of interest particularly with respect to the formation of the unknown thiacyclobutenium ions, e.g., 1, species that are apparent in the mass spectra of thietes.[4]



1

High-potential quinones are used to effect dehydrogenations[5], and 1,4-quinones also frequently act as dienophiles in Diels-Alder reactions[6]. In contrast, 1,2-quinones tend to react as heterodienes with various alkenes to give dihydrodioxins and also as regular carbon dienes to give bicyclic 1,2-diketones[7]. Cycloadditions of o-chloranil with α,β-unsaturated sulfides give adducts involving the heterodiene system. In the attempted dehydrogenation of 2,3,4,10-tetrahydro[3,2-b]-1-benzothiopyran with o-chloranil, the adduct 2 was obtained.[8] Adduct 3 was obtained from o-chloranil and 2-isopropylidene-4,4-dimethyl-3-thietanone[9].



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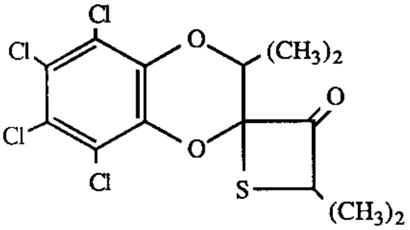
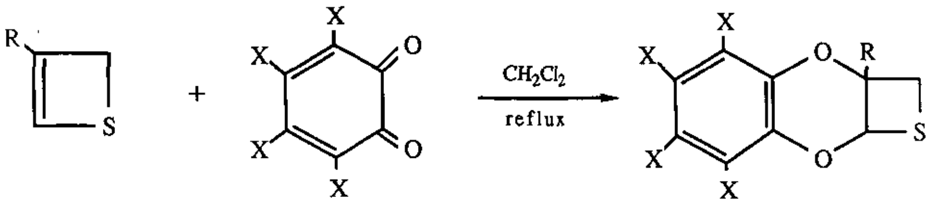


3

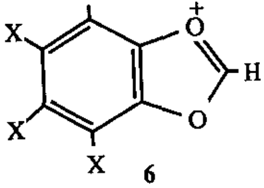
Adducts of o-Quinones with Thietes. Few reactions of thietes are known in which the four-membered ring stays intact.[10] Thiete itself is thermally unstable and yields polymers of thioacrolein[4] although thietes whose double bond is substituted with aryl substituents are considerably more stable[11] as noted also for similarly substituted oxetes.[12] The thiete ring is stable to low-temperature alkylation of sulfur but the resulting sulfonium salts are unstable,[13] and treatment of thiete with TCNE yields a stable 2+2 adduct that rearranges thermally to a thiophene.[14] Treatment of thietes (**4a-e**) with o-chloranil or o-bromanil in methylene chloride gives dark colored solutions from which white solid dihydrobenzo-1,4-dioxins (**5a-h**) precipitate in which the sulfur-containing ring has persisted. The thietes have been prepared previously [4,11] except for 3-ferrocenyl-2H-thiete whose synthesis is described elsewhere[15] and 3-p-tolylthiete.[16]



4a R = Ph
b R = p-$CH_3C_6H_4$
c R = 2-naphthyl
d R = ferrocenyl
e R = H

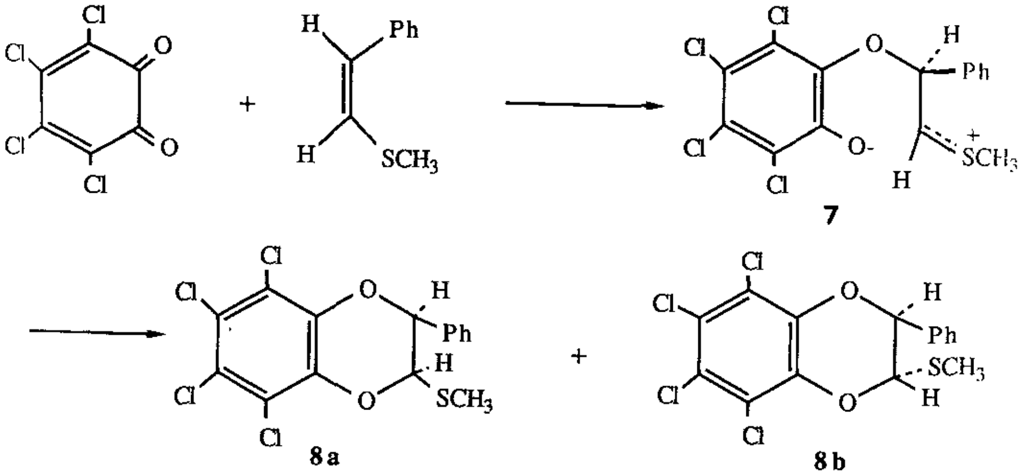
5a R = Ph , X = Cl
b R = p-$CH_3C_6H_4$, X = Cl
c R = 2-naphthyl , X = Cl
d R = ferrocenyl , X = Cl
e R = H , X = Cl
f R = Ph , X = Br
g R = p-$CH_3C_6H_4$, X = Br
h R = 2-naphthyl , X = Br

The adducts were characterized by elemental analysis and by spectroscopic data. Only the adduct of 3-p-tolylthiete gave an unsatisfactory elemental analysis although spectroscopic analysis indicated it was essentially pure. The mass spectrum of **5a**, R=C_6H_5, X=Cl, shows a base peak for the thiete cation (**1**, R=Ph) resulting from a retro-Diels-Alder fragmentation and loss of a hydrogen atom. Interestingly, the mass spectrum of the ferrocenyl derivative, **5**, R=ferrocenyl, X=Cl, shows the ferrocenyl thiete itself and not the cation (**1**, R=ferrocenyl) as the major fragment, suggesting that perhaps the site of ionization involves the ferrocenyl group with the positive charge localized on the iron atom instead of on the sulfur atom. Thus, there is no tendency to lose a hydrogen atom since the thiete cation **1** apparently is formed only when the sulfur atom is the locus of the charge in the cation radical. The observation of abundant fragments at m/e 191 ($C_3H_3SC_5H_4Fe^+$), 135 ($C_3H_3SC_5H_4^+$) and 121 ($C_5H_5Fe^+$) indicates that the charge on the molecular ion resides to a large extent on the ferrocenyl group. The substantial number of ions at m/z 257 in the mass spectra of the dioxins is most likely due to structure **6**, X=Cl, analogous to the known thermal rearrangement products of 1,4-benzodioxanes.[17]



6

The adducts probably are formed at least partly by a two-step process because the chloranil adduct from cis-methyl styryl sulfide yields both cis and trans products (**8a** and **8b**, respectively) as indicated by the ^1H NMR spectrum.[18]



A two-step mechanism has been suggested previously for the cycloaddition of 1,2-benzoquinones to furans[19] No adduct was obtained on refluxing the thiete sulfone, 3-phenyl-2H-thiete 1,1-dioxide, with o-chloranil attesting to the need for electron donation from a sulfur atom as exemplified by intermediate 7. The colors observed when the o-quinone and thiete are mixed may indicate formation of a charge transfer complex or the zwitterion 7. An electron-deficient o-quinone is essential for adduct formation because no reaction was observed with 9,10-phenanthraquinone or 1,2-naphthoquinone. The initial Diels-Alder adducts may have either the exo or endo conformation with respect to the $-SCH_3$ group, one conformer being converted into the other by a flip of the six-membered dioxane ring. The endo conformation is expected to be preferred because in this conformation the electron-donating sulfur atom is closer to the electron-deficient tetrachlorophenyl ring. Also, in a zwitterionic intermediate, Dreiding molecular models show that the electrostatic attraction should be greater in the endo isomer.

