halide. The mixture was stirred vigorously and the hydrogen evolved was measured. Simultaneously, a blank was run in which, instead of 10 mL of alkyl bromide solution, there was added 10 mL of tetrahydrofuran, all other conditions being the same.

The rate of reduction was monitored by the analysis for residual "hydride" in the reaction mixture and the blank at appropriate intervals of time. The reaction proceeded only up to 59% in 48 h. There was no appreciable amount of hydrogen evolution, indicating the absence of any elimination.

Reaction of *n*-Octyl Bromide with Lithium Trimethoxyaluminohydride in THF. In all of these experiments, lithium trimethoxyaluminohydride was synthesized in situ just prior to use by adding 3 mol of anhydrous methanol to 1 mol of lithium aluminum hydride solution in THF.

A clean 100-mL oven-dried flask, equipped with a side arm, fitted with a silicone rubber stopple, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler, was cooled down under a stream of nitrogen. The reaction flask was immersed in a water bath at room temperature (ca. 25 °C). Then 8 mL (8 mmol) of a 1.0 M solution of lithium aluminum hydride was introduced into the reaction flask. This was followed by dropwise addition of 8 mL (24 mmol) of a 3.0 M solution of methanol over a period of 15 min. There was evolved 24 mmol of hydrogen. The resulting solution was stirred for an additional period of 15 min. Finally, 2 mL (2 mmol) of a 1.0 M solution of *n*-nonane (internal standard) followed by 2 mL (2 mmol) of a 1.0 M solution of *n*-octyl bromide was injected. The mixture was vigorously stirred. The mixture was now 0.4 M in $Li(OCH_3)_3AlH$ and 0.1 M in alkyl bromide.

The reaction was monitored by GLC on column A for the formation of *n*-octane and the disappearance of *n*-octyl bromide with time. At 6 h, the reaction was essentially complete, as revealed by the presence of 99% *n*-octane and the absence of *n*-octyl bromide on the gas chromatograph.

Reaction of Sodium Borohydride with *n*-Octyl Iodide in Anhydrous Diglyme. The experimental setup was the same as in the previous experiment. Diglyme (6.5 mL) was introduced into the reaction flask followed by 6 mL (5 mmol) of a 0.83 M sodium borohydride solution in diglyme. Finally, 2.5 mL (5 mmol) of a 2.0 M *n*-nonane solution followed by 5 mL (5 mmol) of an *n*-octyl iodide solution in diglyme was added. The mixture was stirred vigorously. The solution was now 0.25 M in both $NaBH_4$ and alkyl iodide.

At appropriate intervals of time, 1 mL of the reaction mixture was withdrawn by a syringe, quenched with dilute HCl, extracted with ether, and analyzed by GLC on column A for *n*-octane and *n*-octyl iodide. At 0.5 h, 50% of the reaction was essentially complete. At 24 h, reduction had proceeded only to the extent of 89%.

Reaction of Sodium Borohydride with *n*-Octyl Iodide in the Presence of 1-Pentene in Anhydrous Diglyme. A typical reaction setup was assembled as in the case of the previous experiments. Into the reaction flask maintained at ca. 25 °C was injected 4.4 mL of diglyme followed by 6 mL (5 mmol) of a 0.83 M $NaBH_4$ solution, 2.5 mL (5 mmol) of a 2.0 M solution of *n*-nonane, 2.2 mL (20 mmol) of 1-pentene (freshly distilled over $LiAlH_4$), and finally 5 mL (5 mmol) of a 1.0 M solution of *n*-octyl iodide. The reaction mixture was now 0.25 M, in both $NaBH_4$ and *n*-octyl iodide and 1.0 M in 1-pentene. The mixture was vigorously stirred. After 1 h, the reaction flask was cooled in an ice bath at 0 °C, and 6 mL of a 3.0 M NaOH solution was added, followed by dropwise addition of 6 mL of 30% H_2O_2. The mixture was stirred at 50–55 °C for 1 h and then cooled to room temperature. Ether (20 mL) was added and the aqueous layer was saturated with anhydrous K_2CO_3. The dry ethereal layer upon gas chromatographic examination on column B indicated the presence of 3.87 mmol (77%) of *n*-octane and 12.03 mmol of pentanols (the ratio of 1-pentanol to 2-pentanol was 96:4).

Another run of this reaction was conducted under identical conditions except that it was allowed to run for 3 h. Then after the usual oxidation and workup, gas chromatographic examination revealed the presence of 4.5 mmol (90%) of *n*-octane and 13.4 mmol of pentanols.

In both of these experiments, no *n*-octanol was detected on GLC, indicating the absence of the elimination pathway.

Reduction of *n*-Octyl Iodide with Lithium Triethylborohydride. The apparatus was the same as in the previous experiments. Into the reaction flask maintained at 25 °C were injected 5 mL of THF and 5 mL of a 1.0 M solution in THF of lithium triethylborohydride (5 mmol), followed by 5 mL of a 1.0 M solution of *n*-nonane in THF to serve as an internal standard. Finally, 5 mL of a 1.0 M solution in THF of *n*-octyl iodide (5 mmol) was introduced. The reaction mixture was stirred vigorously. After 5 min, 1 mL of the reaction mixture was withdrawn by means of a syringe, quenched with water, extracted with ether, and analyzed by GLC on column A. This revealed the presence of 97% *n*-octane. After 15 min, a 100% yield of *n*-octane was realized. Analysis on column C revealed the complete absence of 1-octene.

Acknowledgment. We acknowledge the generous financial support of the U.S. Army Research Office.

Registry No. Octyl iodide, 629-27-6; octyl bromide, 111-83-1; octyl chloride, 111-85-3; cyclohexyl iodide, 626-62-0; cyclohexyl bromide, 108-85-0; cyclohexyl chloride, 542-18-7; benzyl bromide, 100-39-0; 2-bromooctane, 557-35-7; 3-bromopropene, 106-95-6; butyl bromide, 109-65-9; butyl chloride, 109-69-3; isobutyl bromide, 78-77-3; *sec*-butyl bromide, 78-76-2; cyclopentyl bromide, 137-43-9; $LiAlH_4$, 16853-85-3; $NaAlH_4$, 13770-96-2; $Li(CH_3O)_3AlH$, 12076-93-6; $Li((CH_3)_3CO)_3AlH$, 17476-04-9; $NaBH_4$, 16940-66-2; $LiBH_4$, 16949-15-8; $LiEt_3BH$, 22560-16-3; AlH_3, 7784-21-6; $H_3B{\cdot}SMe_2$, 13292-87-0; 9-BBN, 280-64-8.

Annelations with Tetrachlorothiophene 1,1-Dioxide

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Tetrachlorothiophene 1,1-dioxide is a reactive, cheletropic Diels–Alder reagent. It has been used to annelate, with loss of sulfur dioxide, a large variety of olefinic compounds to form 1,2,3,4-tetrachloro-1,3-cyclohexadiene derivatives. Dehydrochlorination of these forms 1,2,4-trichloro aromatic compounds. Both double bonds in thiophene and *N*-methylpyrrole are annelated. Addition of tetrachlorothiophene dioxide to acyclic 1,5-dienes, which may contain a heteroatom, provides a facile synthesis of tetrachloroisotwistenes (**51**) and heteroisotwistenes (**56**) by a double Diels–Alder reaction. Acyclic 1,6-dienes lead to tetrachlorohomoisotwistene (**59**) and heterohomoisotwistenes (**61**). By use of 1,5-cyclooctadiene, *sym*-dibenzocyclooctatetraene, and 1,5-cyclononadiene, the more complex carbocycles **62**, **65**, and **66** are generated. Tetrabromothiophene dioxide reacts like the tetrachloro compound.

Although many thiophene 1,1-dioxides are known, the preparation of tetrachlorothiophene dioxide has not been reported, though there are unexemplified patent disclosures of it.[2] The compound appeared to offer high re-

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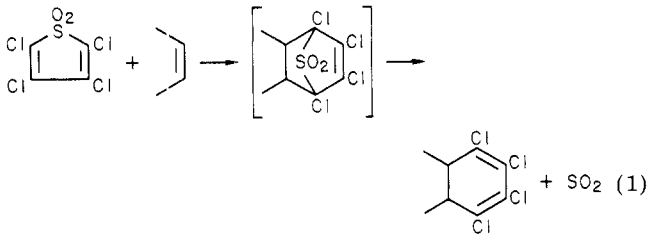
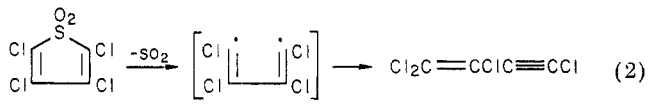
activity as a cheletropic Diels–Alder reagent, more so than the known 3,4-dichlorothiophene dioxide[3] which has been used to annelate maleimides, benzoquinone, and 1,3-dienes, and more than the dimethyl-, diphenyl-, and tetraphenylthiophene dioxides which have been employed in annelating a few other olefinic or acetylenic compounds.[5-7] Unsubstituted thiophene dioxide is unstable but will annelate itself[8] and diethyl acetylenedicarboxylate.[9]

The expectations for tetrachlorothiophene dioxide proved valid. The compound has a combination of stability and reactivity that makes it a useful synthetic reagent. It undergoes Diels–Alder addition with double bonds to form an adduct which spontaneously loses sulfur dioxide to leave the double bond annelated with a tetrachlorobutadienediyl group (eq 1).



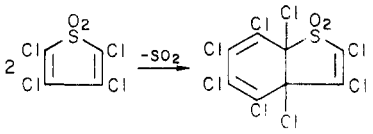
The products can be oxidatively aromatized, treated with base to form 1,2,4-trichloro aromatics, and reductively dechlorinated as part of the synthetic possibilities. Of particular interest is the facile assemblage of polycyclic carbocycles and heterocycles, by means of a double Diels–Alder reaction, through addition of tetrachlorothiophene dioxide to 1,5- and 1,6-dienes. Tetrabromothiophene dioxide, also a new compound, reacts like its tetrachloro analogue.

Synthesis and Stability of Tetrachlorothiophene Dioxide. Tetrachlorothiophene dioxide was prepared by oxidizing tetrachlorothiophene with 3-chloroperbenzoic acid in refluxing 1,2-dichloroethane for 2 days. The compound melts at 91–92 °C and starts to decompose at about 135 °C. Thus, it has ample stability for carrying out reactions and is stable to storage. Pyrolysis at 660 °C and 1 mm yields perchlorovinylacetylene[10] in 67% yield (eq 2).



This decomposition–rearrangement is mechanistically related to the pyrolysis of hexachlorobenzothiophene 1,1-dioxide to perchlorophenylacetylene[11] and to the pyrolysis of octachlorobenzocyclobutene to perchlorostyrene.[12]

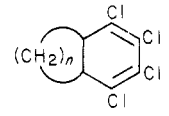
The preparation of tetrachlorothiophene dioxide is accompanied by the formation of **45** in 1.1% yield. This byproduct results from the reaction of tetrachlorothiophene with itself.



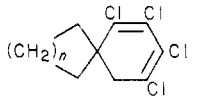
45

Tetrabromothiophene dioxide was made analogously to its tetrachloro analogue.

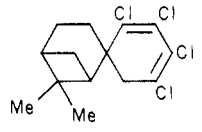
Annelation of Monoolefins. Tetrachlorothiophene dioxide is reactive enough to combine slowly with ethylene at 28 °C to form 1,2,3,4-tetrachloro-1,3-cyclohexadiene (**1**). Many unsaturated compounds react exothermically on slight warming, and the reaction needs to be moderated by cooling or use of solvent. Some illustrative examples of easily generated structures are listed below. A more extensive list, including functionalized compounds, is presented in Table I (compounds 1–44).



