solution resulted. A crystalline precipitate began to form after 2 hr. It was collected after a total of 48 hr at room temperature, washed with water, and dried, giving 13.24 g (55%) of crude cyclohexylcyanoacetamide. Recrystallization from methanol gave an analytical sample, mp 149–150°.

Anal. Calcd for $C_9H_{14}N_2O$: C, 65.03; H, 8.49; N, 16.86. Found: C, 65.08; H, 8.59; N, 17 12.

Acknowledgment. We are indebted to Professor C. G. Swain for helpful comments.

Diels–Alder Reactions of Alkynyltin Compounds with Polychlorocyclopentadienes. Organotin-Substituted Polychloronorbornadienes. Cleavage Reactions and Photochemistry

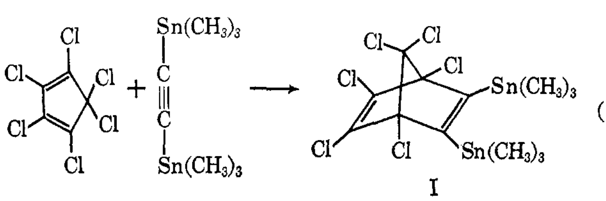
Dietmar Seyferth[1] and Anthony B. Evnin[2]

Contribution from the Department of Chemistry, Massachusetts Institute of Technology Cambridge, Massachusetts 02139. *Received November 12, 1966*

Abstract: The Diels–Alder reaction of hexachlorocyclopentadiene with bis(trimethyltin)acetylene, propynyltrimethyltin, and (phenylethynyl)trimethyltin gave the norbornadienes I, II, and III, respectively. Reaction of 5,5-dimethoxytetrachlorocyclopentadiene with bis(trimethyltin)acetylene resulted in 1,2-bis(trimethyltin)tetrachlorobenzene, but some 1-(trimethyltin)-2,3,4,5-tetrachlorobenzene and 1,2,3,4-tetrachlorobenzene also were formed during work-up. Ultraviolet irradiation of I and II in diethyl ether solution produced the isomeric quadricyclanes XIV and XV, respectively. Proto-, chloro, and bromodestannations of I, II, XIV, and XV were studied, and a number of new norbornadienes (VIII, IX, XI, XII, and XIII) and quadricyclanes (XVI and XVIII) were characterized as products of these cleavage reactions. The thermolysis of II and of 1-(trimethyltin)-2,3,4,5-tetrachlorobenzene was studied. Reaction of the latter with *p*-iodotoluene at 210° gave 2,3,4,5-tetrachloro-4′-methylbiphenyl in 72% yield.

In a previous paper[3] we presented evidence which showed that those Diels–Alder reactions of bis(trimethyltin)acetylene which proceed well represent further examples of Diels–Alder reactions with "inverse electron demand."[4] In agreement with this view, we have found that bis(trimethyltin)acetylene and other organotin-substituted acetylenes react readily with π-electron-deficient hexachlorocyclopentadiene and 5,5-dimethoxytetrachlorocyclopentadiene.

Reaction of equimolar quantities of hexachlorocyclopentadiene and bis(trimethyltin)acetylene in refluxing *n*-butyl ether gave 2,3-bis(trimethyltin)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (I) in 50–70% yield.

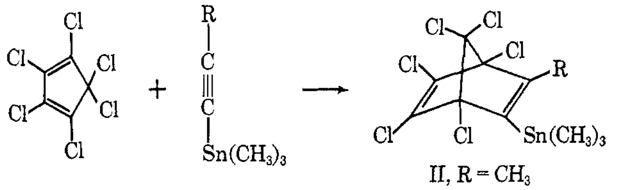


(1)

I

Identification of the adduct, rendered more difficult by the absence of skeletal protons, was made on the basis of elemental analysis, a molecular weight determination, and correlation of the ultraviolet and infrared spectra with those of other norbornadiene systems (see Table I).

Propynyltrimethyltin and (phenylethynyl)trimethyltin also were allowed to react with hexachlorocyclopentadiene. Both gave the expected Diels–Alder adducts. These, II and III, respectively, were identified



II, R = CH_3
III, R = C_6H_5

by the methods mentioned above, but in these cases nmr spectra were useful as well. The spectrum of III is interesting in that the trimethyltin group absorbs at unusually high field, 0.10 ppm (*vs.* 0.35 ppm in I and II), owing to its position above the phenyl substituent which must be skewed to the plane of the 2,3 double bond.

The three Diels–Alder adducts are stable, crystalline solids. On extended standing, however, some decomposition accompanied by formation of methyltin chlorides occurs.[5]

The Diels–Alder reaction of 5,5-dimethoxytetrachlorocyclopentadiene with bis(trimethyltin)acetylene also was investigated. It is known that adducts of this diene with acetylenes aromatize with loss of the bridgehead at moderate temperatures.[6] Loss of the bridgehead

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[1] Alfred P. Sloan Foundation Fellow, 1962–1966.

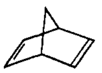
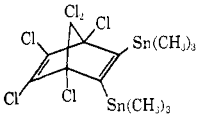
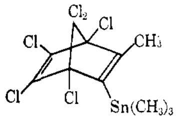
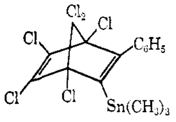
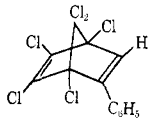
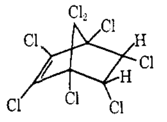
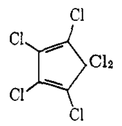
[2] National Institutes of Health Predoctoral Fellow, 1963–1966.

[3] A. B. Evnin and D. Seyferth, *J. Am. Chem. Soc.*, **89**, 952 (1967).

[4] (a) C. W. Smith, D. G. Norton, and S. A. Ballard, *J. Am. Chem. Soc.*, **73**, 5273 (1951); (b) J. Sauer and H. Wiest, *Angew. Chem.*, **74**, 353 (1962); (c) M. G. Ettlinger and C. S. Lewis, *Texas J. Sci.*, **14**, 58 (1962); (d) J. Sauer, A. Mielert, D. Lang, and D. Peter, *Chem. Ber.*, **98**, 1435 (1965).