The chloranil adduct with 3-phenylthiete was oxidized with one equivalent of m-chloroperbenzoic acid to a mixture (92%) of cis and trans sulfoxides; with three equivalents of the peracid, the sulfone was obtained (70%). Oxidation of the less hindered face of the sulfur atom of the endo adduct would give the trans thietane sulfoxide, **9**. Integration of the ^1H NMR spectrum of the mixture of sulfoxides shows that one isomer predominates (82%). The ^1H NMR spectra of the two sulfoxides **9** and **10** and the sulfone **11** are given in Table I. Although the four-membered rings in **9** and **10** are essentially planar (as indicated by Dreiding molecular models) in contrast to the puckered conformation of most thietane 1-oxides[10], the configurations may be assigned on the basis that α-protons cis to the oxygen of the sulfoxide group are at higher field (about 0.5 ppm) than those that are trans.[20] The ^{13}C NMR spectrum of sulfone **11** exhibits the unusual extra shielding of the β-carbon and the extra deshielding of the α-carbon that has been observed in other four-membered cyclic sulfones.[21]

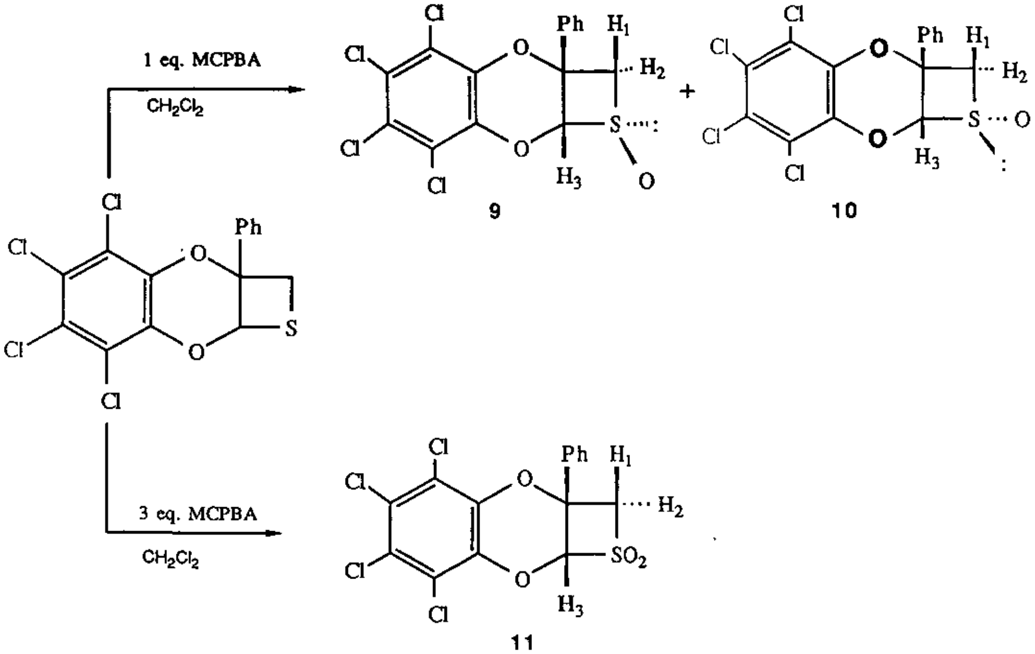


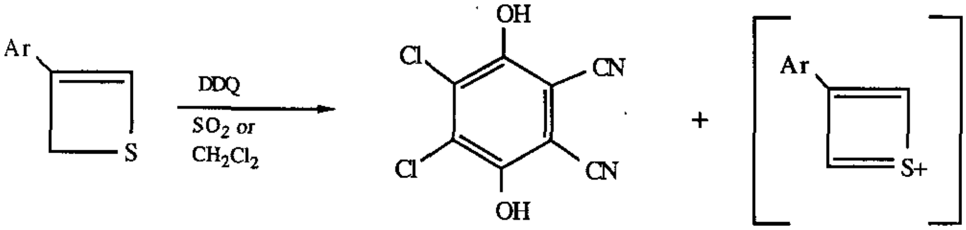
Table I. ^1H NMR Chemical Shifts for Sulfoxides 9 and 10 and Sulfone 11.[a]

	H_1	H_2	H_3	J_{12}(Hz)
9	4.26	3.11	6.03	12.1
10	3.53-3.73	3.53-3.73	5.68	-
11	4.59	4.33	6.45	14.2

[a] See figures **9-11** for numbering of protons.

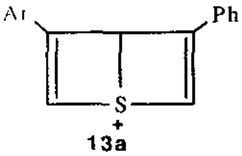
Reactions of Thietes with DDQ and with the Trityl Cation. --- Various hydroaromatic and heterocyclic compounds have been dehydrogenated by p-quinones, e.g. DDQ in perchloric acid.[5,22] Triphenylmethyl (trityl) cation also has been used as a dehydrogenating *reagent; its use with* diethyl sulfide or tetrahydrothiophene gave triphenylmethane and complex mixtures of sulfur-containing compounds.[23] The trityl cation has been extensively used to remove hydride ions from thiapyrans to give thiapyrylium ions.[24]

Treatment of thietes with DDQ or trityl cations gave evidence of dehydrogenation with the formation of good to excellent yields of the hydroquinone or triphenylmethane. For example, treatment of 3-phenyl-2H-thiete with DDQ in liquid sulfur dioxide gave a quantitative yield of the hydroquinone. p-Chloranil did not react. The sulfur-containing intractable solid products were complex and were not able to be characterized. Unstable cationic intermediates (**12**) may be involved.

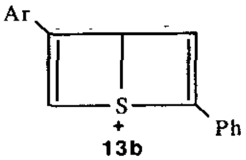


12

Attempts to trap thiete cations **12** with norbornene, diphenylacetylene, 2-naphthol or 3-hexyne were inconclusive. When 3-p-tolyl-2H-thiete[16] was treated with DDQ in the presence of phenylacetylene, the insoluble purple solid obtained showed ions in the mass spectrum at m/z 263 possibly corresponding to the cations **13a** or **13b**(Ar=p-$CH_3C_6H_4$). It was not possible to establish the presence of these species in any other way. No evidence for thiapyrylium ions isomeric with **13a** or **13b** was obtained on work up of the complex mixture. The mass spectrum also showed ions at m/z 161 and 147, corresponding to the p-tolylthiete cation (**12**,Ar=p-$CH_3C_6H_4$-) and the phenylthiete cation (*12*,Ar=C_6H_5-), respectively; *these ions could be formed* by dismutation of **13a** or **13b**. Elemental analysis of the complex product mixture indicates the presence of the DDQ moiety, suggesting the possible occurrence of addition of the hydroquinone to the cation **12**.