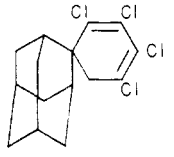
n = 3,4,5,6,10
2–6
from cycloolefins



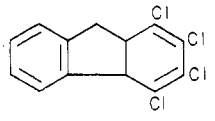
n = 1,3
9, 10
from methylenecycloalkanes



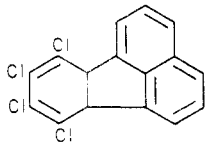
12
from (−)-β-pinene.



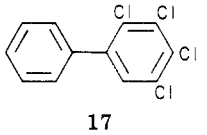
13
from methyleneadamantane



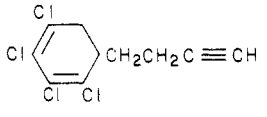
14
from indene



15
from acenaphthylene



17
from PhC≡CH



18
from $CH_2{=}CH(CH_2)_2C{\equiv}CH$

Example 18, from 1-hexen-5-yne, reveals the greater reactivity of alkene vs. alkyne. Reaction is exclusively with the alkene bond as far as NMR reveals. Thus, the kinetically favored product is formed rather than the thermodynamically favored one. Addition to C≡C would have produced an aromatic ring. Selectivity for cis double bonds is shown in the reaction with the cis double bond of *cis*-1,*trans*-5-cyclodecadiene to form **8** (Table I). The reaction with (−)-β-pinene occurred with considerable stereospecificity as a 74% recrystallized yield of a single isomer (**12**) was obtained.

Annelation of 1,4-benzoquinone and 1,4-naphthoquinone produces **35** and **36**. These exist as shown, as demonstrated by NMR and IR, and do not enolize to the aromatic 1,4-diols until treated with base. The 9,10-anthracenediol

(1) Contribution No. 2711.
(2) Bluestone, H. U.S. Patent 2976297, 1961; *Chem. Abstr.* **1967**, *55*, 16567d. U.S. Patent 3073691, 1963; *Chem. Abstr.* **1963**, *59*, 576b.
(3) Bluestone, H.; Bimber, R.; Berkey, R.; Mandel, Z. *J. Org. Chem.* **1961**, *26*, 346.
(4) Bimber, R. M. U.S. Patent 3110739, 1963; *Chem. Abstr.* **1964**, *60*, 2870b.
(5) Melles, J. L. *Recl. Trav. Chim. Pays-Bas* **1952**, *71*, 869.
(6) Whelan, J. M. *Diss. Abstr.* **1959**, *20*, 1180.
(7) Davies, W.; Porter, Q. N. *J. Chem. Soc.* **1957**, 459.
(8) Bailey, W. J.; Cummins, E. W. *J. Am. Chem. Soc.* **1954**, 1932, 1936, 1940. For the best synthesis of thiophene dioxide, see: Chow, Y. L.; Fossey, J.; Perry, R. A. *J. Chem. Soc., Chem. Commun.* **1972**, 501.
(9) Van Tilborg, W. J. M.; Smael, P.; Visser, J. P.; Kouwenhoven, C. G.; Reinhoudt, D. N. *Recl. Trav. Chim. Pays-Bas* **1975**, *94*, 85.
(10) Roedig, A.; Bonse, G.; Helm, R.; Kohlhaupt, R. *Chem. Ber.* **1971**, *104*, 3378.
(11) Brooke, G. M.; King, R. *Tetrahedron* **1974**, *30*, 857.
(12) Roedig, A.; Försch, M.; Haveaux, B.; Scheutzow, D. *Tetrahedron Lett.* **1972**, 2613.

Table I.[a,t] Annelations with Tetrachlorothiophene Dioxide

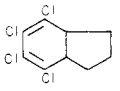
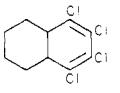
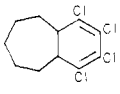
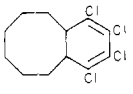
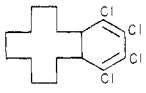
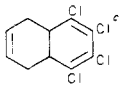
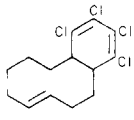
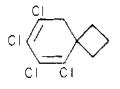
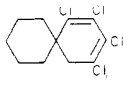
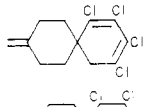
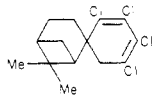
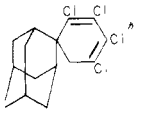
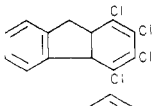
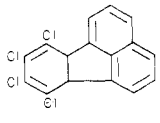
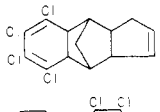
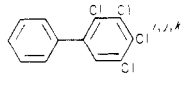
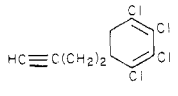
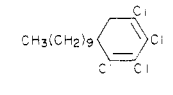
no.	reactant	reaction conditions, temp, °C (time, h)	product	recrystn solvent	mp or bp (mm), °C	yield, %
1	$CH_2=CH_2$	C_6H_6, 80 (200 psi), (4)			74 (0.4) n^{25}_D 1.5748	89
2	cyclopentene	44, (2)		abs EtOH	35-36	74
3	cyclohexene	83, (1)		MeOH	88-89	90
4	cycloheptene	100, (1)		abs EtOH	48-49	92
5	cyclooctene	100, (1)		abs EtOH	56-57	79
6	cyclododecene	100, (16)		Me_2CO	148-150	40
7	1,4-cyclohexadiene	86, (1)		abs EtOH	75.5-76.5	88
8	*cis*-1,*trans*-5-cyclodecadiene[d]	$ClCH_2CH_2Cl$, 80, (1)		abs EtOH	118-119	63
9	methylene-cyclobutane[e]	60, (3)		abs EtOH	37.5-38.3	75
10	methylene-cyclohexane[e]	100, (3)		abs EtOH	66-67	73
11	1,4-dimethylene-cyclohexane[f]	100, (1)		abs EtOH	100-102.5	70
12	(−)-β-pinene	100, (3)		abs EtOH	90.5-91.3 $[\alpha]^{23}_D$ −71.6° ($CHCl_3$)	74
13	methylene-adamantane[g]	130, (4)		Me_2CO	101.5-102.5	27
14	indene	C_6H_6, 45, (1)		MeOH	96-97	80
15	acenaphthylene	C_6H_6, 100, (1)		MeOH	173-174	91
16	*endo*-dicyclo-pentadiene	C_6H_6, 80, (1)		Me_2CO	133-134	65
17	PhC≡CH	cooled in ice		MeOH	90-91	86
18	1-hexen-5-yne[l]	(2)		MeOH	105 (0.35) 28	70
19	1-dodecene[f]	100, (3)			162-163 (0.3) n^{25}_D 1.5155	88

Table I (*Continued*)

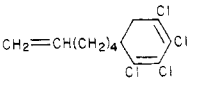
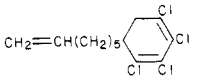
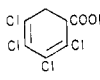
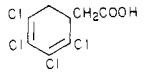
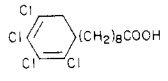
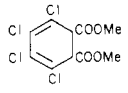
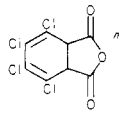
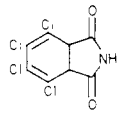
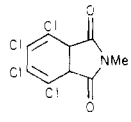
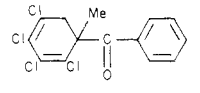
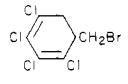
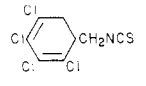
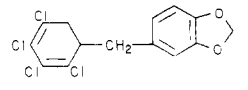
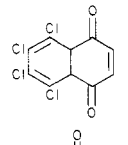
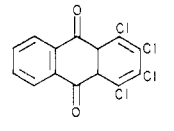
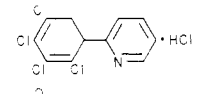
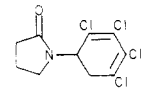
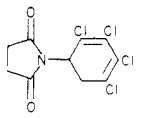
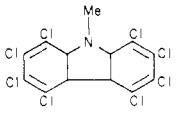
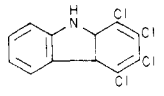
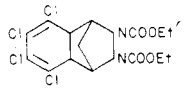
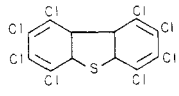
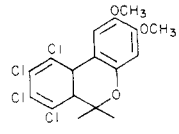
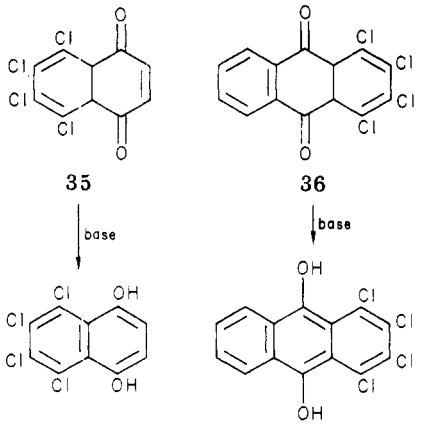
no.	reactant	reaction conditions, temp, °C (time, h)	product	recrystn solvent	mp or bp (mm), °C	yield, %
20	1,7-octadiene[f]	100, (1)			123 (0.25) n^{25}_D 1.5403	69
21	1,8-nonadiene[f]	100, (1)			131 (0.5) n^{25}_D 1.5357	49
22	CH_2=CHCOOH	100, (1)		CCl_4	152-152.6	68
23	CH_2=CHCOOMe	80, (2)		MeOH	75-76	91
24	CH_2=CHCN	78, (17)		MeOH	95-96	83
25	CH_2=$CHCH_2$COOH	100, (16)		hexane	91-92	78
26	CH_2=$CH(CH_2)_8$COOH	100, (1)		hexane	42-43.2	78
27	dimethyl maleate	100, (16)		MeOH	83-85.5	73
28	maleic anhydride	100, (48)		$PhCH_3$	163-165	61
29	maleimide	$ClCH_2CH_2Cl$, 80, (1)		EtOH	255-257	88
30	*N*-methylmaleimide	100, (1)		tetrahydro-furan	230-231	90
31	CH_2=C(Me)COPh[o]	100, (20)		abs EtOH	60.3-61.7	65
32	CH_2=$CHCH_2$Br	70, (2)		hexane	51-52	88
33	CH_2=$CHCH_2$NCS	100, (2)		hexane	42-43	55
34	safrole	100, (1)		hexane	97.8-98.3	75
35	1,4-benzoquinone	$ClCH_2CH_2Cl$, 80, (16)		CCl_4	148-157	74
36	1,4-naphthoquinone	C_6H_6, 80, (16)		CCl_4	177-178	68
37	2-vinylpyridine	(1) C_6H_6, 25 (2) HCl		Me_2CO	223-224	75
38	*N*-vinylpyrrolidone	C_6H_6, 25		MeOH	143-144	84

Table I (*Continued*)

no.	reactant	reaction conditions, temp, °C (time, h)	product	recrystn solvent	mp or bp (mm), °C	yield, %
39	*N*-vinylsuccinimide[p]	100, (0.5)		EtOH	165-166	92
40	*N*-methylpyrrole	$ClCH_2CH_2Cl$, 80, (3)		cyclo-hexane	175.5-176	44
41	indole	C_6H_6, 23, (15)		hexane	118-119	77
42	diethyl 2,3-diaza-norbornene-2,3-dicarboxylate[q]	$ClCH_2CH_2Cl$, 80, (10)		EtOH	162.5-163.5	58
43	thiophene	85, (72)		$CHCl_3$	216.5-217 dec	61
44	precocene II[s]	C_6H_6, 80, (3)		EtOH	160-161	74