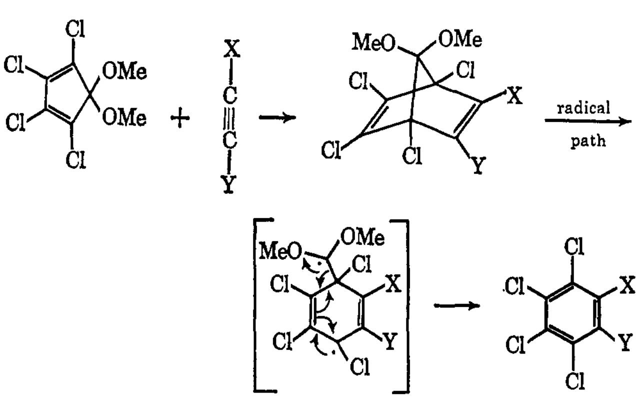
[5] Other examples of such decomposition of halogenated organotin compounds are known: (a) A. N. Nesmeyanov and A. E. Borisov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 146 (1945); (b) F. M. Rabel and R. West, *J. Am. Chem. Soc.*, **84**, 4169 (1962).

Table I. Spectroscopic Correlations

Compound	Ultraviolet (in EtOH or n-hexane), mμ (ϵ)	Infrared, C=C stretch region, cm^{-1}
	λ_{max} 205 (2100); λ_{max} 214 (1480), λ_{max} 220 (870); λ_{sh} 230 (200)	1635, 1543[a]
	λ_{max} 236 (5600); λ_{sh} 257 (1600); λ_{sh} 285 (360)	1605
	λ_{max} 227 (4000); λ_{sh} 276 (280)	1605, 1585
	λ_{max} 255 (3800); λ_{sh} 297 (1300)	1605, 1555
	λ_{max} 223 (11,500); λ_{max} 254 (8920); λ 285 (3300)[b]	
	λ_{max} 212 (6300)[c]	
		1606, 1572[d]

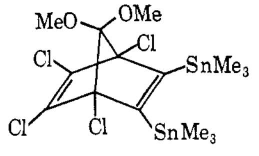
[a] C. F. Wilcox, Jr., S. Winstein, and W. G. McMillan, *J. Am. Chem. Soc.*, **82**, 5450 (1960); the presence of two bands around 1600 cm^{-1} is interpreted as due to a coupled oscillator. [b] A. J. Fry, *J. Org. Chem.*, **31**, 1863 (1966). [c] J. D. Idol, Jr., C. W. Roberts, and E. T. McBee, *ibid.*, **20**, 1743 (1955). [d] H. Gerding, H. J. Prins, and H. van Brederode, *Rec. Trav. Chim.*, **65**, 168 (1946).

can apparently proceed by one of two paths depending on the nature of the groups on the 5,6 double bond and on the polarity of the solvent used. The "radical" path is favored by nonpolar substituents (X and Y) and solvents.[6c,d]



When 5,5-dimethoxytetrachlorocyclopentadiene and bis(trimethyltin)acetylene were heated in refluxing xylene or n-butyl ether for 24–48 hr, the products obtained were 1,2-bis(trimethyltin)tetrachlorobenzene (IV), 1-(trimethyltin)-2,3,4,5-tetrachlorobenzene (V), and 1,2,3,4-tetrachlorobenzene (VI). The total yield of products (IV + V + VI), generally, was 40–60%. The exact mixture of products was found to depend on the work-up procedure used; the highest yield of IV obtained was 35%. The occurence of V and VI was shown to be largely due to secondary reactions during work-up, but their formation in small amounts at intermediate stages cannot be excluded, since crude reaction mixtures, after careful removal of solvent but prior to any other handling, showed traces of absorption in the aryl region of the nmr spectrum. The sensitivity of the Sn–C linkages of IV and V is due to the generally high reactivity of aryltin bonds which is enhanced in these cases by the electron-withdrawing chlorine substituents[7] and the considerable relief of strain resulting from destannation.[8]

None of the initial Diels-Alder adduct, VII, was isolable under the reaction conditions. Its decomposition appears to proceed exclusively by the "radical path."



VII

A study was made of the electrophilic cleavage of the organotin-substituted norbornadienes prepared in this investigation. Treatment of I and II with chlorine, bromine, and hydrogen chloride resulted in instantaneous cleavage of the Sn–C bonds.

Compounds VIII, IX, XI, XII, and XIII have not been reported previously; they were characterized by elemental analysis and by their spectral properties. Hexachloronorbornadiene, X, has been reported previously and some of its reactions have been studied.[9] All of the destannated norbornadienes appeared to be resistant toward further attack by the electrophiles used, unlike norbornadiene itself;[10] this almost certainly is due to withdrawal of electron density by the chlorines. It also must be stressed that no detectable rearrangement of the carbon skeleton occurred during the Sn–C cleavage reactions which probably involve an electrophilic attack at the carbon atoms to which the trimethyltin groups are bound. We suggest that this is either due to the absence of intermediates in the Sn–C cleavage process with significant carbonium ion character or the strong $-I$ effect of the chlorine substituents in I and II.

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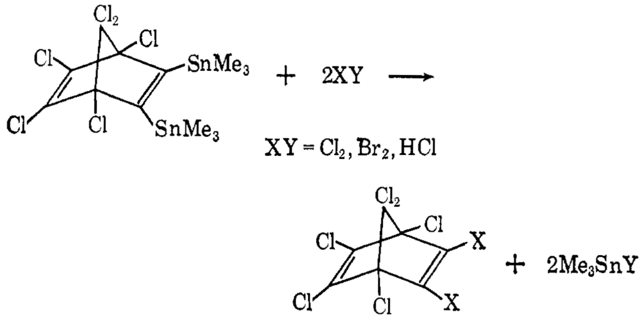
(6) Leading references: (a) H. Feichtinger and H. Linden, German Patent 1,105,862 (1961); *Chem. Abstr.*, **56**, 12803 (1962); (b) J. Diekman, *J. Org. Chem.*, **28**, 2880 (1963); (c) R. W. Hoffmann and H. Hauser, *Tetrahedron*, **21**, 891 (1965); (d) D. M. Lemal, E. P. Gosselink, and S. D. McGregor, *J. Am. Chem. Soc.*, **88**, 582 (1966).

(7) Greatly enhanced susceptibility toward nucleophilic cleavage of the Sn–C bond in perfluoroaryltin compounds has been reported by R. D. Chambers and T. Chivers, *J. Chem. Soc.*, 4782 (1964).