13a



13b

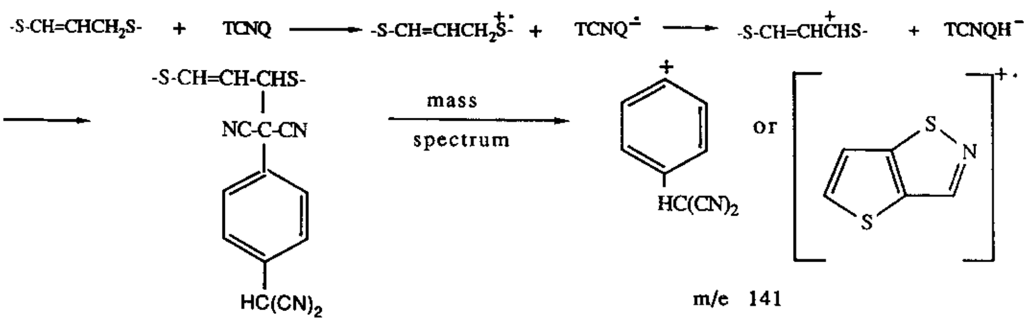
Charge Transfer Complexes of Thietes. --- Colors are observed when thietes are treated with o-bromanil, o-chloranil and DDQ. Colors also are observed with TCNE and TCNQ. These colors are attributed to charge transfer complexes analogous to those reported for a variety of α,β-unsaturated sulfides with TCNE and TCNQ.[25] Treatment of 2H-thiete with TCNE gives a colored solution from which the colorless 2+2 adduct precipitates.[14] No adduct formation is observed with 3-substituted thietes. These colored solutions exhibit absorption bands that are not present in either the donor or acceptor, a property of charge transfer complexes. Application of Job's method of continuous variation[26] for the determination of the stoichiometry of the complexes of 3-phenyl-2H-thiete with DDQ, TCNQ and TCNE gave nearly symmetrical curves with maxima at a mole fraction of 0.5 indicating a stoichiometry of 1:1. Linear plots according to the Benesi-Hildebrand equation[27] are in accord with this stoichiometry, and the formation constants and absorption maxima for the complexes are given in Table II. TCNQ forms the most stable complexes. The solid, black complexes of 3-phenyl-2H-thiete and 3-(2-naphthyl)-2H-thiete were analyzed for the elements, carbon, hydrogen and nitrogen; and the analyses agreed with the 1:1 stoichiometry.

Table II. Absorption Maxima and Formation Constants for Complexes of 3-Substituted Thietes with DDQ, TCNE and TCNQ in Methylene Chloride at Room Temperature.

Acceptor	3-Substituent							
	Ph		$2\text{-}C_{10}H_7$		$2\text{-}C_4H_3S$		$PhCH{=}CHSCH_3$	
	λ_{max}	K, M^{-1}	λ_{max}	K, M^{-1}	λ_{max}	K, M^{-1}	λ_{max}	K, M^{-1}
DDQ	730	1.2	802	1.8	690	3.5	730	6.4
TCNE	650	0.5	690	1.4	697	1.7	650	1.7
TCNQ	691	16	736	52	760	26	667	17

The ^1H NMR spectra in solution of all isolated complexes were broadened and essentially identical with the spectrum of the thiete. The DDQ complexes of 3-phenyl-, 3-(2-naphthyl)-, 3-(2-thienyl)- and 3-ferrocenyl-2H-thiete, the TCNQ complexes of 3-phenyl-3-(2-naphthyl) and 3-p-tolyl-2H-thiete and the TCNE complex of 3-phenyl-2H-thiete gave broad, featureless ESR spectra. Charge transfer also was indicated by the variation of the infrared stretching frequency of the cyano groups in TCNQ[28] [3-substituent, $\bar{\nu}$(CN), degree of charge transfer]: p-tolyl, 2220 cm^{-1}, 0.16; phenyl, 2210 cm^{-1}, 0.39; 2-naphthyl, 2200 cm^{-1}, 0.61; H, 2190 cm^{-1}, 0.84.

The very insoluble blue-black solid (mp>320°C) obtained by treatment of the unsubstituted 2H-thiete with TCNQ showed electrical conductivity (resistivity, compressed pellet, 630 ohm-cm.). Resistivities of other batches of this material varied up to as high as 1700 ohm-cm. Complexes of the other thietes were non-conductors with resistivities greater than 10^6 ohm-cm. The amorphous conducting solid gave no ESR spectrum. The presence of sulfur and nitrogen was shown by sodium fusion analysis. One major distinction between the unsubstituted thiete and the 3-substituted thietes is that the former polymerizes at room temperature to a white solid[4,29], but the latter do not. It is possible that the conducting material involves an oligomer or polymer of thiete. When the preformed white polymer from 2H-thiete was triturated with TCNQ, it became dark. Removal of the excess TCNQ by sublimation at 210°C left a black solid, mp>320°C, that was not conducting and showed no ESR signal. It would appear that the thermal decomposition and polymerization of thiete in the presence of TCNQ in solution is required for the formation of conducting material. The electron impact mass spectrum of the conductor showed ions at m/z 204 (100%, TCNQ), 152, 150 and 125, all of which are observed in the mass spectrum of TCNQ[30]. However, abundant fragments at m/z 141 (72%) [TCNQ + H $-C(CN)_2$], the most intense peak in the mass spectrum except for that at m/z 204, are observed only in the mass spectra of quaternary ammonium salts of the TCNQ anion[30] or in the chemical ionization mass spectrum of TCNQ[31]. This observation of fragments at m/z 141 suggests that a facile removal of hydrogen from the thiete oligomer or polymer is occurring. A thienoisothiazole ion, also of m/z 141, can be formed via cleavage of two carbon-sulfur bonds.



EXPERIMENTAL

Elemental analyses were performed at Microanalysis, Inc., Wilmington, DE. NMR spectra were recorded on a Varian T60, Bruker WM-360, or a narrow bore 250 MHz spectrometer. Infrared spectra were recorded on a Perkin-Elmer 710B spectrometer and ultraviolet spectra were recorded on a Cary 219 or Cary 118 spectrometer. Mass spectra were obtained on a Finnigan 4000 GC/MS Mass Spectrometer Data System (electron impact). Melting points were recorded on a Mel-Temp apparatus and are uncorrected. Hexane was washed successively with sulfuric acid, water, saturated aqueous $NaHCO_3$, and water, dried ($MgSO_4$) and distilled from Linde molecular sieves, type 4A. Ether was dried and distilled from calcium hydride and stored over Linde molecular sieves, type 4A, protected from light. Benzene was dried and distilled from sodium under nitrogen and stored over Linde molecular sieves, type 4A. Acetonitrile and methylene chloride were dried over Linde molecular sieves, type 4A. Spectral grade solvents were used in all ultraviolet and electron spin measurements. 7,7,8,8-Tetracyanoquinodimethane (TCNQ) was prepared by the method of Acker and Hertler[32] and recrystallized three times from acetonitrile prior to its use. 2,3-Dichloro-5,6-dicyano-p-benzoquinone (DDQ) and tetracyanoethylene (TCNE) were recrystallized from methylene chloride.