[a] NMR, UV, and IR data are given in the Experimental Section. [b] Reference 25. Schuphan, I.; Sajko, B.; Ballschmiter, K. *Z. Naturforsch. B* **1972**, *27*, 147. [c] Akhtar, I. A.; Fray, G. I. *J. Chem. Soc. C* **1971**, 2802. [d] Heimbach, P.; Wilke, G. *Justus Liebigs Ann. Chem.* **1969**, *727*, 183. [e] Reference 27. [f] Reference 29. [g] Schleyer, P. v. R.; Nicholas, R. D. *J. Am. Chem. Soc.* **1961**, *83*, 182. [h] One other example of this ring system is known: Kane, V. V. *Synth. Commun.* **1976**, *6*, 237. [i] McBee, E. T.; Diveley, W. R.; Burch, J. E. **1955**, *77*, 385. [j] McBee, E. T.; Idol, J. D., Jr.; Roberts, C. W. *Ibid.* **1955**, *77*, 6674. [k] Hoffmann, R. W.; Häuser, H. *Tetrahedron Lett.* **1964**, 197. [l] Farchan Division, Chemsampco, Inc., Willoughby, OH. [m] References 23 and 24. [n] The acid is known: Nohe, H.; Suter, H. German Patent 2 158 200, 1973; *Chem. Abstr.* **1973**, *79*, 42045. [o] Yakubovich, A. Ya.; Razumovskii, V. V.; Belyaeva, Y. N. *Zh. Obshch. Khim.* **1958**, *28*, 680. *J. Gen. Chem. USSR (Engl. Transl.)* **1958**, *28*, 660. [p] Reference 33. [q] Diels, O.; Blom, J. H.; Koll, W. *Justus Liebigs Ann. Chem.* **1925**, *443*, 242. [r] Reference 16. [s] Parish Chemical Co., Provo, UT. [t] Satisfactory analytical data (±0.4%) for C, H, and Cl, Br, or N were obtained for all new compounds in the table except for **2** (calcd: Cl, 54.97; found: Cl, 54.52).

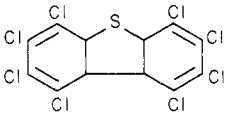
is quickly oxidized by air to 1,2,3,4-tetrachloroanthraquinone.

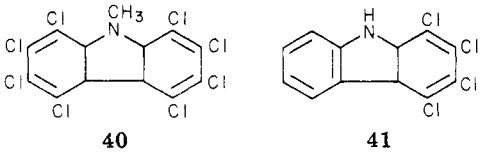


Compound **36** has been represented as the hydrolysis product of the Diels–Alder adduct of 1,4-naphthoquinone and 5,5-dimethoxytetrachlorocyclopentadiene.[13] It was not isolated or characterized but oxidized to the anthraquinone.

Compound **3** has been aromatized by heating with chloranil at 140 °C in xylene to form 1,2,3,4-tetrachloro-5,6,7,8-tetrahydronaphthalene.

Annelation of Aromatic Heterocycles. The reactivity of tetrachlorothiophene dioxide is further demonstrated by its reaction with thiophene. A 61% yield of the diadduct **43** is formed when the dioxide is refluxed with excess thiophene for 72 h. The diadduct was the only product





isolated since monoannelation breaks the aromaticity of the ring and creates a product more reactive than thiophene itself. By comparison, thiophene is reported to add 2 mol of hexachlorocyclopentadiene when the reactants are heated together at 150–160 °C for 14 days.[14] Similarly, *N*-methylpyrrole reacts at 22 °C to form **40**, and indole yields **41**. Furans undergo an addition–rearrangement reaction which will be reported separately.

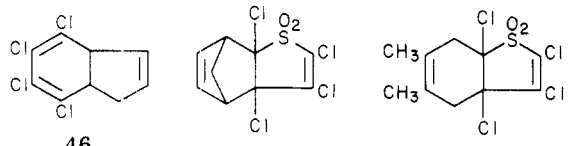
Reaction with 1,3-Dienes. Addition of tetrachlorothiophene dioxide to conjugated dienes can occur in two

(13) Kniel, P. *Helv. Chim. Acta* **1963**, *46*, 492.

(14) Hamadait, H.; Neeman, M. Israel Patent 9749, 1957; *Chem. Abstr.* **1958**, *52*, 1263e.

(15) Lemal, D. M.; Gosselink, E. P.; McGregor, S. D. *J. Am. Chem. Soc.* **1966**, 582. Schmerling, L. U.S. Patent 3660473, 1972; *Chem. Abstr.* **1972**, *77*, 48052k. Roedig, A.; Neukom, T. *Chem. Ber.* **1974**, *107*, 3463.

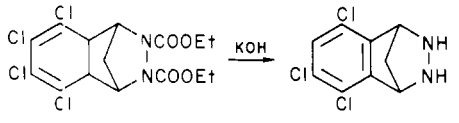
ways. Thus, with excess cyclopentadiene, annelation of one double bond took place in 44% yield to form **46**, and



46 47 48

Diels–Alder addition of the diene to one double bond of tetrachlorothiophene dioxide occurred to give **47** in 25% yield. 3,4-Dichlorothiophene dioxide reacts similarly,[3] but the predominant product corresponds to **47**. With 2,3-dimethylbutadiene and tetrachlorothiophene dioxide, the Diels–Alder adduct **48** was the isolated product.

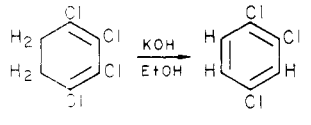
Dehydrochlorination of the Adducts. Mackenzie, Lay, and Telford[16] added 5,5-dimethoxytetrachlorocyclopentadiene to diethyl 2,3-diazanorbornene-2,3-dicarboxylate, followed by acid hydrolysis of the acetal and decarbonylation, to form **42**, which can also be made from the diazanorbornene and tetrachlorothiophene dioxide. They observed that alkaline hydrolysis caused dehydrochlorination to give the aromatic compound **42a** (eq 3).



(3)

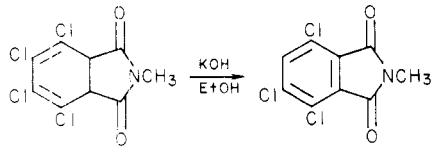
42 42a

The dehydrochlorination of the tetrachlorothiophene dioxide adducts to 1,2,4-trichloro aromatic compounds is a general reaction, as illustrated by eq 4 and 5.



(4)

1



(5)

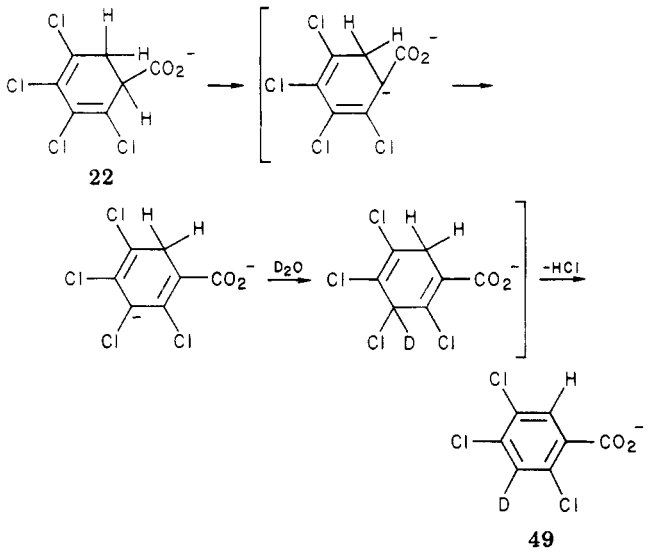
30 50

Similarly, when 2,3,4,5-tetrachloro-2,4-cyclohexadiene-1-carboxylic acid (**22**) is dissolved in aqueous sodium hydroxide, sodium 2,4,5-trichlorobenzoate is formed in 98% yield, identified by the melting point and NMR of the free acid and conversion to the amide, mp 167 °C. If this reaction is carried out in D_2O using NaOD, the result is at least 96% insertion of D at position 3 with no replacement of H with D at position 6 as far as NMR shows. Integrals of the NMR spectra of the deuterated (**49**) and undeuterated (**22**) acids were compared in $(CD_3)_2SO$ at 27% concentration. The singlet for 6-H at 7.76 ppm was not diminished in the deuterated acid. The singlet for 3-H in the undeuterated acid appears at 7.56 ppm. These assignments follow those in Sadtler spectrum no. 11569 and result from comparison with the position of the singlet for 2,3,4,5-tetrachlorobenzoic acid (Sadtler spectrum no. 11570).

The deuteration may be rationalized according to Scheme I.

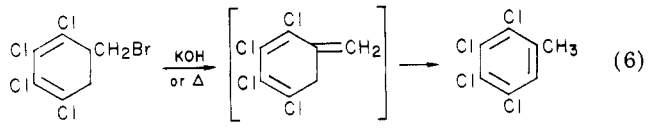
Dehydrobromination of the annelation product of allyl bromide (**32**) with potassium hydroxide, or by boiling the

Scheme I



22 49

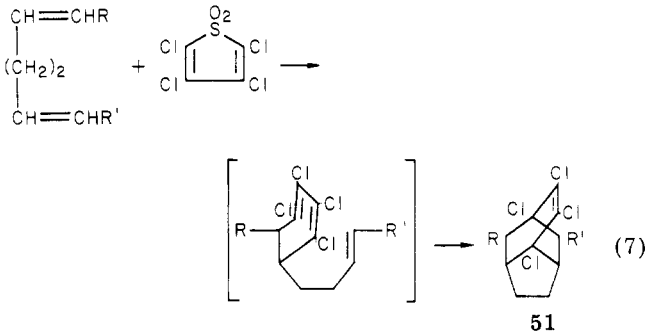
compound, provides a route to 2,3,4,5-tetrachlorotoluene[15] (eq 6).



(6)

32

Isotwistenes. Annelation of one double bond of a 1,5-acyclic diene with tetrachlorothiophene dioxide produces a tetrachloro-1,3-cyclohexadienyl group in that position which is then available for an intramolecular Diels–Alder reaction with the remaining double bond of the diene to form an isotwistene (**51**) in 50–60% yield (eq 7). The initial annelation takes place at slightly elevated



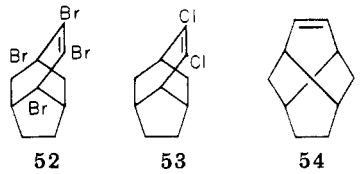
(7)

51

a, R = R′ = H; b, R = H, R′ = CH_3; c, R = R′ = CH_3

temperatures, but the intramolecular reaction, also exothermic, may require raising the temperature to 150–175 °C.

Similarly, tetrabromothiophene dioxide and 3,4-dichlorothiophene dioxide react with 1,5-hexadiene to form **52** and **53**.