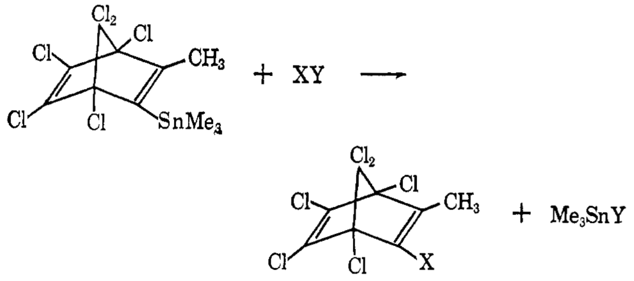
(8) Relief of strain has been shown to have a powerfully accelerating effect on electrophilic Sn–C cleavage: O. Buchman, M. Grosjean, J. Nasielski, and B. Wilmet-Devos, *Helv. Chim. Acta*, **47**, 1689 (1964). The strain in IV can be estimated to be in the neighborhood of 20 kcal since models indicate crowding analogous to that in o-di-t-butylbenzene: C. Hoogzand and W. Hübel, *Tetrahedron Letters*, 637 (1961).

(9) (a) H. Bluestone, U. S. Patent 2,676,132 (1954); *Chem. Abstr.*, **48**, 8474 (1954); (b) R. E. Lidov, U. S. Patent 2,717,851 (1955); *Chem. Abstr.*, **50**, 2914 (1956); (c) M. Kleiman, U. S. Patent 2,736,730 (1956); *Chem. Abstr.*, **50**, 10780 (1956); (d) A. F. Plate and G. Tarasova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 873 (1957); (e) J. A. Claisse, D. I. Davies, and C. K. Alden, *J. Chem. Soc., Org. Sect.*, 1498, 1540 (1966).

(10) S. Winstein and M. Shatavsky, *Chem. Ind.* (London), 56 (1956).



VIII, X = Cl
IX, X = Br
X, X = H



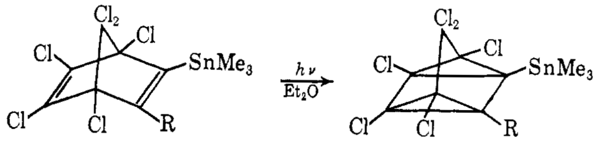
XI, X = Cl
XII, X = Br
XIII, X = H

Attempts to cleave only one of the vinyltin bonds of I using 1 equiv of bromine or iodine were unsuccessful, although varied reaction conditions (low temperature, high dilution, high-speed stirring) were investigated. This is in contrast to the selective cleavage of one Sn–C bond of various *o*-bis(trimethyltin)benzenes with iodine at room temperature and bromine at −75°.[3] The mechanistic implications of this are not clear.

The photochemistry of main group organometallic compounds is an area that has received only scant attention to date. In the case of heavy metal derivatives, this is due to the facile destruction of the metal–carbon bonds upon irradiation which is a result of the relatively low dissociation energies of the bonds involved and the possibility of obtaining different, stable oxidation states of the metal by transfers of electrons. However, the photochemistry of vinyl derivatives of heavy metals appears to be an area worth studying. The ultraviolet-catalyzed isomerization of (*trans*-ClCH=CH)$_2$Hg to the *cis,cis* isomer has been reported by Russian workers[11] and we have described the nondestructive ultraviolet-catalyzed isomerization of propenyltin compounds.[12] This suggested that a study of the photochemistry of the organotin-substituted norbornadienes might be of interest.

The photochemical transformation of norbornadienes to quadricyclanes[13] is well known.[14] Several Diels–Alder adducts of hexachlorocyclopentadiene and acetylenes had been reported not to undergo this reaction,[15] but very recently the isomerization of hexachloronorbornadiene to the corresponding quadricyclane was described by English workers.[9e]

We have found that irradiation of I and II in diethyl ether solution with a high-pressure mercury lamp results in their conversion to the corresponding quadricyclanes, 2,3-bis(trimethyltin)-1,4,5,6,7,7-hexachloroquadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptane (XIV) and 2-(trimethyltin)-1,4,5,6,7,7-hexachloro-3-methylquadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptane (XV), in isolated yields of 45%. The actual yield of photoproducts is considerably higher; however, their isolation requires column chromatography and fractional recrystallization and is complicated by their tendency to decompose to tars and methyltin chlorides. They can be handled in air, but for extended storage, temperatures below 0° and an inert atmosphere are recommended. They do not reconvert to the norbornadienes I and II at ambient temperature and attempts to observe such conversion at higher temperatures were complicated by Sn–C homolysis and other side reactions. Characterization of the quadricyclanes XIV and XV was made by ultraviolet, infrared, and nmr spectral correlations (Table II). Molecular weight data and elemental analysis established that XIV was isomeric with I. The presence of only end absorption in the ultraviolet region and the absence of C=C stretch bands in the infrared spectra of XIV and XV in particular were significant.



XIV, R = SnMe$_3$
XV, R = CH$_3$

Reactions of the C–Sn linkages in these organotin-substituted quadricyclanes were examined both in order to assess their utility as routes to other quadricyclanes and to determine whether rearrangement of the quadricyclic skeleton would occur during Sn–C bond fission. The reactivity of quadricyclane itself has been demonstrated by Dauben and Cargill.[16]

The reactions of the quadricyclane XV with hydrochloric acid in methanol and with bromine are much slower than those of the isomeric norbornadiene with these reagents. In both cases, however, Sn–C cleavage was observed. Treatment of XV with 1 equiv of methanolic HCl (conditions under which II was cleaved very rapidly) led to 70% recovery of the quadricyclane after 71 hr. When a large excess of HCl was used, Sn–C cleavage was complete in about 36 hr, and the protodestannated quadricyclane XVI (Table II) was obtained in high yield. In addition to the spectroscopic evidence for its structure, its thermal conversion to the isomeric diene, 1,2,3,4,7,7-hexachloro-5-methylbicyclo[2.2.1]hepta-2,5-diene, provides further confirmation of the quadricyclane skeleton. Treatment of XIV with an excess of hydrochloric acid similarly produced 1,2,3,4,7,7-hexachloroquadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptane (XVII).

When quadricyclane XV was treated with 1 equiv of bromine in ether–methanol solution, a mixture of four

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(11) A. N. Nesmeyanov, A. E. Borisov, and A. N. Abramova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 289 (1947).

(12) D. Seyferth and L. G. Vaughan, *J. Organometal. Chem.* (Amsterdam), **1**, 138 (1963).

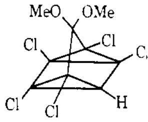
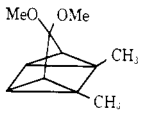
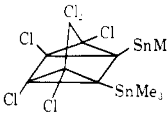
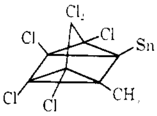
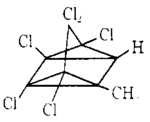
(13) We use the nomenclature recently favored by Smith: C. D. Smith, *J. Am. Chem. Soc.*, **88**, 4273 (1966).