4,5,6,7-Tetrachloro-2a,8a-dihydro-2a-phenyl-2H-thiacylobuta[b][1,4]-benzodioxin (**5a**, R=Ph, X=Cl). --- 3-Phenyl-2H-thiete,[11] **4a**, (0.148 g, 1.00 mmol) and o-chloranil (0.250 g, 1.00 mmol) were dissolved in methylene chloride (5 ml) to give a black solution which was then refluxed for 24 h. A white solid precipitated from the solution; both solution and precipitate were chromatographed (methylene chloride-hexane, 1:1, neutral alumina, 30 cm) to give a white granular solid (0.345 g, 0.875 mmol, 88%): mp 157-158°C; ^1H NMR ($CDCl_3$) δ 7.46 (m, 5 H, aromatic), 6.10 (s, 1 H, CH), 3.52 (d, J = 10.6 Hz, 1 H, CH_2), 3.38 (d, J = 10.6 Hz, 1 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 139.8, 139.2, 138.6, 129.3, 129.1, 126.9, 126.2, 124.2, 122.6, 121.9, 88.0 (s), 84.8 (d, J=178.9 Hz), 35.7 (t, J=151.3 Hz); IR (KBr) 1420 (vs, C-O), 1395 (m), 1355 (m), 1280 (m), 1260 (m), 1210 (m), 1040 (s), 990 (m), 940 (m), 880 (m), 850 (m), 780 (m), 760 (m) cm^{-1}; UV (Et_2O) 297 (log ε = 3.28), 214 (4.87) nm; MS (m/z, rel. intensity, %) 398 (0.88) , 396 (1.91), 395 (1.61), 394 (6.17), 392 (M^+, 4.45), 263 (3.40), 261 (13.5) 259 (25.6), 257 ($C_7HCl_4O_2^+$, 21.6), 149 (7.01), 148 ($C_9H_8S^+$, 25.6), 147 ($C_9H_7S^+$ 100), 135 ($C_8H_7S^+$, 24.0), 121 (5.61), 120 (5.65), 118

(7.24), 115 ($C_9H_9^+$, 14.3), 105 (17.7), 103 ($C_8H_7^+$, 70.1), 91 (10.8), 89 (8.12), 77 (63.7). A sample was recrystallized from ether: Anal. Calcd. for $C_{15}H_8Cl_4O_2S$: C, 45.72; H, 2.05. Found: C, 45.73; H, 2.21.

In a similar manner, the following adducts of 3-aryl-2H-thietes and o-chloranil were prepared.

4,5,6,7-Tetrachloro-2a,8a-dihydro-2a-p-tolyl-2H-thiacyclobuta[b][1,4]-benzodioxin (**5b**, R = p-$CH_3C_6H_4$, X = Cl). --- 3-p-Tolyl-2H-thiete,[16] **4b** (0.241 g, 1.49 mmol), and o-chloranil (0.403 g; 1.64 mmol) gave the adduct (0.497 g, 1.21 mmol): mp 115-116°C; ^1H NMR ($CDCl_3$) δ 7.30 (dd, 4 H, aromatic), 6.03 (s, 1 H, CH), 3.54 (d, J = 10.6 Hz, 1 H, CH_2), 3.30 (d, J = 10.6 Hz, 1 H, CH_2), 2.42 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 139.8, 139.5, 138.5, 136.3, 129.7, 126.9, 126.1, 124.2, 122.5, 121.9, 88.0, 84.7, 35.6, 21.2; IR (KBr), 1420 (vs, C-O), 1390 (s), 1340 (w), 1260 (m), 1205 (m), 1090 (m), 985 (m), 940 (m), 875 (m), 845 (m), 800 (m), 760 (m) cm^{-1}; UV (Et_2O) 259 (log ε = 3.25), 214 (4.88) nm.

4,5,6,7-Tetrachloro-2a,8a-dihydro-2a-(2-naphthyl)-2H-thiacyclobuta[b][1,4]-benzodioxin (**5c**, R = 2-$C_{10}H_7$, X = Cl). --- 3-(2-Naphthyl)-2H-thiete,[11] **4c** (0.173 g, 0.875 mmol), and o-chloranil (0.249 g, 1.05 mmol) gave the adduct (0.334 g, 0.752 mmol, 86%): mp 183-184°C; ^1H NMR ($CDCl_3$) δ 7.63 (m, 7 H, aromatic), 6.13 (s, 1 H, CH), 3.58 (d, J = 10.6 Hz, 1 H, CH_2), 3.33 (d, J = 10.6 Hz, 1 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 139.9, 138.6, 136.2, 133.4, 132.8, 129.4, 128.5, 127.7, 127.1, 126.9, 126.3, 123.7, 122.7, 122.0, 121.7, 88.3, 84.7, 35.5; IR (KBr) 1420 (vs, C-O), 1390 (s), 1320 (m), 1270 (m), 1200 (s), 1070 (s), 1030 (vs), 1000 (m), 985 (s), 960 (m), 930 (m), 875 (m), 870 (m), 855 (m), 805 (s), 780 (w), 740 (m), 700 (m) cm^{-1}; UV (Et_2O) 224 (log ε = 5.02) nm. A sample was recrystallized from ether: Anal. Calcd. for $C_{19}H_{10}Cl_4O_2S$: C, 51.38; H, 2.27. Found: C, 51.30; H, 2.55.