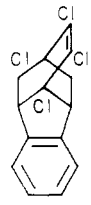
52 53 54

Determination of the ^{13}C NMR of **51a**, **52**, and **53** showed seven kinds of carbon atoms in support of the structure. Had the intramolecular Diels–Alder reaction taken place in the reverse direction, twistenes (**54**) with

(16) Lay, W. P.; Mackenzie, K.; Telford, J. R. *J. Chem. Soc. C* **1971**, 3199.

five kinds of carbon atoms would have formed. In accord with the assigned structure, Krantz and Lin have shown that the intramolecular Diels–Alder reactions of 5-(3-butenyl)-1,3-cyclohexadiene and of 5-(4-pentenyl)-1,3-cyclohexadiene above 200 °C form isotwistene and homoisotwistene, respectively, not twistene and homotwistene.[17]

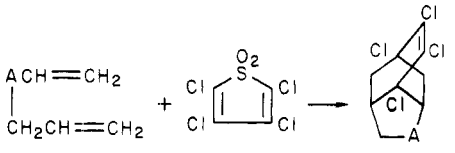
By reaction of tetrachlorothiophene dioxide with 1,2-divinylbenzene at 80 °C, the more complex ring system represented by **55** is built up. The structure is supported



55

by ^{13}C NMR which shows nine kinds of carbon atoms, whereas the twistene isomer would show seven. Only one example of this ring system has been reported.[18]

Heteroisotwistenes. The 1,5-diene chains may be interrupted by a heteroatom. Reaction with tetrachlorothiophene dioxide then yields heteroisotwistenes (**56**) (eq 8). The intramolecular Diels–Alder reaction involving allyl



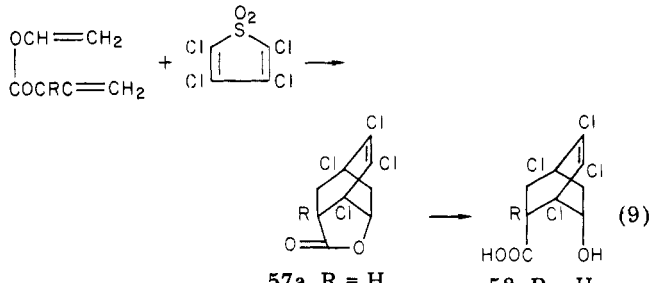
(8)

56

a, A = O; b, A = S

vinyl ether took place below 100 °C, but the sulfide required a temperature of about 150 °C. The thiaisotwistene has been oxidized to the sulfone.

Vinyl acrylates produce lactones (**57**) which can be hydrolyzed to hydroxy acids (**58**) (eq 9).



(9)

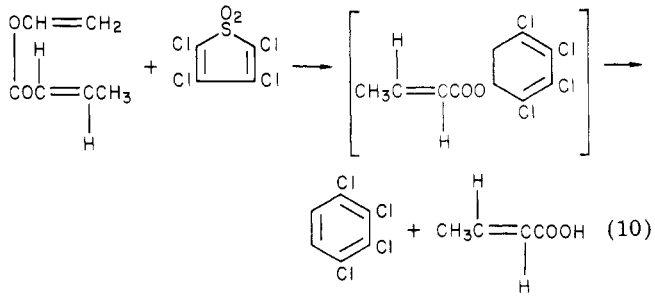
57a, R = H
b, R = CH_3

58, R = H

The assignments of the structures as heteroisotwistenes rather than heterotwistenes rests upon analogy with **51a**, **52**, **53**, and **55**.

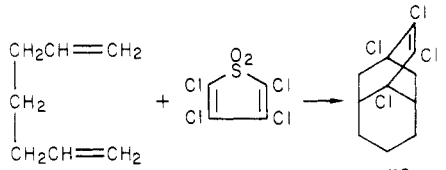
When vinyl crotonate is used, an intramolecular Diels–Alder reaction does not take place, as crotonic acid is spontaneously lost at 100 °C and 1,2,3,4-tetrachlorobenzene is formed (eq 10).

Homoisotwistenes. By using acyclic 1,6-dienes instead of 1,5-dienes, homoisotwistenes are obtained. Thus, 1,6-heptadiene gives **59** (eq 11). Presumably, this type of



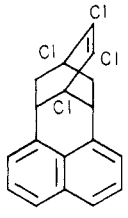
(10)

reaction could also be used to prepare more complex ring systems. 1,8-Divinylnaphthalene should yield **60**.



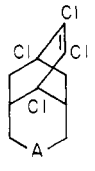
(11)

59



60

The reaction can utilize readily available diallyl compounds to form heterohomoisotwistenes. Thus, diallyl ether, diallyl sulfide, *N,N*-diallylacetamide, *N,N*-diallylcyanamide, and *N,N*-diallylaminoacetonitrile form the following compounds (**61a–e**) which have been transformed to **61f–i**.



61

a, A = O
b, A = S ⟶ f, A = SO_2
c, A = NAc ⟶ g, A = NH
d, A = NCN ⟶ h, A = $NCONH_2$
e, A = CH_2CN ⟶ i, A = $CH_2CH_2NH_2$

The ring system of **61a** is known only as a cyclic anhydride.[19] The ring systems represented by the other compounds are new.

In accord with the assigned structures, ^{13}C NMR showed **59** to have eight kinds of carbon atoms and **61a,b,g** seven kinds. Had the intramolecular Diels–Alder reaction taken place in the reverse direction, the homotwistenes would have had two fewer types of carbon atoms.

Tetracycles from Cyclic 1,5-Dienes. With 1,5-cyclooctadiene, halogenated thiophene dioxides form hexahydro-4,1,5-[1]propanyl[3]ylidene-1*H*-indenes (eq 12).

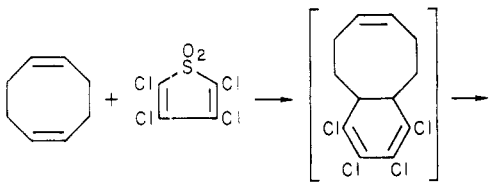
The reaction proceeds vigorously on slight warming, and the product separates in 90% yield from excess diene. The reaction even proceeds slowly at room temperature, indicating that a proximity effect and entropic assistance

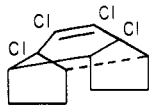
(17) Krantz, A.; Lin, C. Y. *J. Am. Chem. Soc.* **1973**, *95*, 5662. For a review of intramolecular Diels–Alder reactions see Oppolzer, W. In "New Synthetic Methods"; Verlag Chemie: Weinheim and New York, 1979; Vol. 6, pp 1–48; *Angew. Chem.* **1977**, *89*, 10; *Angew Chem., Int. Ed. Engl.* **1977**, *16*, 10.

(18) Föhlisch, B.; Schupp, E.; Dukek, U.; Schwaiger, G. *Justus Liebigs Ann. Chem.* **1973**, 1861.

(19) Tichy, M.; Hamsikova, E.; Blaha, K. *Collect. Czech. Chem. Commun.* **1976**, *41*, 1935.

(20) Fray, G. I.; Oppenheimer, A. W. *J. Chem. Soc., Chem. Commun.* **1967**, 599.



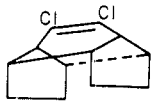


(12)

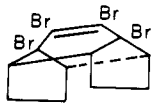
62

greatly facilitate the intramolecular Diels–Alder reaction. Compound **62** has been synthesized previously in five steps and 19% overall yield starting with 1,5-cyclooctadiene and tetrachloro-5,5-dimethoxycyclopentadiene.[21] The same investigators made the unchlorinated analogue of **62** by refluxing 1,5-cyclooctadiene with α-pyrone,[21] and the tetraphenyl derivative by refluxing 1,5-cyclooctadiene with tetraphenylcyclopentadienone.[20,21]

The addition of 3,4-dichlorothiophene dioxide at 80 °C and of tetrabromothiophene dioxide at 100 °C to 1,5-cyclooctadiene produces **63** and **64**.



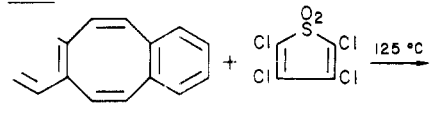
63

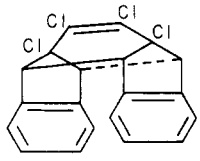


64

Although tetrachloro-α-pyrone[23] is not as reactive as tetrachlorothiophene dioxide, it added to 1,5-cyclooctadiene at 140 °C (1.5 h) to form **62** in 93% yield with loss of carbon dioxide. At 100 °C (17 h) the yield was 46%. Tetrachloro-α-pyrone might function as a substitute for tetrachlorothiophene dioxide in many instances by operating at a higher temperature. The pyrone has been used to annelate methyl acrylate[23,24] and ethylene.[25] Products different from those obtained with tetrachlorothiophene dioxide were produced when the pyrone was reacted with maleic anhydride, cyclopentadiene, and dicyclopentadiene.[23,24]

By using dibenzo[*a*,*e*]cyclooctene, a dibenzo analogue (**65**) of **62** can be assembled (eq 13).



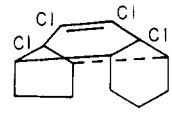


(13)

65

The ^{13}C NMR is consistent with **65** and shows six types of carbon atoms. In the ^{1}H NMR spectrum, the aromatic protons appear as a singlet at 6.80 ppm. By comparison, *o*-xylene gives a singlet at 7.10 ppm. Compound **65** represents a new ring system, but the hydrocarbon with a third benzo group located at the upper double bond of the ring system of **65** has been made by the photolysis of tribenzo[12]annulene.[22]

Another new ring system (**66**) is generated by the reaction of tetrachlorothiophene dioxide with 1,5-cyclononadiene.



66

Experimental Section

The ^{1}H NMR spectra were determined on Varian instruments using Me_4Si as internal standard. For the ^{13}C NMR spectra, a Bruker WH-90 instrument and Me_4Si were used and values are given in parts per million. IR spectra (KBr wafer) were measured in a Perkin-Elmer Model 21 spectrometer. Melting and boiling points are uncorrected.

Tetrachlorothiophene. This laboratory procedure was adapted from patents.[26] In a 1-L, three-necked flask equipped with a mechanical stirrer, simple still head, thermometer, and Glas-Col heater was placed 400 mL (2.55 mol) of hexachloro-1,3-butadiene[27] which was then heated to 160 °C. Sulfur (245 g, 7.66 mol) was added. The mixture was heated to 220–225 °C. After about 1.5 h, sulfur monochloride began to distill over. Heating was continued for 7 h. The mixture was then kept at about 200 °C for 15 h (overnight). Heating was then continued at 220–225 °C for 7 h. By this time, distillation of sulfur monochloride had ceased, and 206 mL containing a little hexachlorobutadiene had collected.

The product in the still pot was transferred to a single-necked flask and given a simple distillation at about 90 °C (6–7 mm) which removed tar and gave 438 g of distillate. The material was then fractionated through a 1 × 65 cm column having a spinning band of Teflon fluorocarbon resin to give 350 g (62%) of tetrachlorothiophene: bp 93–94 °C (7.7 mm); mp 29 °C. Additional product can be crystallized from the foreshot near this boiling point.

Tetrachlorothiophene 1,1-Dioxide. To a solution of 126 g (0.62 mol) of 85% 3-chloroperbenzoic acid[27] dissolved in 960 mL of warm 1,2-dichloroethane was added 55.5 g (0.25 mol) of tetrachlorothiophene. The solution was heated under reflux on a steam bath for 48 h. The solution was cooled, 3-chlorobenzoic acid was filtered off, the cake was washed with cold 1,2-dichloroethane, and the filtrate was washed with 10% sodium carbonate solution until free of acid. After the filtrate was dried ($MgSO_4$), the solvent was removed, finally under vacuum. A little hexane was added to the residue, the mixture was cooled, and the crystals were filtered off. Recrystallization from hexane gave 32 g (50%) of the sulfone: mp 90–91 °C, 91–92 °C after sublimation; IR 1608, 1565 (conjugated cyclic C=C), 1344, 1170 (SO_2) cm^{-1}; UV 325 (ϵ 2310), 234 (ϵ 4190) nm.

Anal. Calcd for $C_4Cl_4O_2S$: C, 18.92; Cl, 55.87. Found: C, 19.23; Cl, 55.84.