(14) For a recent review see W. L. Dilling, *Chem. Rev.*, **66**, 373 (1966).

(15) (a) R. J. Gritter, E. Sabatino, and S. Sacharow, U. S. Dept. of Commerce, PB Report 150, 407 (1960); *Chem. Abstr.*, **58**, 3327 (1963); (b) W. E. Noland and L. R. Smith, *J. Am. Chem. Soc.*, **82**, 2021 (1960).

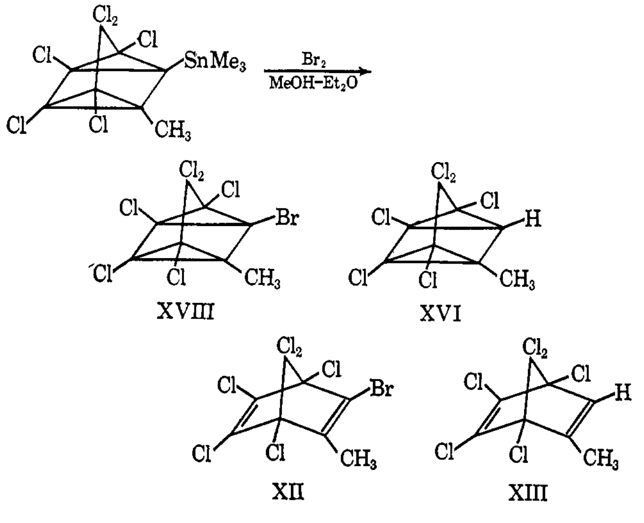
(16) See Table II, footnote *e*.

Table II. Quadricyclanes: Spectroscopic Correlations

Compound	Ultraviolet (in EtOH or *n*-heptane),[a] mμ (ε)	Nmr, ppm	Ref
	λ_{end} 205 (400)		*e*
		*H* 2.87	*f*
	λ_{end} 210 (380)	C-CH_3, 1.22;[b] 5,6-*H*, 1.18	*g*
	λ_{end} 245 (370)	0.33	
	λ_{end} 240 (500)	C-CH_3, 1.32;[c] Sn-CH_3, 0.37	
 XVI	λ_{end} 232 (240)	C-CH_3, 1.34;[d] *H*, 2.81	

[a] Note ultraviolet data for isomeric norbornadienes in Table I. [b] Nmr of isomeric norbornadiene shows C-CH_3 at 1.70 ppm, vinyl *H* at 6.58 ppm. [c] Nmr of isomeric norbornadiene shows C-CH_3 at 2.03 ppm, Sn-CH_3 at 0.37 ppm. [d] Nmr of isomeric norbornadiene shows C-CH_3 at 1.97 ppm, vinyl *H* at 6.20 ppm; its ultraviolet spectrum shows $\lambda_{\max}$ 222 mμ (ε 3150) and $\lambda_{\max}$ 265 mμ (ε 550). [e] W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961). [f] D. M. Lemal, E. P. Gosselink, and S. D. McGregor, *J. Am. Chem. Soc.*, **88**, 582 (1966). [g] P. G. Gassman, D. H. Aue, and D. S. Patton, *ibid.*, **86**, 4211 (1964).

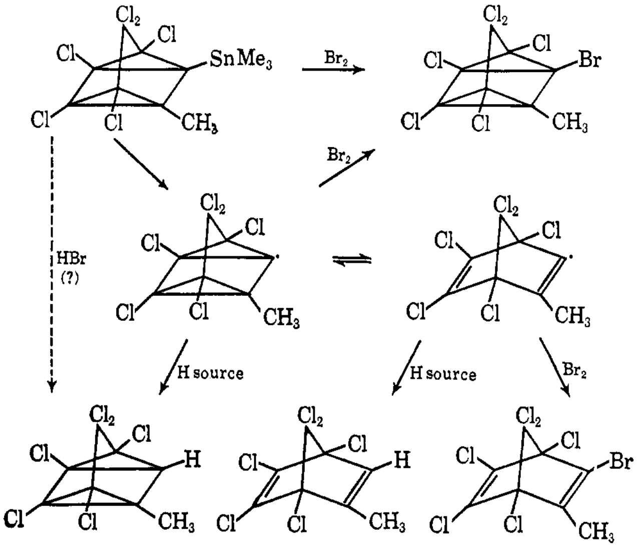
products resulted. Three of the components could be isolated by a combination of column chromatography and glpc; these were identified as 2-bromo-1,4,5,6,7,7-hexachloro-3-methylbicyclo[2.2.1]hepta-2,5-diene (XII) and the protodestannated species XVI and XIII. The fourth product could not be isolated, but its nmr absorption at 1.42 ppm, the exact position of the C-CH_3 protons in the nmr spectrum of the photoproduct of XII, suggests that it is 2-bromo-1,4,5,6,7,7-hexachloro-3-methylquadricyclo[2.2.1.$0^{2,6}$.$0^{3,5}$]heptane (XVIII). The combined yield of these products was 75%, and XVIII, XII, XIII, and XVI were present in the approximate ratio of 1:1:1:2. The reaction was carried out again using rigorously dried and purified solvents and atmosphere; in this case XVIII, XII, and XIII were formed in approximately equal amounts, but only traces of XVI were present. When chloroform was used as the solvent, XVIII and XII were obtained in 1:5 ratio, but *no* products of protodestannation were observed.



In the addition reactions of halogens and hydrogen halides, mechanistic considerations frequently are complicated by the simultaneous occurrence of polar and radical paths. With hydrogen chloride, however, radical-chain processes are unfavorable due to the high H-Cl bond energy and are not observed in additions to olefins, even in the presence of radical initiators. Therefore, it is reasonable to interpret the protodestannation of XV as involving attack of a proton at C-2, followed by cleavage of the Sn-C bond (probably assisted by chloride ion). Apparently this occurs without rearrangement of the quadricyclane skeleton. It should be noted that formation of a positive charge at the 2 position of a quadricyclane is not as favorable as it is in the doubly cyclopropylcarbinyl 7 position.

The stability of the C-C bonds in the destannated quadricyclanes XVI, XVII, and XVIII to attack by electrophiles (XVI also is inert to bromine in carbon tetrachloride) is in marked contrast to the behavior of unhalogenated quadricyclanes.[16] The similar lack of reactivity to electrophiles of highly halogenated norbornadienes indicates that in both systems this is the result of the withdrawal of considerable electron density from the rings by the chlorine substituents. The extremely low field absorption, 2.81 ppm, of the cyclopropyl hydrogen of XVI supports the contention that the bicyclic system is deficient in electron density.