4,5,6,7-Tetrachloro-2a,8a-dihydro-2a-ferrocenyl-2H-thiacyclobuta[b][1,4]-benzodioxin (**5d**, R = ferrocenyl, X = Cl). --- 3-Ferrocenyl-2H-thiete,[15] **4d** (0.100 g, 0.400 mmol), and o-chloranil (0.403 g, 1.64 mmol) gave the adduct (0.120 g, 0.239 mmol, 59%). After chromatography of the crude sample, a solution in methylene chloride (25 ml) was stirred with zinc dust, filtered and the solvent removed to give an orange, granular solid: mp 155-156°C; ^{1}H NMR ($CDCl_3$) δ 5.97 (s, 1 H, CH), 4.27 (m, 9 H, cyclopentadienyl), 3.42 (d, J = 10.5 Hz, 1 H, CH_2), 3.20 (d, J = 10.5 Hz, 1 H, CH_2); ^{13}C NMR ($CDCl_3$), δ 140.3, 139.0, 126.9, 126.1, 122.7, 121.9, 87.1, 85.5, 69.2, 69.1, 66.2, 65.3, 35.4; IR (KBr) 1780 (w), 1720 (w), 1690 (w), 1660 (m), 1630 (w), 1425 (vs, C-O), 1390 (s), 1380 (s), 1315 (m), 1280 (m), 1260 (m), 1225 (m), 1220 (m), 1060 (s), 1020 (s), 985 (s), 935 (m), 865 (s), 820 (s), 780 (m), 760 (w), 700 (m) cm^{-1}; UV (Et_2O) 432 (log ε = 2.05), 296 (3.40), 214 (4.92) nm; MS (m/z, rel. intensity, %) 504 (5.20), 503 (1.62), 502 (12.8), 501 (1.53), 500 (M^+,10.0), 258 (3.74), 257 ($C_7HCl_4O_2^+$, 15.6), 256 ($C_{13}H_{12}FeS^+$, 100), 254 (7.30), 191 ($C_8H_7FeS^+$, 28.4), 190 (3.51), 166 (2.65), 165 (4.89), 147 (6.96), 145 (4.72), 137 (3.46), 136 (6.53), 135 ($C_8H_7S^+$, 77.0), 134 (16.3), 121 ($C_5H_5Fe^+$, 33.4), 115 (5.85), 113 (4.73), 111 (9.26), 105 (4.01), 103 (5.42), 102 (7.58), 97 (7.61), 91 (33.9), 89 (28.4), 85 (4.41), 84 (6.59), 83 (6.78), 81 (7.27), 77 (8.59), 73 (5.44), 71 (9.07), 69 (14.6). A sample was recrystallized from ether: Anal. Calcd. for $C_{19}H_{12}Cl_4FeO_2S$: C, 45.46; H, 2.41. Found: C, 45.59; H, 2.47.

4,5,6,7-Tetrachloro-2a,8a-dihydro-2H-thiabicyclobuta[b][1,4]-benzodioxin (**5e**, R = H, X = Cl). --- A solution of potassium t-butoxide (2.60 g, 23.0 mmol) in dry DMF (25 ml) was added dropwise over 15 min to a cold (-20°C) solution of trimethyl-3-thietanylammonium iodide[4] (3.00 g, 11.6 mmol) in dry DMF (25 ml) in an atmosphere of nitrogen. After the addition was completed, the reaction mixture was allowed to warm to -12°C and was stirred at -10° to -12°C for 30 min. The mixture was poured into a chilled separatory funnel containing ice-cold water saturated with NaCl (100 ml) and cold ether (100 ml). The layers were separated and the aqueous layer was extracted with cold ether (3x25 ml). The ether extracts were combined, washed with cold 5% hydrochloric acid saturated with NaCl and the ether layer was separated and dried (at -30°C) over anhydrous $CaSO_4$. The next day the thiete solution was filtered and o-chloranil (2.85 g, 11.6 mmol) dissolved in methylene chloride (75 ml) was added. The reaction mixture was stirred at room temperature for 24 h, the solvent removed under reduced pressure and the crude product dissolved in a minimum amount of methylene chloride and purified by chromatography (methylene chloride-hexane, 1:1, neutral alumina, 30 cm) to give a white crystalline solid (1.18 g, 3.71 mmol, 32%): mp 161-162°C; ^{1}H NMR ($CDCl_3$) (a complex ABMX spectrum) δ

6.00 (t, 1 H, O-CH-S), 5.60 (q, 1H,CH$_2$-$\underline{\text{CH}}$-O), 3.40, 3.24 (m, m, 2H, CH$_2$);^{13}C NMR (CDCl$_3$) δ 139.5, 138.4, 126.4, 122.3, 122.0, 82.1; 73.4, 31.8; IR (KBr) 1440 (m, C-O), 1405 (m), 1270 (m), 1060 (m), 870 (m) cm^{-1}; UV (Et$_2$O) 296 (log ε = 3.15), 213 (4.80) nm. A sample was obtained by recrystallization from methylene chloride-ether: Anal. Calcd. for $C_9H_4Cl_4O_2S$: C, 33.99; H, 1.27. Found: C, 33.77; H, 1.47.

5,6,7,8-Tetrachloro-2,3-dihydro-2-methylthio-3-phenyl-1,4-benzodioxin (cis and trans) (**8a**,**8b**). --- A solution of methyl styryl sulfide (0.819 g, 5.46 mmol) and o-chloranil (1.54 g, 6.26 mmol) in methylene chloride (10 ml) was refluxed for 48 h. Initially the reaction mixture was black but it later became red. The mixture was chromatographed (methylene chloride-hexane, 1:1, neutral alumina, 30 cm) to give a white granular mixture of cis and trans isomers, **8a** and **8b** (1.32 g, 3.34 mmol, 61%): mp 171-174°C; ^{1}H NMR (CDCl$_3$) δ 7.30 (m, 3.5H, aromatic), 7.23 (m, 1.6H, aromatic), 5.63 (d, J = 2 Hz, 0.67 H, C$\underline{\text{H}}$SCH$_3$), 5.40 (d, J = 4 Hz, 0.33H, C$\underline{\text{H}}$SCH$_3$), 5.37 (d, J = 2 Hz, 0.67 H, C$\underline{\text{H}}$Ph), 5.20 (d, J = 4 Hz, 0.33 H, C$\underline{\text{H}}$Ph), 2.17 (s, 1.0 H, -SCH$_3$), 2.03 (s, 2.0 H, -SCH$_3$); ^{13}C NMR (CDCl$_3$) δ 140.2, 139.3, 137.7, 136.7, 135.5, 133.9, 129.2, 129.1, 128.9, 128.7, 126.3, 125.7, 125.1, 124.9, 121.6, 121.1, 120.6, 120.4, 84.4, 82.9, 77.9, 77.4, 13.4, 13.1; IR (KBr) 1410 (vs, C-O), 1400 (m), 1280 (m), 1260 (m), 1200 (m), 1080 (m), 1060 (m), 1000 (m), 980 (m), 940 (m), 910 (m), 890 (m) cm^{-1}; UV (Et$_2$O) 297 (log ε = 3.55), 214 (4.80) nm. A sample was obtained by recrystallization from ether: Anal. Calcd. for $C_{15}H_{10}Cl_4O_2S$: C, 45.48; H, 2.54. Found: C, 45.53; H, 2.47.