Byproduct 45 from Oxidation of Tetrachlorothiophene. From the oxidation of a total of 246 g of tetrachlorothiophene by heating with 3-chloroperbenzoic acid in 1,2-dichloroethane for 72 h, the third crop of crystals from hexane contained a byproduct. The tetrachlorothiophene dioxide was boiled out at 100 °C (0.5 mm), and the residue was recrystallized from hexane to give 2.74 g (1.1%) of 2,3,3a,4,5,6,7,7a-octachloro-3a,7a-dihydrobenzo[*b*]-thiophene (**45**): mp 156–157 °C.

Anal. Calcd for $C_8Cl_8O_2S$: C, 21.65; Cl, 63.93. Found: C, 21.33; Cl, 64.24.

Tetrabromothiophene 1,1-Dioxide. Tetrabromothiophene[26] (16 g, 0.04 mol) was added to 20.3 g (0.1 mol) of 85% 3-chloroperbenzoic acid dissolved in 150 mL of 1,2-dichloroethane, and

(21) Akhtar, I. A.; Fray, G. I.; Yarrow, J. M. *J. Chem. Soc.* **1968**, 812.
(22) Staab, H. A.; Graf, F.; Junge, B. *Tetrahedron Lett.* **1966**, 743. Tausch, M. W.; Elian, M.; Bucur, A.; Cioranescu, E. *Chem. Ber.* **1977**, *110*, 1744.
(23) Leon, E. U.S. Patent 3092641, 1963; *Chem. Abstr.* **1964**, *60*, 2092c.
(24) Leon, E. U.S. Patent 3274131, 1966; *Chem. Abstr.* **1967**, *66*, 65190u.
(25) Kauer, J. C. *Prepr., Div. Pet. Chem., Am. Chem. Soc.* **1970**, *15*(2), 1314–1318.
(26) Osgood, E. R.; Limpel, L. E.; Annis, R. L.; Turner, N. J. U.S. Patent 3354179, 1967; *Chem. Abstr.* **1968**, *68*, 104965p. Geering, E. J. U.S. Patent 2900394, 1959; *Chem. Abstr.* **1960**, *54*, 572g.
(27) Aldrich Chemical Co., Milwaukee, WI.

the solution was heated on a steam bath for 72 h. 3-Chlorobenzoic acid was filtered from the cooled solution, and the filtrate was washed twice with 5% sodium bicarbonate solution. The solution was dried ($MgSO_4$), treated with decolorizing charcoal, filtered, and evaporated at room temperature. Recrystallization of the residue from CCl_4 gave 11.4 g (66%) of the sulfone: mp 201–202 °C; IR 1570, 1531 (d, conjugated, cyclic C=C), 1188, 1176 (d, SO_2) cm^{-1}.

Anal. Calcd for $C_4Br_4O_2S$: Br, 74.03; S, 7.43. Found: Br, 73.90; S, 7.40.

Pyrolysis of Tetrachlorothiophene Dioxide. Tetrachlorothiophene dioxide (10 g) was distilled at 1 mm through a pyrolysis apparatus[28] heated to 660 °C, and the product (7.3 g) was collected in a trap cooled with liquid nitrogen. Distillation gave 5.0 g (67%) of 1,1,2,4-tetrachloro-1-buten-3-yne:[10] bp 24 °C (0.1 mm); mp −12 °C; IR as reported.[10] The pot residue was 1.5 g of syrup.

Compounds of Table I. These reactions were usually run on a 0.01–0.02-mol scale. In any scale-up, the exothermicity of the reactions should be kept in mind so that the temperature may be controlled by use of solvent or cooling.

NMR (ppm, in $CDCl_3$ except where noted), UV, and IR data: **1**, 2.77 (s); **2**, 3.18 (m, 2 CH); **3**, 1.52 (m, center CH_2CH_2), 1.67 (m, 2 CH_2), 2.85 (m, 2 CH); **4**, 3.03 (m, 2 CH); **5**, 2.87 (m, 2 CH); UV ($CHCl_3$) 295 (ε 6060), 285 (ε 6180) nm; **6**, 2.67 (m, 2 CH); **7**, 2.42 (m, 2 CH_2), 3.08 (m, 4a,8a-H_2), 5.77 (m, CH=CH); **8**, 1.3–3.1 (m's, 14 H), 5.46 (m, CH=CH); IR 2985, 2915, 2849 (CH), 1603 cm^{-1} (cyclic diene), no absorption for trans CH=CH; **9**, 1.8–2.7 (m's, 3 CH_2 of cyclobutane ring), 2.99 (s, CH_2 of diene ring); **10**, 2.84 (s, CH_2 of diene ring); **11**, 1.6–2.4 (m, 4 CH_2 of cyclohexane ring), 2.85 (s, CH_2 of diene ring), 4.64 (s, $=CH_2$); **12**, 1.11 (s, CH_3), 1.23 (s, CH_3), 1.5–2.6 (m's, 8 H), 2.84 (s, CH_2 of diene ring); **13**, 1.5–2.7 (m's, 14 H), 3.00 (s, CH_2 of diene ring); **14**, 3.17–3.75 (m, CH_2 + CH, half of AB), 4.35 (CH, half of AB, J = 9 Hz), 7.15–7.65 (m, 4 H, aromatic); **16**, 1.67 (AB, bridge CH_2), 2.1–3.5 (m, 8 H), 5.68 (unsymmetrical m, CH=CH of cyclopentene ring); **18** (CD_3CN), 2.18 (s, ≡CH), 2.1–3.3 (m's); IR 3311 (≡CH), 2950 (CH), 2119 (C≡C), 1608 (C=C) cm^{-1}; **20**, 1.1–3.35 (m's, 11 H), 4.8–6.2 (vinyl pattern); **21**, 1.2–3.3 (m's, 13 H), 4.8–6.2 (vinyl pattern); **23**, 3.12–3.70 (m, 3 H), 3.82 (s, CH_3); **28**, 4.35 (s); **32**, 3.05 (m, 3 H), 3.50 (m, CH_2Br); **35**, 4.16 (s, 2 CH), 6.87 (s, CH=CH); IR 3077 (=CH), 2924 (CH), 1686 (C=O), 1600, 1558, 1511 (C=C) cm^{-1}; **40**, 2.57 (s, CH_3), 3.90 (AB, J = 7 Hz, 4 CH); **41**, 4.23 (s, removed by D_2O, NH), 4.58 (AB, J = 11 Hz); **43**, 4.43 (AB, J = 6.4 Hz); **44**, 1.28 (s, CH_3), 1.54 (s, CH_3), 2.98, 4.31 (AB, J = 7 Hz, 2 CH of diene ring), 3.83 (s, 2 CH_3O), 6.37 (s, H, aromatic), 6.64 (s, H, aromatic, between CH_3O and O).

1,2,3,4-Tetrachloro-5,6,7,8-tetrahydronaphthalene. Compound **3** (1.63 g, 6 mmol), 1.55 g (6.3 mmol) of chloranil, and 5 mL of xylene were heated at 140 °C for 1 h. The xylene was evaporated, and the residue was extracted with 5% potassium hydroxide solution to remove tetrachlorohydroquinone. The product remaining was recrystallized from acetic acid to give 1.18 g (73%) of the title compound: mp 174–176 °C (lit.[40] mp 174 °C).

Addition to Cyclopentadiene. To 2.54 g (0.01 mol) of tetrachlorothiophene dioxide and 5 mL of dichloromethane in a flask fitted with a reflux condenser was added 2 mL of cyclopentadiene through the condenser. The reaction was exothermic. The volatiles were removed under vacuum, the residue was stirred with hexane, and 0.90 g of crystals was filtered off. Recrystallization of this product from absolute ethanol gave 0.81 g (25%) of 2,3,3a,7a-tetrachloro-3a,4,7,7a-tetrahydro-4,7-methanobenzo[*b*]-thiophene 1,1-dioxide (**47**): mp 168–169 °C; NMR ($CDCl_3$) 2.38 (AB, J = 10 Hz, CH_2), 3.50 (d with further splitting, 2 CH), 6.33 (m, symmetrical, CH=CH).

Anal. Calcd for $C_9H_6Cl_4O_2S$: C, 33.78; H, 1.89; Cl, 44.31. Found: C, 33.51; H, 1.94; Cl, 44.20.

The hexane filtrate was reduced in volume and 1.17 g (44%) of 4,5,6,7-tetrachloro-3a,7a-dihydroindene (**46**), mp 43–44 °C, was crystallized out: NMR ($CDCl_3$) 2.6–4.1 (m's, CH_2, 2 CH), 5.91 (m, CH=CH).

Anal. Calcd for $C_9H_6Cl_4$: C, 42.23; H, 2.36; Cl, 55.40. Found: C, 42.38; H, 2.39; Cl, 55.18.

Diels–Alder Addition with 2,3-Dimethylbutadiene. 2,3-Dimethylbutadiene[27] (3 mL) and 2.54 g (0.01 mol) of tetrachlorothiophene dioxide were heated under reflux on a steam bath for 15 min. The excess diene was removed and the residue was recrystallized from absolute ethanol to give 1.70 g (50.5%) of 2,3,3a,7a-tetrachloro-3a,4,7,7a-tetrahydro-5,6-dimethylbenzo[*b*]-thiophene 1,1-dioxide (**48**): mp 121–122 °C; NMR ($CDCl_3$) 1.72 (s, 2 CH_3), 2.86 (m, CH_2), 3.12 (AB, J = 18 Hz, CH_2).

Anal. Calcd for $C_{10}H_{10}Cl_4O_2S$: C, 35.74; H, 3.00; Cl, 42.20. Found: C, 35.90; H, 3.01; Cl, 42.22.

3,4,6-Trichloro-*N*-methylphthalimide. To 0.35 g (53 mmol) of potassium hydroxide dissolved in 50 mL of ethanol was added 1.50 g (5 mmol) of 3,4,5,6-tetrachloro-1,2-dihydro-*N*-methylphthalimide (**30**), and the solution was heated for 30 min. The solution was evaporated, and the residue was washed with water and then recrystallized from ethanol to give 0.49 g (37%) of 3,4,6-trichloro-*N*-methylphthalimide: mp 148–151 °C; NMR ($CDCl_3$) 3.19 (s, CH_3), 7.74 (1 H, aromatic).

Anal. Calcd for $C_9H_4Cl_3NO_2$: C, 40.87; H, 1.52; N, 5.30. Found: C, 40.60; H, 1.61; N, 5.10.

2,3,4,5-Tetrachlorotoluene. To a solution of 3.11 g of 5-bromomethyl-1,2,3,4-tetrachloro-1,3-cyclohexadiene (**32**, 0.1 mol) in 12 mL of ethanol was added 0.70 g (0.0106 mol) of potassium hydroxide in 5 mL of ethanol. The ethanol was evaporated from the mixture, and the residue was washed with water to leave 2.08 g (90%) of product. Recrystallization from hexane gave 1.65 g (72%) of 2,3,4,5-tetrachlorotoluene: mp 96.5–97.3 °C (lit.[15] mp 96–97 °C); NMR ($CDCl_3$) 2.35 (s, CH_3), 7.22 (s, 1 H).

Tetrachloroisotwistene (51a). 1,5-Hexadiene[29] (10 mL) and 5.08 g (0.02 mol) of tetrachlorothiophene dioxide were heated under reflux in an oil bath at 80 °C for 3 h. The product was distilled, mostly at 117 °C (0.4 mm), and then recrystallized to give 2.73 g (50%) of 5,6,7,7a-tetrachloro-2,3,3a,4,5,7a-hexahydro-1,5-methano-1*H*-indene: mp 73–73.5 °C; ^1H NMR ($CDCl_3$) 1.6–2.5 (m's), no CH=CH; ^{13}C NMR ($CDCl_3$) C-2 29.9 (t), C-1 45.9 (d), C-4 49.6 (t), C-5 65.0 (s), C-7a 78.6 (s), C=C 127.0, 132.1.