The occurrence of protodestannation as well as of bromodestannation in the reaction of the quadricyclane XV with bromine in methanol-ether suggests that radical as well as polar pathways might be involved. This is quite reasonable in view of the reported difficulty of suppressing radical-chain reactions in the bromination



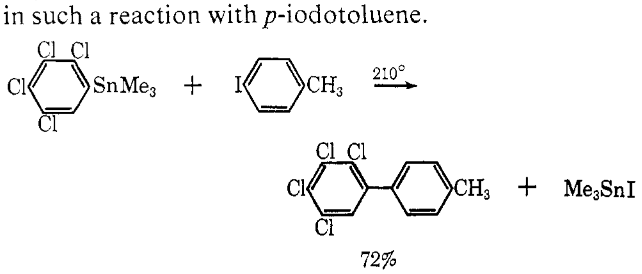
of olefins. The product mixture obtained in the brominolysis of XV can be accounted for by the sequence shown above, although in the absence of further evidence, this represents no more than a hypothesis. This scheme implies that highly halogenated quadricyclane radicals undergo isomerization to norbornadienyl radicals.

An attempt was made to photoisomerize 2-bromo-1,4,5,6,7,7-hexachloro-3-methylbicyclo[2.2.1]hepta-2,5-diene to the corresponding quadricyclane under the conditions described above. Although the quadricyclane was formed, it proved impossible to separate it from unconverted starting material. Very strong evidence for its presence in the reaction mixture was given by an nmr absorption at 1.42 ppm, by correlations of infrared and ultraviolet spectral data, and by thermal conversion of the reaction product mixture to pure starting material.

A brief study also was made of the thermal decomposition of the norbornadiene II. When heated at about 230° for 4 hr, it decomposed to give trimethyltin chloride (51%), and products of both hydrogen and chlorine abstraction by an intermediate 2-norbornadienyl radical, XIII and XI, respectively. Decomposition of II or of its quadricyclic isomer also was observed in the course of glpc analysis. Injection of samples of either compound onto an SE-30 glpc column at about 200° resulted in the elution of complex mixtures, the highest boiling component of which was identified as XIII. In this connection it is of interest to note that thermal decomposition of $Me_3SnC(CF_3)=C(CF_3)SnMe_3$ at 150° produced $Me_3SnC(CF_3)=CHCF_3$ as a major product.[17] Presumably in both of these cases methyl groups attached to tin provide the hydrogen atoms which appear in the final product.

The thermal stability of 1-trimethyltin-2,3,4,5-tetrachlorobenzene was considerably greater. When it was heated at 230° for 3 hr, approximately 50% was recovered unchanged. A trace amount of trimethyltin chloride was formed, but the major reaction which occurred was the disproportionation to give tetramethyltin and dimethylbis(2,3,4,5-tetrachlorophenyl)tin.

In previous papers[3,18] we described a novel coupling reaction occurring between aryl iodides and aryltrimethyltin compounds. We have used 1-(trimethyltin)-2,3,4,5-tetrachlorobenzene (prepared in this study) in such a reaction with *p*-iodotoluene.



Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified nitrogen or argon using magnetic stirring, unless otherwise indicated.

Infrared spectra were recorded on either a Perkin-Elmer Infracord 337 or 237 spectrophotometer, ultraviolet spectra with a Cary 14 instrument. Nmr spectra were obtained with a Varian Associates A-60 spectrometer. Chemical shifts are given in parts per million downfield from TMS, which was employed as an internal standard.

Elemental analyses were performed by Dr. S. M. Nagy, MIT Microchemical Laboratory, the Galbraith Laboratories, Knoxville, Tenn., and the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Diels–Alder Reaction of Bis(tetramethyltin)acetylene and Hexachlorocyclopentadiene. A solution of 19.10 g (54.3 mmoles) of bis(trimethyltin)acetylene, 14.56 g (53.4 mmoles) of hexachlorocyclopentadiene (Hooker Chemical Co., redistilled, $n^{25}D$ 1.5622), and 0.5 g of hydroquinone in 300 ml of di-*n*-butyl ether (Union Carbide Corp., distilled from sodium) was heated at reflux for 25 hr. The solution darkened rapidly and was black after 1 hr. Removal of volatiles at reduced pressure [to 70° (0.05 mm)] left a black, solid residue. The latter was washed with cold methanol, dissolved in pentane and decolorized with active charcoal. Concentration of this solution, addition of methanol, and cooling gave 20.63 g of off-white crystals, mp 84–88°; an additional 1.46 g, mp 82–87°, was obtained from the methanol washings, to give a total yield of 22.1 g (66%). One recrystallization from pentane–methanol gave colorless crystals, mp 89–90°, of I.

Anal. Calcd for $C_{13}H_{18}Cl_6Sn_2$: C, 25.01; H, 2.91; Cl, 34.07; mol wt, 624. Found: C, 24.95; H, 2.78; Cl, 33.76; mol wt, 640 (vapor pressure osmometer).

The nmr spectrum of I (in CCl_4) showed a singlet at 0.35 ppm with satellites $J_{Sn^{117}-H^1} = 54$ and $J_{Sn^{119}-H^1} = 56$ cps. The infrared spectrum (CCl_4, CS_2) showed bands at 2980 (m), 2920 (m), 1605 ($\nu_{CCl=CCl}$, m), 1260 (w), 1195 (w), 1160 (w), 1135 (m), 1098 (m), 1020 (m), 863 (s), 835 (m), 775 (vs), 720 (m), 685 (m), 650 (w), and 520 (s) cm^{-1}.

The Diels–Alder reaction of bis(trimethyltin)acetylene and hexachlorocyclopentadiene also was carried out in refluxing xylene (24 hr) and in refluxing toluene (114 hr); the yields of I were 53 and 16%, respectively.

In some cases, especially when slightly impure acetylide was employed, the residue from the distillation of volatiles was an oil. Chromatography through alumina (Woelm, neutral, activity 1) or silica gel (Brinkmann G) columns using pentane as eluent gave, after solvent removal, crystalline product.