4,5,6,7-Tetrabromo-2a,8a-dihydro-2a-phenyl-2H-thiacyclobuta[b][1,4]-benzodioxin (**5f**, R = Ph, X = Br). --- A solution of 3-phenyl-2H-thiete,[11] **4a**, (0.201 g, 1.36 mmol) and o-bromanil (0.576 g, 1.36 mmol) in methylene chloride (5 ml) was refluxed for 24 h. A black solution was produced immediately upon mixing the reagents. The solution became purple and a white precipitate appeared. It was purified by chromatography (methylene chloride-hexane, 1:1, neutral alumina, 30 cm) to give a white granular solid (0.687 g, 1.20 mmol, 88%): mp 165-166°C; ^{1}H NMR (CDCl$_3$) δ 7.50 (m, 5 H, aromatic), 6.07 (s, 1 H, CH), 3.49 (d, J = 10.5 Hz, 1 H, CH$_2$), 3.25 (d, J = 10.5 Hz, 1 H, CH$_2$); ^{13}C NMR (CDCl$_3$) δ 141.4, 140.4, 139.3, 129.3, 129.1, 124.2, 122.2, 121.5, 116.2, 115.6, 88.4, 85.5, 35.9; IR (KBr) 1410 (s, C-O), 1360 (m), 1340 (m), 1320 (w), 1280 (m), 1240 (m), 1210 (m), 1040 (s), 960 (m), 915 (m), 860 (m), 780 (m), 760 (m), 690 (m) cm^{-1}; UV (Et$_2$O) 298 (log ε =

3.21), 2.70 (3.28), 222 (4.78) nm. A sample was recrystallized from ether: Anal. Calcd. for $C_{15}H_8Br_4O_2S$: C, 31.50; H, 1.41. Found: C, 31.74; H, 1.55.

In a similar manner the following two adducts of 3-aryl-2H-thietes with o-bromanil were prepared.

4,5,6,7-Tetrabromo-2a,8a-dihydro-2a-p-tolyl-2H-thiacyclobuta[b][1,4]-benzodioxin (**5g**, R = p-$CH_3C_6H_4$; X = Br). --- 3-p-Tolyl-2H-thiete,[16] **4b**,(0.343 g, 3.36 mmol) and o-bromanil (1.42 g, 3.36 mmol) gave the adduct (1.24 g, 2.12 mmol, 63%): mp 153-154°C; ^{1}H NMR ($CDCl_3$) δ 7.33 (dd, 4 H, aromatic), 6.03 (s, 1 H, CH), 3.46 (d, J = 10.5 Hz, 1 H, CH_2), 3.23 (d, J= 10.5 Hz, 1H, CH_2), 2.42 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 141.4, 140.3, 139.3, 136.4, 129.7, 124.2, 122.1, 121.4, 116.1, 115.5, 88.4, 85.5, 35.8, 21.2; IR (KBr) 1405 (s, C-O), 1390 (m), 1360 (m), 1270 (m), 1230 (m), 1040 (s), 1010 (m), 960 (s), 900 (s), 840 (m), 830 (m), 800 (s) 760 (m), 700 (m) cm^{-1}; UV (Et_2O) 298 (log ε = 3.28), 270 (3.32), 222 (4.87) nm.

4,5,6,7-Tetrabromo-2a,8a-dihydro-2a-(2-naphthyl)-2H-thiacyclobuta[b][1,4]-benzodioxin (**5h**, R = 2-$C_{10}H_7$, X = Br). --- 3-(2-Naphthyl)-2H-thiete, **4c**, (0.598 g, 3.02 mmol) and o-bromanil (1.27 g, 3.01 mmol) gave the adduct (1.39 g, 2.23 mmol, 88%): mp 183-184°C; ^{1}H NMR ($CDCl_3$) δ 7.70 (m, 7 H, aromatic), 6.17 (s, 1 H, CH), 3.61 (d, J = 10.5 Hz, 1 H, CH_2), 3.32 (d, J = 10.5 Hz, 1 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 141.5, 140.4, 136.3, 133.4, 132.9, 129.4, 128.5, 127.7, 127.1, 126.9, 123.6, 122.3, 121.7, 121.6, 116.2, 115.6, 88.6, 85.4, 35.7; IR (KBr) 1435 (m, C-O), 1360 (m), 1340 (m), 1290 (m), 1055 (s), 1010 (s), 975 (s), 960 (m), 940 (m), 915 (m), 900 (m), 860 (m), 845 (m), 815 (m), 805 (m), 750 (m), 710 (m) cm^{-1}; UV (Et_2O) 225 (log ε = 5.13) nm. A sample was recrystallized from ether: Anal. Calcd. for $C_{19}H_{10}Br_4O_2S$: C, 36.69; H, 1.62. Found: C, 37.13; H, 1.95.

4,5,6,7-Tetrachloro-2a,8a-dihydro-2a-phenyl-2H-thiacyclobuta[b][1,4]-benzodioxin-1-oxide (**9**,**10**). --- A solution of 4,5,6,7-tetrachloro-2a,8a-dihydro-2a-phenyl-2H-thiacyclobuta[b][1,4]-benzodioxin, **5a**, (0.507 g, 1.29 mmol) and m-chloroperbenzoic acid (0.256 g, 1.29 mmol, 85%) in methylene chloride (20 ml) was stirred under nitrogen for 12 h at room temperature. The reaction mixture was washed with aqueous $NaHSO_3$ (3x25 ml, 10%), aqueous $NaHCO_3$ (3x25 ml, 10%), and water (3x25 ml). The organic layer was separated, dried over anhydrous $MgSO_4$, filtered, and the solvent removed in vacuo to leave a mixture of sulfoxide isomers as a white powder (0.485 g, 1.18 mmol, 92%): mp 205-206°C; ^1H NMR ($CDCl_3$) δ 7.37 (m, 5.01 H, aromatic), 6.03 (s, 0.82 H, CH), 5.68 (s, 0.18 H, CH), 4.26 (d, J = 12.1 Hz, 0.82 H, CH_2), 3.53-3.73 (m, 0.35 H, CH_2), 3.11 (d, J = 12.1 Hz, 0.82 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 138.0, 137.9, 136.4, 136.1, 136.0, 129.9, 129.8, 129.5, 126.9, 126.8, 124.9, 124.4, 121.5, 120.9, 96.7, 84.5, 83.4, 75.0, 55.8, 55.0; IR (KBr) 1405 (vs, C-O), 1370 (m), 1315 (m), 1300 (w), 1290 (s), 1160 (s), 1145 (s), 1105 (m), 1060 (vs, S=O), 1000 (m), 980 (w), 940 (m), 935 (m), 880 (s), 840 (m), 810 (s), 760 (m), 740 (m), 690 (m) cm^{-1}; MS (m/z, rel. intensity, %) 412 (M+4, 2.64), 410 (M+2, 5.23), 365 (8.59), 364 (14.4), 363 (35.5), 362 (36.7), 361 (100), 359 ($C_{15}H_7Cl_4O_2^+$, 17.0), 350 (18.9), 348 (34.8) 346 ($C_{14}H_6Cl_4O_2^+$, 26.8), 333 (6.07), 331 (6.19), 321 (17.0), 319 (31.0), 317 ($C_8HCl_4O_3S^+$, 23.1), 313 (7.55), 311 (6.66), 298 (6.47), 296 (6.22), 285 (12.6), 283 (10.6), 261 (18.4), 259 (34.4), 257 ($C_7HCl_4O_2^+$, 29.8), 167 (7.13), 164 ($C_9H_8OS^+$, 11.6), 163 (8.21), 149 (9.84), 147 (8.52), 135 (25.0), 116 (19.5), 115(35.5), 105 (8.36), 103 (6.82), 77 (5.49). A sample was recrystallized from ether-methylene chloride: Anal. Calcd. for $C_{15}H_8Cl_4O_3S$: C, 43.93; H, 1.97. Found: C, 43.43; H, 1.75.