Anal. Calcd for $C_{10}H_{10}Cl_4$: C, 44.16; H, 3.71; Cl, 52.14; M_r 272. Found: C, 44.56; H, 3.77; Cl, 52.10; M_r 271 (cryoscopic in benzene).

Methyltetrachloroisotwistene (51b). Use of 10 mL of *cis*- and *trans*-1,5-heptadiene[29] in the above procedure gave a 48% yield of the 4-methyl derivative of **51a**: mp 41–42 °C (from methanol); NMR ($CDCl_3$) 1.01 (d, J = 7 Hz, CH_3), 1.5–2.6 (m's, 9 H).

Anal. Calcd for $C_{11}H_{12}Cl_4$: C, 46.19; H, 4.23; Cl, 49.58. Found: C, 46.43; H, 4.20; Cl, 49.31.

Dimethyltetrachloroisotwistene (51c). 2,6-Octadiene[29] (3 mL, mixed geometric isomers) and 2.54 g of tetrachlorothiophene dioxide were heated on a steam bath for 18 h. The excess diene was then removed, and the residue was heated at 175 °C for 1.5 h. Recrystallization of the product from absolute ethanol gave 1.71 g (57%) of **51c**, the 4,8-dimethyl derivative of **51a**: mp 68–70 °C; NMR ($CDCl_3$) 1.03 (d, J = 7 Hz, 2 CH_3), 1.4–2.6 (m, 8 H).

Anal. Calcd for $C_{12}H_{14}Cl_4$: C, 48.04; H, 4.70; Cl, 47.26. Found: C, 47.41; H, 4.55; Cl, 47.36.

Tetrabromoisotwistene (52). Tetrabromothiophene 1,1-dioxide (4.32 g, 0.01 mol), 5 mL of 1,5-hexadiene,[29] and 5 mL of 1,2-dichloroethane were refluxed for 4 h. The volatiles were removed, and the residue was heated to 160 °C to complete ring closure. This occurred with an exotherm to 200 °C. The cooled product was recrystallized twice from hexane to give 3.06 g (68%) of **52**: mp 102–103 °C; NMR ($CDCl_3$) 1.5–2.7 (m's, no $CH=CH_2$);

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^{13}C NMR C-2 30.9 (t), C-1 47.8 (d), C-4 51.2 (t), C-5 60.6 (s), C-7a 75.3 (s), C=C 122.8, 127.4.

Anal. Calcd for $C_{10}H_{10}Br_4$: C, 26.70; H, 2.24; Br, 71.06. Found: C, 26.73; H, 2.02; Br, 71.14.

Dichloroisotwistene (53). 3,4-Dichlorothiophene 1,1-dioxide[3] (11.1 g, 0.06 mol), 20 mL of benzene, and 12 mL of 1,5-hexadiene were heated under reflux on a steam bath for 16 h. The volatiles were removed, the residue was extracted with hot hexane, and 2 g of resin was filtered off. The filtrate was distilled to give 4.32 g, bp 77–78 °C (0.8 mm), and a pot residue of 2.65 g. The distillate was crystallized from methanol at low temperature to give 2.02 g (16.6%) of 6,7-dichloro-2,3,3a,4,5,7a-hexahydro-1,5-methano-1*H*-indene: mp 36–37 °C; ^1H NMR ($CDCl_3$) 1.8–2.8 (m's); ^{13}C NMR ($CDCl_3$) C-2 31.1 (t), C-1 36.1 (d), C-4 38.5 (t), C-5 39.9 (d), C-7a 52.3 (d), C=C 125.8, 130.0. The material in the mother liquor was heated at 200 °C to complete ring closure and then yielded 0.7 g (5.7%) more of product.

Anal. Calcd for $C_{10}H_{12}Cl_2$: C, 59.13; H, 5.96; Cl, 34.91. Found: C, 58.77; H, 5.87; Cl, 35.10.

Compound 55. 1,2-Divinylbenzene[30] (1.95 g, 0.015 mol), 2 mL of benzene, and 2.54 g of tetrachlorothiophene dioxide were heated under reflux on a steam bath for 30 min. The reaction was vigorous. The benzene was removed and the residue was recrystallized from acetone to give 2.30 g (72%) of 1,2,3,9a-tetrachloro-4,4a,9,9a-tetrahydro-3,9-methano-3*H*-fluorene in 2 crops: mp 161–162 °C; ^1H NMR (220 MHz, $CDCl_3$) 2.16 (half of AB, J = 12.7 Hz), 2.36 (half of AB appearing as a triplet with further splitting; one H of CH_2 coupled with CH), 3.32 (d, J = 10 Hz, CH; in the 60 MHz spetrum, these lines are split to doublets, J = 2.5 Hz, indicating weak coupling with the second H of CH_2), 7.25 ppm (m, 4 H, aromatic); ^{13}C NMR ($CDCl_3$) ,C-4 45.5 (t), C-4a 52.4 (d), C-3 67.2 (s), C-9a 80.6 (s), C-5 124.1, C-6 127.4, C=C 128.0, 134.5, C-4b 146.9.

Anal. Calcd for $C_{14}H_{10}Cl_4$: C, 52.54; H, 3.15; Cl, 44.31. Found: C, 52.71; H, 3.09; Cl, 44.23.

Tetrachlorooxaisotwistene (56a). Allyl vinyl ether[31] (3 mL) and 2.54 g (0.01 mol) of tetrachlorothiophene 1,1-dioxide were warmed under reflux to produce a vigorous reaction. Heating on a steam bath was continued for 1 h. The excess ether was removed, and the residue was recrystallized from absolute ethanol in 3 crops which were combined and recrystallized again to give 2.20 g (80%) of 3a,4,5,6-tetrachloro-2,3,3a,6,7,7a-hexahydro-3,6-methanobenzofuran: mp 100–101 °C; NMR ($CDCl_3$) 2.2–2.6 (m, 5 H), 3.8–4.5 (m, 3 H).

Anal. Calcd for $C_4H_8Cl_4O$: C, 39.46; H, 2.94; Cl, 51.76. Found: C, 39.71; H, 2.95; Cl, 51.74.

Tetrachlorothiaisotwistene (56b) and Its 1,1-Dioxide. To 5.08 g (0.02 mol) of tetrachlorothiophene dioxide in 5 mL of 1,2-dichloroethane was added slowly 3.00 g (0.03 mol) of allyl vinyl sulfide.[32] The reaction was exothermic. After subsidence, the mixture was heated on a steam bath for 1 h, the volatiles were removed, and the residue was heated at 150 °C for 10 min. The product was recrystallized from absolute ethanol to give 4.35 g (75%) of 3a,4,5,6-tetrachloro-2,3,3a,6,7,7a-hexahydro-3,6-methanobenzo[*b*]thiophene: mp 94.3–95 °C; NMR ($CDCl_3$) 2.0–2.9 (m's, 6 H), 3.37 (AB, J = 4 Hz, CH_2S).

Anal. Calcd for $C_9H_8Cl_4S$: C, 37.27; H, 2.78; S, 11.05. Found: C, 37.52; H, 2.71; S, 10.91.

The above sulfide (2.32 g, 0.008 mol), 10 mL of acetic acid, and 2.4 mL of 30% hydrogen peroxide were heated on a steam bath for 3 h. Water was added to the cooled mixture, and 2.3 g (89%) of the product was filtered off. Recrystallization twice from ethanol gave 1.68 g of the 1,1-dioxide, mp 236–245 °C.

Anal. Calcd for $C_9H_8Cl_4O_2S$: C, 33.57; H, 2.50; S, 9.96. Found: C, 33.76; H, 2.49; S, 10.00.

Lactone 57a from Vinyl Acrylate and Its Hydrolysis. Vinyl acrylate[33] (6 mL) and 5.08 g (0.02 mol) of tetrachlorothiophene dioxide were heated under reflux on a steam bath for 16 h. Dichloromethane was then added to the cooled mixture, and polymer was filtered off. The solvent and excess ester were removed from the filtrate, and the residue was recrystallized from carbon tetrachloride to give 3.24 g (56%) of 3a,4,5,6-tetrachloro-2,3,3a,6,7,7a-hexahydro-2-oxo-3,6-methanobenzofuran: mp 168–169 °C; NMR ($CDCl_3$) 2.3–3.1 (m's, 5 H), 4.75 (m, CHO).

Anal. Calcd for $C_9H_6Cl_4O_2$: C, 37.54; H, 2.10; Cl, 49.25. Found: C, 37.35; H, 2.40; Cl, 49.28.

The above lactone (1.73 g, 6 mmol) was suspended in 15 mL of hot ethanol, and 0.44 g (6.6 mmol) of potassium hydroxide dissolved in 5 mL of ethanol was added. The solution was diluted with water, hydrochloric acid was added, and the precipitated acid was filtered off to give 1.58 g (86%). This was recrystallized from 1,2-dichloroethane to give 1.20 g (65%) of 1,4,5,6-tetrachloro-7-hydroxybicyclo[2.2.2]oct-5-ene-2-carboxylic acid (**58**): mp 160.5–161.5 °C; NMR (CD_3CN) 1.85–2.95 (m's, 2 CH_2), 3.18 (ddd, CH), 3.83 (ddd, CH), 7.00 (COOH + OH).

Anal. Calcd for $C_9H_8Cl_4O_2$: C, 35.33; H, 2.64; Cl, 46.25. Found: C, 35.39; H, 2.59; Cl, 46.31.

Lactone 57b from Vinyl Methacrylate. Vinyl methacrylate[33] (2 mL) and 2.54 g (0.01 mol) of tetrachlorothiophene dioxide were heated under reflux on a steam bath for 3 h. The cooled mixture was stirred with a little hexane, and 1.06 g (35%) of product was filtered off. This was recrystallized from hexane to give 0.94 g (31%) of **57b**: mp 133–134 °C; NMR ($CDCl_3$) 1.26 (s, CH_3), 1.98, 2.66 (AB, J = 14 Hz, CH_2 next to CH_3), 2.45 (m, CH_2), 4.77 (t, CH).

Anal. Calcd for $C_{10}H_8Cl_4O_2$: C, 39.77; H, 2.67; Cl, 46.96. Found: C, 39.81; H, 2.71; Cl, 47.01.

Tetrachlorohomoisotwistene (59). 1,6-Heptadiene[29] (6 mL) and 5.08 g (0.02 mol) of tetrachlorothiophene dioxide were warmed under reflux. The vigorous reaction was moderated by cooling and then heated on a steam bath for 1 h. The excess diene was removed under vacuum to leave a syrup which NMR indicated to be mainly 1,2,3,4-tetrachloro-5-(4-pentenyl)-1,3-cyclohexadiene. This was heated in an oil bath at 170 °C for 1 h and then cooled. Absolute ethanol was added, and the crystals present were filtered off and recrystallized from petroleum ether to give 1.5 g (26%) of 6,7,8,8a-tetrachloro-1,2,3,4,4a,5,6,8a-octahydro-1,6-methanonaphthalene: mp 82.5–83.5 °C; ^1H NMR ($CDCl_3$) 1.25–2.8 (m's, no CH=CH_2); ^{13}C NMR [$CDCl_3$, $Cr(acac)_3$] C-3 13.2 (t), C-2 25.3 (t), C-1 39.8 (d), C-5 43.1 (t), C-6 66.6 (s), C-8a 73.8 (s), C=C 131.5, 132.2 (s's).

Anal. Calcd for $C_{11}H_{12}Cl_4$: C, 46.19; H, 4.23; Cl, 49.58. Found: C, 46.18; H, 4.25; Cl, 49.22.