Diels–Alder Reaction of Propynyltrimethyltin and Hexachlorocyclopentadiene. A solution of 6.64 g (32.7 mmoles) of propynyltrimethyltin, 10.87 g (40.0 mmoles) of hexachlorocyclopentadiene, and 0.2 g of hydroquinone in 50 ml of xylene was heated at reflux for 44 hr. After 1 hr the reaction mixture was black. Removal of solvent and starting materials by trap-to-trap distillation at 0.3 mm (pot temperature to 80°) left an oily, black residue. This was adsorbed on a few grams of silica gel and filtered through a 7 × $^7/_8$ in. column of silica gel using pentane (500 ml) as eluent. Evaporation of the pentane left 10.42 g of oil from which 9.72 g of off-white crystals, mp 80.5–83.5°, were obtained by crystallization from methanol–ether at 0°. Recrystallization from this solvent pair gave colorless prisms, mp 83–85°.

Anal. Calcd for $C_{11}H_{12}Cl_6Sn$: C, 27.78; H, 2.54; Cl, 44.73. Found: C, 27.97; H, 2.86; Cl, 44.61.

Spectral data were in agreement with the assigned structure of 2-(trimethyltin)-1,4,5,6,7,7-hexachloro-3-methylbicyclo[2.2.1]hepta-2,5-diene (II). The nmr spectrum (CCl_4) of the product showed a singlet at 2.03 ($C-CH_3$) and at 0.36 ppm ($Sn-CH_3$) with relative areas of 1:3. The $Sn-CH_3$ absorption had satellites at $J_{Sn^{117}-H^1} = 55$ and $J_{Sn^{119}-H^1} = 57$ cps. The infrared spectrum (CCl_4) showed bands at 2985 (w), 2910 (w), 1605 ($\nu_{CCl=CCl}$, m), 1585 ($\nu_{CMe=CSn}$ w), 1550 (w), 1435 (m), 1385 (w), 1193 (w), 1150 (s), 1128 (m), 1091 (s), 1042 (m), 1010 (m), 992 (m), 938 (m), 900 (s), 858 (s), 683 (s), 648 (w), and 525 (s) cm^{-1}.

Diels–Alder Reaction of (Phenylethynyl)trimethyltin and Hexachlorocyclopentadiene. A solution of 2.59 g (9.84 mmoles) of (phenylethynyl)trimethyltin, 2.85 g (10.45 mmoles) of hexachlorocyclopentadiene, and 0.1 g of hydroquinone in 50 ml of xylene was heated at reflux for 29 hr. After removal of the solvent and unconverted starting materials at reduced pressure, the oily, black residue was dissolved in pentane and decolorized with charcoal. Attempted crystallization from pentane–methanol was unsuccessful. The reaction mixture was filtered through a short silica gel column using pentane as eluent. Concentration of the chromatographed solution, addition of methanol, and cooling (several days) resulted in formation of 1.10 g (21%) of off-white crystals, mp 97–102°. Recrystallization from this solvent mixture gave colorless crystals, mp 101.5–102.5°.

Anal. Calcd for $C_{16}H_{14}Cl_6Sn$: C, 35.74; H, 2.62; Cl, 39.56. Found: C, 35.73; H, 2.75; Cl, 39.76.

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(17) W. R. Cullen, D. S. Dawson, and G. E. Styan, *J. Organometal. Chem.* (Amsterdam), 3, 406 (1965).

(18) D. Seyferth, C. Sarafidis, and A. B. Evnin, *ibid.*, 2, 437 (1964).

The nmr spectrum of the adduct (in CCl_4) showed a broad, complex multiplet at 7.0–7.52 ppm (Ar–H) and a singlet (Sn–C*H*$_3$) at 0.10 ppm ($J_{Sn^{117}-H^1}$ = 56 and $J_{Sn^{119}-H^1}$ = 58 cps). The infrared spectrum (in CCl_4) had bands at 3070 (w), 3330 (w), 2980 (w), 2920 (w), 1605 (m) 1555 (m), 1485 (m), 1450 (m), 1250 (w), 1190 (w), 1145 (m), 1130 (m), 1085 (s), 1045 (s), 1020 (m), 900 (w), 880 (s), 850 (s), 700 (sh), 695 (s), 685 (s), 650 (w), 620 (w), 580 (w), 510 (w), 555 (w), and 525 (w) cm^{-1}. The spectral data are in agreement with the assigned structure, 2-(trimethyltin)-1,4,5,6,7,7-hexachloro-3-phenylbicyclo[2.2.1]hepta-2,5-diene (III).

Diels–Alder Reaction of Bis(trimethyltin)acetylene and 5,5-Dimethoxytetrachlorocyclopentadiene. A solution of 5.70 g (21.6 mmoles) of 5,5-dimethoxytetrachlorocyclopentadiene,[19] 7.13 g (20.2 mmoles) of bis(trimethyltin)acetylene, and 0.1 g of hydroquinone in 50 ml of xylene was heated at reflux for 26 hr. The reaction flask was wrapped in aluminum foil to minimize exposure to light. Removal of volatiles at 0.1 mm (pot temperature to 70°) left a black oil and some solids. This residue was dissolved in pentane; the extracts were concentrated, diluted with methanol, and chilled. A total of 3.50 g of crystalline solid, mp 113–117°, was obtained. Recrystallization from pentane–methanol gave 3.15 g (28%) of crystals, mp 118–120°, identified as 1,2-bis(trimethyltin)tetrachlorobenzene.

Anal. Calcd for $C_{12}H_{18}Cl_4Sn_2$: C, 26.62; H, 3.35; Cl, 26.19. Found: C, 26.51; H, 3.39; Cl, 25.89.

The nmr spectrum (CCl_4) showed a singlet at 0.43 ppm ($J_{Sn^{117}-H^1}$ = 52; $J_{Sn^{119}-H^1}$ = 54 cps). The ultraviolet spectrum (ethanol) had λ_{max} 217 mμ (ϵ 51,000) and λ_{max} 294 mμ (ϵ 400). The infrared spectrum (CCl_4, CS_2 composite) showed bands at 2980 (m), 2915 (m), 1550 (m), 1390 (w), 1325 (m), 1265 (s), 1200 (w), 1190 (m), 1135 (s), 1095 (s), 1055 (m), 1015 (w), 835 (m), 810 (s), 775 (s), 715 (m), 630 (w), 580 (w), and 515 (s) cm^{-1}.

The dark mother liquor from the crystallization was adsorbed on 5 g of alumina (Woelm, neutral, activity 1) and chromatographed using pentane as eluent. Removal of solvent gave 0.95 g of aromatic, white needles which were found *via* their nmr spectrum to be an approximately 10:1 mixture of 1,2,3,4-tetrachlorobenzene and 1-(trimethyltin)-2,3,4,5-tetrachlorobenzene (comparison with authentic samples). Recrystallization from ether–methanol–water gave 0.60 g of colorless crystals, mp 44–46° (melting point of pure 1,2,3,4-tetrachlorobenzene is 47.5°).