4,5,6,7-Tetrachloro-2a,8a-dihydro-2a-phenyl-2H-thiacyclobuta[b][1,4]-benzodioxin-1,1-dioxide (11). --- 4,5,6,7-Tetrachloro-2a,8a-dihydro-2a-phenyl-2H-thiacyclobuta[b][1,4]-benzodioxin, **5a**, (0.400 g, 1.02 mmol) and m-chloroperbenzoic acid (0.607 g, 3.06 mmol, 85%) in methylene chloride (25 ml) were stirred under nitrogen at room temperature for 24 h. The methylene chloride solution was washed with aqueous $NaHSO_3$ (3x25 ml, 10%), $NaHCO_3$ (3x25 ml, 10%), and water (3x25 ml), separated, dried over $MgSO_4$, filtered, and the solvent removed in vacuo. A white solid was obtained which was recrystallized from 1:1 methylene chloride-hexane (0.298 g, 0.700 mmol, 70%): mp 211.5-213°C; ^1H NMR ($CDCl_3$) δ 7.44 (m, 5 H, aromatic), 6.45 (s, 1 H, CH), 4.59 (d, J = 14.2 Hz, 1 H, CH_2) 4.33 (d, J = 14.2 Hz, 1 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 136.3, 135.6, 134.3, 130.2, 129.7, 127.2, 126.8, 125.1, 121.4, 120.8, 99.8 (d, J_{CH}=171.5 Hz), 71.0 (s), 70.0 (dd, J_{CH}=142.9, 147.7 Hz); IR (KBr) 1425 (vs, C-O), 1390 (m), 1325 (m, SO_2), 1260 (vs), 1160 (m, SO_2), 1060 (s,br), 805 (s, br), 695 (m) cm^{-1}; MS (m/z, rel. intensity, %) 428 (0.38), 426 (1.20), 424 (M^+, 0.74), 333 (0.94), 261 (0.95), 259 (2.53), 257 (2.06), 181 (3.44), 180 ($C_9H_8O_2S^+$, 18.2), 167 (2.74), 165 (3.69), 163 (7.00), 135 (6.02), 132 (10.9), 131 (9.13), 130 (2.46), 118 (3.82), 116 (20.8), 115 ($C_9H_7^+$, 100), 105 ($PhCO^+$, 48.2), 104 (17.7), 103 (46.2), 102 (12.3), 91 (5.66), 89 (13.1), 78 (5.07), 77 (41.3), 76 (6.10). A sample was recrystallized from 1:1 methylene chloride-ether: Anal. Calcd. for $C_{15}H_8Cl_4O_4S$: C, 42.38; H, 1.66. Found: C, 42.20; H, 1.94.

Attempted Dehydrogenation of 3-Aryl-2H-Thietes.

1. With DDQ. --- 3-Phenyl-2H-thiete (0.444 g, 3.00 mmol) in methylene chloride (50 ml) was added (20 min) to DDQ (0.681 g, 3.00 mmol) in methylene chloride (50 ml) to give a green solution. After 1 h the solvent was removed to give a green solid that turned brown on standing. After 24 h, methylene chloride (100 ml) was added to the brown solid some of which dissolved. The insoluble material (0.423 g, 1.8 mmol, 60%) was identified as 2,3-dichloro-5,6-dicyano-1,4-benzohydroquinone by comparison of its properties with those of an authentic sample obtained by oxidation of cinnamyl alcohol with DDQ:[33] mp 250°C; ^{13}C NMR (DMSO-d_6) δ 150.9, 129.2, 113.7, 101.6; IR (KBr) 3700-2700 (s, br, OH), 2250 (s, CN), 1440 (s, C-O); UV (EtOH, 100%) 400 ($\log \varepsilon = 3.48$), 248 (4.09), 206 (4.09) nm. Control experiments showed that the hydroquinone was formed in more than traces only when the thiete was present. The solution of methylene chloride, after removal of the hydroquinone, was concentrated to give a black solid containing nitrogen, sulfur and chlorine (sodium fusion). The black material is complex as indicated by the mass spectrum which showed over 100 fragments from mass 640 to 74. The infrared spectrum indicated the presence of a cyano group (2225 cm^{-1}). It was not possible to separate the components of the mixture by chromatography. Similar experiments with the phenyl, p-tolyl and 2-naphthylthietes in methylene chloride either in the presence or absence of perchloric or fluoroboric acid also gave the hydroquinone and intractable product mixtures. No dehydrogenation occurred with chloranil. The best conversion (100%) to the hydroquinone occurred when liquid sulfur dioxide was used as solvent, but there were at least ten other products as indicated by thin layer chromatography. Attempts to trap intermediates in these reactions by addition of diphenylacetylene, phenylacetylene, norbornene and 2-naphthol were unsuccessful. When 3-p-tolyl-2H-thiete was treated with DDQ in methylene chloride in the presence of phenylacetylene, the purple solid that was obtained showed fragments in the mass spectrum attributable to both the 3-phenyl- and 3-p-tolylthiacyclobutenium cations (m/z 147 and 162, respectively) and a fragment at m/z

263 possibly due to an adduct of phenylacetylene with the 3-p-tolylthiacyclobutenium cation because its mass is the sum of the two components (C_8H_6+$C_{10}H_9S$). An elemental analysis of the purple solid, corresponding to the composition $C_{19.7}H_{13}Cl_{1.5}N_{1.6}O_{2.0}S_{1.0}$ also supports the presence of DDQ, the tolylthiete and phenylacetylene: Anal. Calcd. for $C_{19.7}H_{13}Cl_{1.5}N_{1.6}OS$: C, 60.76; H, 3.37; Cl, 13.66; N, 5.76; S, 8.24. Found: C, 60.64; H, 3.32; Cl, 13.72; N, 5.91; S, 8.22.