Tetrachlorooxahomoisotwistene (61a). The reaction was run as described for 1,6-heptadiene but by using 6 mL of diallyl ether instead. The product was recrystallized from methanol to give 3.75 g (65%) of 4a,5,6,7-tetrachloro-3,4,4a,7,8,8a-hexahydro-4,7-methano-1*H*-2-benzopyran: mp 117–118.4 °C; ^1H NMR ($CDCl_3$) 1.8–2.5 (m's, 6 H), 3.87 (AB, J = 12 Hz, CH_2OCH_2); ^{13}C NMR [$CDCl_3$, $Cr(acac)_3$] C-4 40.8 (d), C-8 43.0 (t), C-7 66.1 (s), C-1 66.6 (t), C-4a 70.8 (s), C=C 130.0, 133.4 (s's).

Anal. Calcd for $C_{10}H_{10}Cl_4O$: C, 41.70; H, 3.50; Cl, 49.24. Found: C, 41.93; H, 3.55; Cl, 49.11.

Tetrachlorothiahomoisotwistene (61b) and Its Dioxide (61f). The reaction was run as described for 1,6-heptadiene, but 6 mL of diallyl sulfide[27] was used instead, and the heating at 170 °C was carried out for 3 h. The product was recrystallized from hexane (decolorizing charcoal) to give 4.0 g (66%) of 4a,5,6,7-tetrachloro-3,4,4a,7,8,8a-hexahydro-4,7-methano-1*H*-2-benzothiopyran: mp 130.5–131.3 °C; ^1H NMR ($CDCl_3$) 2.0–2.7 (m's overlapping half of AB pattern, 8 H), 3.46 (half of AB pattern, J = 13.5 Hz, CH_2S); ^{13}C NMR [$CDCl_3$, $Cr(acac)_3$] C-1 27.9 (t), C-4 38.9 (d), C-8 41.8 (t), C-7 66.4 (s), C-4a 72.3 (s), C=C 131.4, 133.2 (s's).

Anal. Calcd for $C_{10}H_{10}Cl_4S$: C, 39.50; H, 3.32; S, 10.54. Found: C, 39.86; H, 3.28; S, 10.30.

The above sulfide (1.52 g, 5 mmol), 10 mL of acetic acid, and 2.0 mL of 30% hydrogen peroxide were heated on a steam bath for 3 h. Water was added to the cooled mixture and 1.49 g of product was filtered off. Recrystallization from ethanol gave 1.18 g (70%) of the sulfone (**61f**), mp 229–233 °C.

Anal. Calcd for $C_{10}H_{10}Cl_4O_2S$: C, 35.74; H, 3.00; S, 9.54. Found: C, 36.06; H, 3.11; S, 9.66.

***N*-Acetyltetrachloroazahomoisotwistene (61c).** *N,N*-Diallylacetamide[34] was made by adding 40 mL of acetic anhydride dropwise to a stirred, cooled solution of 38 g of diallylamine in 100 mL of ether. Distillation gave 50.2 g (92%) of the amide: bp 63–65 °C (1.7 mm); n^{25}_D 1.4639.

N,N-Diallylacetamide (3 mL) and 2.54 g (0.01 mol) of tetrachlorothiophene dioxide were heated 1 h on a steam bath and 30 min at 170 °C. The cooled product crystallized and was washed with methanol to give 2.10 g. Recrystallization from ethanol left

1.94 g (59%) of 2-acetyl-6,7,8,8a-tetrachloro-1,2,3,4,4a,5,6,8a-octahydro-4,7-methanoisoquinoline: mp 204–205 °C; NMR ($CDCl_3$) 1.85–2.4 (m's, 6 H), 2.20 (s, CH_3), 3.14, 4.58 (AB, J = 14 Hz, CH_2N), 3.70 (s, CH_2N); NMR [$(CD_3)_2SO$] 1.6–2.6 (m, 6 H), 2.12 (s, CH_3), 2.95, 4.40 (AB, J = 13.5 Hz, CH_2N), 3.50, 3.80 ppm (AB, J = 14.5 Hz, CH_2N).

Anal. Calcd for $C_{12}H_{13}Cl_4NO$: C, 43.80; H, 3.98; N, 4.26. Found: C, 43.93; H, 4.00; N, 4.30.

Tetrachloroazahomoisotwistene (61g). The above acetyl derivative (3.92 g, 0.012 mol), 25 mL of ethanol, and 25 mL of hydrochloric acid were refluxed for 16 h. The mixture was cooled, and 3.55 g (92%) of the amine hydrochloride was filtered off; mp >350 °C.

Anal. Calcd for $C_{10}H_{12}Cl_5N$: Cl, 54.80. Found: Cl, 55.02.

The hydrochloride was dissolved in 100 mL of hot water, and sodium carbonate solution was added to precipitate the free base which was filtered off, recrystallized from methanol, and dried at 100 °C (0.5 mm) to give 2.73 g (79%) of 4a,5,6,7-tetrachloro-1,2,3,4,4a,7,8,8a-octahydro-4,7-methanoisoquinoline: mp 109–110 °C; NMR ($CDCl_3$) 1.55 (s, removed by D_2O, NH), 1.8–2.5 (m's, 6 H), 2.98 (AB, J = 12 Hz, CH_2NCH_2).

Anal. Calcd for $C_{10}H_{11}Cl_4N$: C, 41.85; H, 3.86; N, 4.88. Found: C, 42.13; H, 3.80; N, 4.79.

***N*-Cyanotetrachloroazahomoisotwistene (61d).** The reaction was run as described for 1,6-heptadiene, but 6 mL of diallylcyanamide[35] was used instead. The product was washed with CCl_4 and then recrystallized from ethyl acetate to give 3.51 g (56%) of 4a,5,6,7-tetrachloro-3,4,4a,7,8,8a-hexahydro-4,7-methanoisoquinoline-2(1*H*)-carbonitrile in two crops: mp 208.5–209.2 °C; NMR ($CDCl_3$) 2.30 (m, 6 H), 3.52 (AB, J = 13 Hz, CH_2NCH_2).

Anal. Calcd for $C_{11}H_{10}Cl_4N_2$: C, 42.34; H, 3.23; N, 8.98. Found: C, 42.33; H, 3.35; N, 9.02.

Hydrolysis of 61d to the Amide (61h). The above nitrile (3.12 g, 0.01 mol), 16 mL of ethanol, and 16 mL of hydrochloric acid were heated under reflux for 3.5 h. The ethanol was then removed, and the product was filtered off and extracted with hot water to remove amine hydrochloride. The residue was recrystallized from 1-propanol to give 1.92 g (58%) of the carbonamide **61h**, mp 238–239 °C.

Anal. Calcd for $C_{11}H_{12}Cl_4N_2O$: C, 40.03; H, 3.66; N, 8.49. Found: C, 39.96; H, 3.81; N, 8.40.

***N*-Cyanomethyltetrachloroazahomoisotwistene (61e).** *N*,*N*-Diallylaminoacetonitrile[35] (3 mL) and 2.54 g (0.01 mol) of tetrachlorothiophene dioxide were heated on a steam bath for 1 h and then at 170 °C for 10 min. The cooled product crystallized and was rinsed with cold 1,2-dichloroethane to give 2.45 g (75%). Recrystallization from 1,2-dichloroethane gave 2.05 g (63%) of 4a,5,6,7-tetrachloro-3,4,4a,7,8,8a-hexahydro-4,7-methanoisoquinoline-2(1*H*)-acetonitrile: mp 158–158.5 °C; NMR ($CDCl_3$) 2.1–2.5 (m's, 6 H), 2.85 (AB, J = 11.5 Hz, CH_2NCH_2), 3.62 (s, CH_2CN).

Anal. Calcd for $C_{12}H_{12}Cl_4N_2$: C, 44.21; H, 3.71; N, 8.59. Found: C, 44.40; H, 3.75; N, 8.72.

***N*-(2-Aminoethyl)tetrachloroazahomoisotwistene (61i).** The above nitrile (5 g), 50 mL of absolute ethanol, 1 g of Raney nickel, and 3 g of ammonia were charged into a shaker tube, and hydrogenation was carried out at 1000 psi and 125 °C for 2 h. The solution was filtered from the catalyst and evaporated, and the residue was redissolved in absolute ethanol. Addition of 2 mL of hydrochloric acid precipitated the amine hydrochloride. This was filtered off and dissolved in water. The solution was filtered, and sodium hydroxide solution was added to liberate the free amine which was filtered off and dried. Recrystallization from hexane left 2.0 g (40%) of 4a,5,6,7-tetrachloro-3,4,4a,7,8,8a-hexahydro-4,7-methanoisoquinoline-2(1*H*)-ethanamine: mp 95–96 °C; NMR ($CDCl_3$) 1.27 (s, NH_2, removed by D_2O), 1.9–3.0 (m's, 14 H); IR 3436, 3390 (NH_2), 2967, 2907, 2857 (CH), 1603 (C=C) cm^{-1}.

Anal. Calcd for $C_{12}H_{16}Cl_4N_2$: C, 43.67; H, 4.89; Cl, 42.96; N, 8.49. Found: C, 43.79; H, 4.89; Cl, 42.99; N, 8.45.

Tetracycle 62. 1,5-Cyclooctadiene[27] (5 mL) and 2.54 g (0.01 mol) of tetrachlorothiophene 1,1-dioxide were warmed on a steam bath. An exothermic reaction ensued and was cooled in ice to keep the temperature from rising above 100 °C. After temperature subsidence, the mixture was heated on a steam bath for 1 h. The product crystallized out. The mixture was cooled in ice, and the product was filtered off and washed with hexane to give 2.67 g (89.5%). Recrystallization from acetone left 2.35 g (79%) of 5,6,7,7a-tetrachloro-2,3,3a,4,5,7a-hexahydro-4,1,5-[1]propanyl-[3]ylidene-1*H*-indene: mp 184–185 °C (lit.[20] mp 183.5–185 °C); IR 2994, 2959 (CH), 1618 (C=C) cm^{-1}; NMR ($CDCl_3$, Varian XL-100) 2.06 (broadened peak, 4 CH_2), 2.21 (sharper peak, 4 CH).

Tetracycle 63. 1,5-Cyclooctadiene[27] (5 mL), 2 mL of benzene, and 3.70 g of 3,4-dichlorothiophene dioxide[1] were heated on a steam bath for 1.5 h. The mixture turned black. The volatiles were removed under vacuum, and the residue was extracted with hot hexane which left behind 0.25 g of black powder. The hexane solution was treated with decolorizing charcoal, and the solution was evaporated. The residue was recrystallized from acetone to give 3.05 g (66.5%) of **63**: mp 152–153 °C; NMR ($CDCl_3$) 1.63 (m, 4 CH_2), 2.08 (broadened s, 4 CH next to CH_2), 2.48 (broadened s, 2 CH next to CCl).

Anal. Calcd for $C_{12}H_{14}Cl_2$: C, 62.90; H, 6.16; Cl, 30.94. Found: C, 62.99; H, 6.20; Cl, 31.10.

Tetracycle 64. Tetrabromothiophene 1,1-dioxide (2.16 g, 5 mmol) and 3 mL of 1,5-cyclooctadiene[27] were heated on a steam bath for 1 h. Product crystallized from the hot solution. The excess diene was removed, and the residue was recrystallized from benzene to give 1.34 g (56%) of **64**: mp 237.2–238.5 °C; NMR ($CDCl_3$) 2.20 (s, CH_2), 2.37 (s, CH).

Anal. Calcd for $C_{12}H_{12}Br_4$: C, 30.29; H, 2.54; Br, 67.17. Found: C, 30.44; H, 2.84; Br, 67.22.