In another experiment, a solution of 22.2 mmoles and 20.8 mmoles of bis(trimethyltin)acetylene and 5,5-dimethoxytetrachlorocyclopentadiene, respectively, in 120 ml of di-*n*-butyl ether was heated at reflux for 36 hr. Removal of the solvent left a crystalline solid. Thorough washing with methanol left as residue 3.90 g (35%) of slightly tan crystals, mp 117–120° (1,2-bis(trimethyltin)-tetrachlorobenzene). Refrigeration of the mother liquor at −20° produced two additional crops of crystals, 0.83 g (mp 60–80°) and 0.39 g (mp 55–62°). Sublimation of the last two crops [40° (0.05 mm)] gave colorless crystals, mp 64–68°. Recrystallization of the latter from ether–methanol resulted in formation of fluffy needles of 1-(trimethyltin)-2,3,4,5-benzene, mp 65.5–68.3°.

Anal. Calcd for $C_9H_{10}Cl_4Sn$: C, 28.55; H, 2.66; Cl, 37.42; mol wt, 379. Found: C, 28.73; H, 2.79; Cl, 37.67; mol wt, 400 (vapor pressure osmometer).

The nmr spectrum of this compound (CCl_4) had absorptions at 7.27 (Ar-*H*) and 0.40 ppm (Sn–C*H*$_3$) with relative areas of 1:9. The trimethyltin absorption had satellites, $J_{Sn^{117}-H^1}$ = 52 and $J_{Sn^{119}-H^1}$ = 54 cps. The ultraviolet spectrum (ethanol) had λ_{max} 210 mμ (ϵ 86,500), λ_{sh} 237 (11,200), λ_{sh} 274 (231), λ_{max} 283 (317), and λ_{max} 292 (264). It may be noted that 1,2,3,4-tetrachlorobenzene shows a similar pattern for the long wavelength absorption: λ 274 mμ (ϵ 260), λ 280 mμ (ϵ 330), and λ 291 mμ (ϵ 290).[20] The infrared spectrum (CCl_4) had absorption at 3075 (w), 2980 (m), 2920 (m), 1550 (m), 1520 (m), 1395 (s), 1320 (s), 1290 (w), 1260 (s), 1235 (m), 1205 (w), 1190 (s), 1165 (w), 1145 (m), 1095 (w), 1070 (s), 1010 (w), 880 (m), 845 (s), 630 (m), and 530 (s) cm^{-1}.

In order to establish the occurrence of Sn–C cleavage during column chromatography, a sample of pure 1,2-bis(trimethyltin)tetrachlorobenzene was dissolved in ether and adsorbed on some of the alumina used in the work described above. After 10 hr the alumina was extracted with ether. The solvent was removed, and the nmr spectrum of the residue (in CCl_4) was recorded. The ratio of Ar–*H* (7.3 ppm) to Sn–C*H*$_3$ (0.4 ppm) was 3:18, indicating that 60% destannation had occurred.

An authentic sample of 1,2,3,4-tetrachlorobenzene was prepared by cleavage of the Sn–C bond of 1.2 mmoles of 1-(trimethyltin)-2,3,4,5-tetrachlorobenzene with hydrochloric acid in ether–methanol medium. The product, mp 46.5–48°, had an infrared spectrum identical with that obtained above. Its nmr spectrum showed a singlet at 7.31 ppm.

Anal. Calcd for $C_6H_2Cl_4$: C, 33.37; H, 0.94; Cl, 65.69. Found: C, 33.41; H, 0.71; Cl, 65.67.

Cleavage Reactions of 2,3-Bis(trimethyltin)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (I). a. With Chlorine. To a solution of 8.08 mmoles of I in 50 ml of chloroform was added dropwise at room temperature a solution of *ca.* 17 mmoles of chlorine in chloroform. The chlorine color was discharged instantaneously. Solvent and trimethyltin chloride were removed at reduced pressure to leave a yellow oil. The latter was dissolved in pentane, filtered, and concentrated. Addition of methanol and chilling produced 2.44 g of crude product. Recrystallization from pentane–methanol gave pure octachlorobicyclo[2.2.1]hepta-2,5-diene, mp 87.5–88.5°.

Anal. Calcd for C_7Cl_8: C, 22.86; Cl, 77.14. Found: C, 22.87; Cl, 77.30.

Its ultraviolet spectrum (*n*-heptane) had λ_{max} 233 mμ (ϵ 4430), λ_{sh} 239 mμ (ϵ 3630), and λ_{sh} 265 mμ (ϵ 320). The infrared spectrum (CCl_4, CS_2 composite) had bands at 1610 (m), 1585 (m), 1145 (s), 1095 (s), 1055 (w), 1000 (m), 920 (w), 905 (w), 865 (w), 760 (s), 700 (s), 685 (s), and 675 (s) cm^{-1}.

b. With Bromine. To 8.97 mmoles of I in 100 ml of chloroform was added dropwise a solution of 18.8 mmoles of bromine in methanol. Instantaneous discharge of the bromine color was observed. Work-up similar to that in part a gave 3.85 g (94%) of 2,3-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene, mp 98.5–100.5°.

Anal. Calcd for $C_7Br_2Cl_6$: C, 18.41; Br, 35.00; Br + Cl, 81.58. Found: C, 18.58; Br, 34.76; Br + Cl, 81.40.

Its ultraviolet spectrum (*n*-heptane) showed λ_{max} 237 mμ (ϵ 4565), λ_{sh} 244 mμ (ϵ 4196), and λ_{max} 271 mμ (ϵ 465). The infrared spectrum (CCl_4) had bands at 1605 (m), 1575 (m), 1230 (w), 1120 (s), 1083 (s), 1075 (s), 1045 (w), 1005 (w), 920 (w), 900 (s), 700 (s), 670 (m), 640 (s), and 620 (m) cm^{-1}. The bands at 1605 and 1575 cm^{-1} are $\nu_{C=C}$ for the CCl=CCl and CBr=CBr moieties, respectively.

c. With Hydrochloric Acid. To a solution of 3.94 mmoles of I in 50 ml of diethyl ether was added dropwise an excess of concentrated HCl diluted with methanol. Subsequent addition of 1:1 aqueous-alcoholic potassium fluoride precipitated trimethyltin fluoride. The organic layer was dried and concentrated. Passage through a column of alumina and evaporation resulted in isolation of 0.905 g (77%) of colorless oil, n^{28}D 1.5469. Microdistillation gave a sample with n^{25}D 1.5520 (lit.[9d] n^{20}D 1.5550). The nmr spectrum of the product (in CCl_4) showed a singlet at 6.68 ppm.