2. With Triphenylcarbenium Tetrafluoroborate. --- Liquid sulfur dioxide (35 ml) was added to a mixture of 3-phenyl-2H-thiete (0.149 g, 1.00 mmol) and triphenylcarbenium tetrafluoroborate (0.344, 1.04 mmol) cooled to -78°C. The mixture was allowed to warm to -10°C and was stirred for 3 h. The sulfur dioxide was removed by evaporation. Anhydrous ether was added and an insoluble sulfur-containing (sodium fusion) gray solid (0.115 g) was removed. The infrared spectrum of this solid indicated the presence of tetrafluoroborate ion (1060 cm^{-1}) and phenyl rings (3100, 3050, 1620, 1530, 1460, 760, 710 cm^{-1}). The mass spectrum showed fragments corresponding to triphenylmethane (m/z 244) and 3-phenylthiacyclobutenium ion (m/z 147) in addition to many fragments up to m/z 605. The ether solution yielded triphenylmethane (mp 92-94°C; lit.,[34] mp 92.1°C) (0.120 g, 0.494 mmol, 49%) separated by column chromatography. Thin layer chromatography indicated the presence of six to 12 other components. Use of triphenylmethyl chloride instead of the carbocation gave no triphenylmethane and the starting thiete (in this case the 2-naphthyl) was recovered. Other runs with trityl cation gave results similar to those above.

Charge Transfer Complexes of Thietes.

1.Stoichiometry and Formation Constants. --- For the purpose of determining the stoichiometry by the continuous variation method of Job[26], stock solutions of donor and acceptor in methylene chloride were prepared. Combined molarities were 0.01320 M for 3-phenyl-2H-thiete - DDQ and 0.001188 M for 3-phenyl-2H-thiete - TCNE. For the determintion of stability constants by the Benesi-Hildebrand equations,[27] the concentration of acceptors in methylene chloride ranged from 9.90×10^{-4} to 5.94×10^{-3} M and the concentration of donors ranged from 3.62×10^{-2} to 1.15×10^{-1} M. The results are given in Table II.

2. Isolated Charge Transfer Complexes of Thietes. --- Typically, the thiete in methylene chloride was added dropwise under nitrogen to a solution of the acceptor (DDQ, TCNE) in methylene chloride chilled in an ice bath. Most of the complexes with TCNQ were prepared in warm acetonitrile except that of 2H-thiete itself which was prepared in methylene chloride. After the addition of thiete was complete, residual starting material was removed by filtration. When methylene chloride was the solvent, the methylene chloride filtrate was concentrated under reduced pressure to give the colored complex. When acetonitrile was the solvent, the reaction mixture was cooled for 12 h in a nitrogen atmosphere. The TCNQ complexes precipitated. The TCNQ complex of 2H-thiete, prepared in ether-methylene chloride, precipitated in low yield when the reaction mixture was allowed to stand. The following complexes were obtained. **TCNQ-2H-Thiete** (The composition of this material is uncertain). Blue or blue-black solid, insoluble in NMR solvents; mp > 320°C; IR (KBr) 2190 (m, br, CN) cm^{-1}; MS (m/z, rel. intensity, %) 204 (100, TCNQ+) 141 (72, $C_5H_3NS_2^+$ and/or $C_9H_5N_2^+$), 71 (4, $C_3H_3S^+$); ESR (solid, RT) no signal; Resistivity (compressed powder) 630-1700 ohm-cm. **TCNQ-3-Phenyl-2H-thiete.** 41%. Black needles; mp 248-250°C (color changes at 190°C from black to orange); ^1H NMR (CD_3CN) (broadened) δ 7.31-7.53 (m), 6.96 (s), 4.18 (s); ^{13}C NMR (broad, no resolution); IR (KBr) 2210 (m, CN) cm^{-1}; UV (CH_3CN) $E^{1\%}_{cm}$ 842 (9.66), 8.22 (6.75), 760 (4.54), 742 (5.31), 678 (2.08), 662 (1.84), 392 (2400), 296 (616), 222 (440) nm; ESR (solid, RT) g= 2.0032; Resistivity (compressed powder) > 10^6 ohm-cm. Anal. Calcd. for $C_{21}H_{12}N_4S$: C, 71.57; H, 3.43; N, 15.90. Found: C, 71.77; H, 3.64; N, 16.11. **TCNQ-3-p-Tolyl-2H-thiete.** 42%. Black needles; mp 150-152°C; ^1H NMR (CD_3CN) (broadened) δ 7.18 (m), 6.94 (s), 6.87 (s), 4.15 (s), 2.31 (s); IR(KBr) 2220 (m, CN) cm^{-1}; UV (CH_3CN) ($E^{1\%}_{cm}$) 842 (6.35), 822 (4.50), 760 (3.05), 742 (3.57), 678 (1.55), 662 (1.48), 392 (1850), 296 (529) 222 (3720); ESR (solid, RT) g=2.0032. **TCNQ-3-(2-Naphthyl)-2H-thiete.** 41%. Black needles mp 145-147°C (dec); ^1H NMR (CD_3CN)(broadened) δ 7.45-7.99 (m), 7.09 (s), 4.29 (s); IR (KBr) 2200 (m,.CN) cm^{-1}; UV (CH_3CN) ($E^{1\%}$cm) 842 (16.7), 822 (11.6), 760 (7.80), 742 (9.12), 678 (3.52), 662 (3.07), 392 (1830), 322 (108), 277 (604), 268 (536), 221 (1300); ESR (solid, RT) g= 2.0032. **DDQ-3-Phenyl-2H-thiete.** Green solid; mp 59-60° (dec); ^1H NMR ($CDCl_3$) (broadened) δ 7.24 (s), 6.80 (s), 4.17 (s); ^{13}C NMR ($CDCl_3$) extremely broadened, unresolved; IR (KBr) 2225 (w, CN), 1660 (m, CO) cm^{-1}; UV (CH_2Cl_2) 730 (6800) nm; ESR (solid or 2.70 x 10^{-2}M in CH_2Cl_2, RT) g= 2.0052. **DDQ-3-(2-Naphthyl)-2H-thiete.** 94%. Deep green solid; mp 139-147°C; ^1H NMR ($CDCl_3$) δ 7.49 (m), 6.86 (s), 4.16 (s); IR (KBr) 2225 (m, CN), 1660 (m, CO); UV (CH_2Cl_2) 802 (7140) nm; ESR (solid or

1.74×10^{-2}M in CH_2Cl_2, RT) g= 2.0052. **DDQ-3-(2-Thienyl)-2H-thiete).** 79%. Dark green solid; mp 97-98°C (dec); ^{1}H NMR ($CDCl_3$) δ 6.90 (m), 6.56 (s), 4.06 (s); IR (KBr) 2225 (m, CN), 1730 (m, C=O) cm^{-1}; UV (CH_2Cl_2) 690 (6060) nm; ESR (solid, RT) g=2.0053. **DDQ-3-Ferrocenyl-2H-thiete.** Tan solid; mp > 320°C; ^{1}H NMR (DMSO-d_6) δ 4.73 (br m) 4.10 (br m); IR (KBr) 2225 (m, CN), 1650 (m) cm^{-1}. ESR (solid, RT) g=2.0057. **TCNE-3-Phenyl-2H-thiete.** 93%; purple solid; mp 60-63°C (dec); IR (KBr) 2220 (w, CN) cm^{-1}; UV (CH_2Cl_2) 650 nm (ε=3050) and absorptions identical with those of 3-phenyl-2H-thiete and TCNE; ESR (solid, room temperature) g=2.0032; no hyperfine splitting.

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