Tetracycle 62 from Tetrachloro-α-pyrone. Tetrachloro-α-pyrone[23] (11.7 g, 0.05 mol) and 12.2 mL of 1,5-cyclooctadiene were heated in an oil bath at 140 °C for 1.5 h. A brisk evolution of carbon dioxide occurred. The mixture was cooled, and the crystals were filtered off and washed with cold hexane to give 10.93 (93%) of product. Recrystallization from acetone gave 10.26 g (88%) of **62** in 2 crops, mp 184–185 °C for each.

When the reaction was run by heating the reactants on a steam bath for 17 h, evolution of carbon dioxide was not evident, and the yield was 45.7% before recrystallization.

Hexacycle 65 from Dibenzo[*a*,*e*]cyclooctene. Dibenzo[*a*,*e*]cyclooctene[36,37] (1.02 g, 5 mmol) and 1.40 g (5.5 mmol) of tetrachlorothiophene dioxide were heated in a flask in an oil bath at 125 °C for 5 h. The mixture melted and then crystallized as product formed. Recrystallization from CCl_4 gave 1.12 g (57%) of 1,2,3,9a-tetrachloro-4,4a,9,9a-tetrahydro-4,3,9-([1,2]benzeno-metheno)-3*H*-fluorene: mp 275–276 °C; NMR ($CDCl_3$) 3.58 (s, 4 CH), 6.80 ppm (s, 8 H, aromatic); ^{13}C NMR ($CDCl_3$) C-4b 59.6 (d), C-6 85.5 (s), C-4a 146.7 (s), C-1, C-2 124.8, 126.2, C-7 130.7 (s).

Anal. Calcd for $C_{20}H_{12}Cl_4$: C, 60.95; H, 3.07; Cl, 35.98. Found: C, 60.71; H, 3.36; Cl, 35.71.

Tetracycle 66. 1,5-Cyclononadiene[38] (1.83 g, 0.015 mol), prepared by isomerizing 1,2-cyclononadiene,[39] 3 mL of 1,2-dichloroethane, and 2.54 g (0.01 mol) of tetrachlorothiophene dioxide were heated under reflux on a steam bath for 30 min. After the vigorous reaction, the solvent was removed, and the residue was heated in a flask on an oil bath at 150 °C for 10 min. This caused an exotherm to 190 °C. The product was recrystallized twice from ethanol to give 1.80 g (58%) of 6,7,8,8a-tetrachloro-1,2,3,4,4a,5,6,8a-octahydro-5,1,6-[1]propanyl[3]ylidenenaphthalene: mp 124.5–127 °C; NMR ($CDCl_3$) 1.2–2.6 (m's, no CH=); IR 2994, 2959, 2915 (CH), 1618 (C=C) cm^{-1}.

Anal. Calcd for $C_{13}H_{14}Cl_4$: C, 50.04; H, 4.52; Cl, 45.44. Found: C, 50.05; H, 4.59; Cl, 45.18.

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Registry No. **1**, 35608-94-7; **2**, 72524-26-6; **3**, 72524-27-7; **4**, 72524-28-8; **5**, 72524-29-9; **6**, 72524-30-2; **7**, 33332-93-3; **8**, 72524-31-3; **9**, 72524-32-4; **10**, 72524-33-5; **11**, 72524-34-6; **12**, 72541-90-3; **13**, 72524-35-7; **14**, 72524-36-8; **15**, 72541-91-4; **16**, 72524-37-9; **17**, 33284-53-6; **18**, 72524-38-0; **19**, 72524-39-1; **20**, 72524-40-4; **21**,

72448-16-9; **22**, 72524-41-5; **23**, 14370-25-3; **24**, 72524-42-6; **25**, 72524-43-7; **26**, 72524-44-8; **27**, 72524-45-9; **28**, 72524-46-0; **29**, 72524-47-1; **30**, 72524-48-2; **31**, 72524-49-3; **32**, 72524-50-6; **33**, 72524-51-7; **34**, 72524-52-8; **35**, 72524-53-9; **36**, 72524-54-0; **37**, 72524-55-1; **38**, 72524-56-2; **39**, 72524-57-3; **40**, 72524-58-4; **41**, 72524-59-5; **42**, 72581-28-3; **43**, 72524-60-8; **44**, 72524-61-9; **45**, 72524-62-0; **46**, 72524-63-1; **47**, 72524-64-2; **48**, 72524-65-3; **49**, 72541-92-5; **50**, 72524-66-4; **51a**, 72541-93-6; **51b**, 72524-67-5; **51c**, 72524-68-6; **52**, 72524-69-7; **53**, 72541-94-7; **55**, 72541-95-8; **56a**, 72524-70-0; **56b**, 72524-71-1; **56b** 1,1-dioxide, 72524-72-2; **57a**, 72524-73-3; **57b**, 72524-74-4; **58**, 72524-75-5; **59**, 72524-76-6; **61a**, 72541-96-9; **61b**, 72524-77-7; **61c**, 72524-78-8; **61d**, 72524-79-9; **61e**, 72524-80-2; **61f**, 72524-81-3; **61g**, 72524-82-4; **61g**·HCl, 72524-83-5; **61h**, 72524-84-6; **61i**, 72524-85-7; **62**, 18517-93-6; **63**, 72524-86-8; **64**, 72524-87-9; **65**, 72524-88-0; **66**, 72524-89-1; tetrachlorothiophene, 6012-97-1; tetrachlorothiophene 1,1-dioxide, 72448-17-0; tetrabromothiophene 1,1-dioxide, 72524-90-4; 1,2,3,4-tetrachloro-5,6,7,8-tetrahydronaphthalene, 1203-38-9; 2,3,4,5-tetrachlorotoluene, 1006-32-2; 3,4-dichlorothiophene, 17249-76-2; hexachloro-1,3-butadiene, 87-68-3; tetrabromothiophene, 3958-03-0; 1,1,2,4-tetrachloro-1-buten-3-yne, 5658-91-3; cyclopentadiene, 542-92-7; 2,3-dimethylbutadiene, 513-81-5; 1,5-hexadiene, 592-42-7; *cis*-1,5-heptadiene, 7736-34-7; *trans*-1,5-heptadiene, 7736-22-3; 2,6-octadiene (*E,E* isomer), 18152-32-4; 2,6-octadiene (*E,Z* isomer), 29801-67-0; 2,6-octadiene (*Z,Z* isomer), 18680-11-0; 1,2-divinylbenzene, 105-06-6; allyl vinyl ether, 3917-15-5; allyl vinyl sulfide, 41049-25-6; vinyl acrylate, 2177-18-6; vinyl methacrylate, 4245-37-8; 1,6-heptadiene, 3070-53-9; diallyl ether, 557-40-4; diallyl sulfide, 592-88-1; *N,N*-diallylacetamide, 6296-61-3; diallylcyanamide, 538-08-9; (*N,N*-diallylamino)acetonitrile, 72524-91-5; 1,5-cyclooctadiene, 111-78-4; tetrachloro-α-pyrone, 10269-62-2; dibenzo[*a,e*]cyclooctene, 262-89-5; 1,5-cyclononadiene, 57357-81-0; sodium 2,4,5-trichlorobenzoate, 72524-92-6; CH_2=CH_2, 74-85-1; cyclopentene, 142-29-0; cyclohexene, 110-83-8; cycloheptene, 628-92-2; cyclooctene, 931-88-4; cyclododecene, 1501-82-2; 1,4-cyclohexadiene, 628-41-1; *cis*-1,*trans*-5-cyclodecadiene, 1124-78-3; methylenecyclobutane, 1120-56-5; methylenecyclohexane, 1192-37-6; 1,4-dimethylenecyclohexane, 4982-20-1; (−)-β-pinene, 18172-67-3; methyleneadamantane, 875-72-9; indene, 95-13-6; acenaphthylene, 208-96-8; *endo*-dicyclopentadiene, 1755-01-7; PhC≡CH, 536-74-3; 1-hexen-5-yne, 14548-31-3; 1-dodecene, 112-41-4; 1,7-octadiene, 3710-30-3; 1,8-nonadiene, 4900-30-5; CH_2=CHCOOH, 79-10-7; CH_2=CHCOOMe, 96-33-3; CH_2=CHCN, 107-13-1; CH_2=$CHCH_2COOH$, 625-38-7; CH_2=$CH(CH_2)_8COOH$, 112-38-9; dimethyl maleate, 624-48-6; maleic anhydride, 108-31-6; maleimide, 541-59-3; *N*-methylmaleimide, 930-88-1; CH_2=C(Me)COPh, 769-60-8; CH_2=$CHCH_2Br$, 106-95-6; CH_2=$CHCH_2NCS$, 57-06-7; safrole, 94-59-7; 1,4-benzoquinone, 106-51-4; 1,4-naphthoquinone, 130-15-4; 2-vinylpyridine, 100-69-6; *N*-vinylpyrrolidone, 88-12-0; *N*-vinylsuccinimide, 2372-96-5; *N*-methylpyrrole, 96-54-8; indole, 120-72-9; diethyl 2,3-diazanorbornene-2,3-dicarboxylate, 14011-60-0; thiophene, 110-02-1; precocene II, 644-06-4.

Addition-Rearrangement Reactions of Halogenated Thiophene Dioxides with Furans

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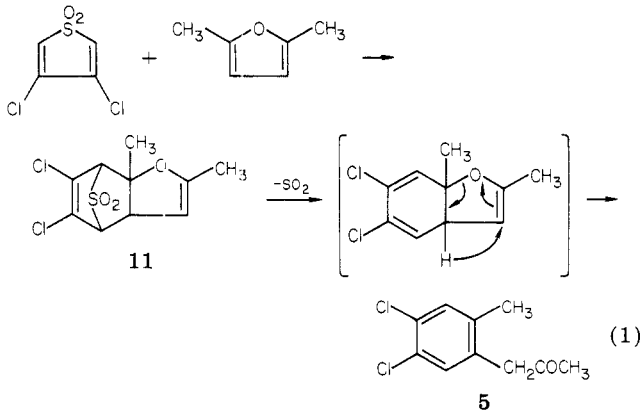
Dichloro-, tetrachloro-, and tetrabromothiophene dioxides undergo novel addition–rearrangement reactions with furans to form halobenzyl carbonyl compounds.

Halogenated thiophene 1,1-dioxides undergo addition–rearrangement reactions with furans to form halobenzyl carbonyl compounds (**1–10**, Table I). No precedent for this rearrangement has been found in furan chemistry. In the case of 2,5-dimethylfuran and 3,4-dichlorothiophene dioxide,[2] the primary adduct **11** precipitates from solution



11 (1) 5

and can be isolated if the reaction is stopped after 1–2 min. Warming the reaction results in loss of sulfur dioxide and rearrangement of the annelation product to yield the benzyl ketone **5** (eq 1).

The reaction and rearrangement also proceed with tetrachloro- and tetrabromothiophene dioxides[3a] to give products corresponding to **5**. Intermediates corresponding to **11** have not been observed, however. A variety of substituted furans has been employed to give the halogenated benzyl ketones listed in Table I (compounds **1–10**). The products (**8, 9**) from tetrachlorothiophene dioxide and methyl 2-furoate or 2-acetylfuran exist in the enolic form, as shown, rather than the ketonic form (NMR and IR data are detailed in the Experimental Section). Hydrolysis of **8** gives the corresponding tetrachloro-α-hydroxycinnamic acid.

The reactions with the substituted furans listed in Table I generally proceed in high yield. Reaction of furan itself, however, differs from these examples. The normal rearrangement product, (2,3,4,5-tetrachlorophenyl)acetaldehyde, has been isolated in 8% yield. A second product (**12**, 27% yield) results from furan acting as a 1,3-diene accepting one double bond of tetrachlorothiophene dioxide (TCTD), and the resulting intermediate acting as a donor

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