Anal. Calcd for $C_7H_2Cl_6$: C, 28.13; H, 0.67; Cl, 71.20. Found: C, 28.34; H, 0.77; Cl, 70.26.

Cleavage Reactions of 2-(Trimethyltin)-1,4,5,6,7,7-hexachloro-3-methylbicyclo[2.2.1]hepta-2,5-diene. a. With Chlorine. To an ether solution of 0.60 g of the norbornadiene was added dropwise a solution of chlorine in methanol until a yellow color persisted in the reaction mixture. Removal of solvents and trimethyltin chloride under vacuum left a yellow oil. The latter was dissolved in pentane; the solution was filtered, concentrated, treated with methanol, and chilled. 2-Methylheptachlorobicyclo[2.2.1]hepta-2,5-diene, 0.305 g (70%), mp 91.5–93°, was obtained. An analytical sample had mp 92.3–93.3°.

Anal. Calcd for $C_8H_3Cl_7$: C, 27.66; H, 0.87; Cl, 71.47. Found: C, 27.93; H, 0.70; Cl, 71.26.

Its nmr spectrum (CCl_4) showed a singlet at 1.95 ppm. The ultraviolet spectrum (ethanol) had λ_{max} 228 mμ (ϵ 3900) and λ_{sh} 270 mμ (ϵ 285). The infrared spectrum showed the expected absorptions at 1605 and 1645 cm^{-1}, bands attributable to the CCl=CCl and CMe=CCl units.

b. With Bromine. A similar reaction was carried out between 0.127 g (0.266 mmole) of the norbornadiene and methanolic bromine. Work-up gave a nearly quantitative yield of 2-bromo-1,4,5,-6,7,7-hexachloro-3-methylbicyclo[2.2.1]hepta-2,5-diene, mp 98.5–100.5°.

Anal. Calcd for $C_8H_3BrCl_6$: C, 24.53; H, 0.77. Found: C, 24.13; H, 1.01.

The nmr spectrum of the product showed a singlet at 1.95 ppm. The ultraviolet spectrum (ethanol) had λ_{max} 224 mμ (ϵ 4100) and

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[19] J. S. Newcomer, and E. T. McBee, *J. Am. Chem. Soc.*, **71**, 949 (1949).

[20] W. R. Jondorf, D. V. Park, and R. T. Williams, *Biochem. J.*, **69**, 181 (1958).

λ_{sh} 277 mμ (ϵ 340). C=C stretching frequencies were present at 1600 and 1640 cm^{-1} in the infrared spectrum.

c. With Hydrochloric Acid. A solution of 0.170 g (0.36 mmole) of the norbornadiene in 5 ml of ether was treated with methanolic HCl (0.42 mmole), overnight at room temperature. Removal of volatiles left a yellow oil. An analytical sample was collected by glpc (F & M 700, isothermal at 205°, 7.5% General Electric Co. SE-30 on Chromosorb P); it had n^{25}D 1.5440.

Anal. Calcd for $C_8H_4Cl_6$: C, 30.71; H, 1.29. Found: C, 30.74; H, 1.46.

Its nmr spectrum (CCl_4) consisted of a quartet (J = 2.2 cps) at 6.20 ppm and a doublet at 1.97 ppm, with relative areas of 1:3. The ultraviolet spectrum (ethanol) had λ_{max} 222 mμ (ϵ 3150) and λ_{max} 265 mμ (ϵ 550). The infrared spectrum (liquid film) showed $\nu_{C=C}$ at 1600 and 1635 cm^{-1}. The near infrared spectrum showed an absorption at 1.645 μ. (It has been reported that absorption at 1.644 μ is characteristic of the vinyl proton of 1,2,3,4-tetrachloro-7,7-dimethoxybicyclo[2.2.1]hepta-2,5-diene.[21])

Irradiation of 2,3-Bis(trimethyltin)-1,4,5,6,7,7-hexachlorobicyclo-[2.2.1]hepta-2,5-diene (I). A solution of 3.093 g (4.95 mmoles) of I in 300 ml of diethyl ether in a quartz flask was irradiated for 24 hr with a 100-w, high-pressure mercury, external source, Hanovia lamp which was maintained about 2 in. from the reaction vessel. External cooling was provided with an electric fan, and the solution was stirred with a magnetic stirring unit. The course of the reaction was followed by thin layer chromatography (tlc) using silica gel–pentane. After 3 hr, a new compound with R_f slightly lower than that of I was the major component of the reaction mixture. A photostationary equilibrium appeared to have been reached after 17 hr. Removal of solvent at 0.3 mm (pot temperature to 30°) left a brown oil which was chromatographed on a silica gel G column using pentane as eluent. A clean separation was not obtained, but the norbornadiene I was concentrated into the first few fractions. A total of 2.145 g (70%) of oils and solids was eluted. Fractional crystallization of the initial fractions and recrystallization of the later fractions from pentane–methanol gave 1.389 g (45%) of colorless crystals (free of I by tlc), mp 120–125° dec. Recrystallization gave 2,3-bis(trimethyltin)-1,4,5,6,7,7-hexachloroquadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptane (XIV), mp 136–139° dec. An analytical sample had mp 139–141° dec.

Anal. Calcd for $C_{13}H_{18}Cl_6Sn_2$: C, 25.01; H, 2.91; Cl, 34.07; mol wt, 624. Found: C, 25.08; H, 2.96; Cl, 34.40; mol wt, 612 (vapor pressure osmometer, in benzene).

Ultraviolet and nmr spectral data are given in Table II. The infrared spectrum of the product showed bands at 2985 (m), 2920 (m), 1400 (w), 1310 (w), 1295 (w), 1280 (m), 1195 (w), 1180 (s), 1175 (s), 1145 (m), 1045 (w), 1030 (m), 925 (w), 900 (m), 835 (s), 775 (s), 720 (m), 595 (w), and 530 (m) cm^{-1}.

Irradiation of 2-(Trimethyltin)-1,4,5,6,7,7-hexachloro-3-methylbicyclo[2.2.1]hepta-2,5-diene (II). The reaction was carried out as described above using 3.34 g (7.05 mmoles) of II in 250 ml of diethyl ether (22.5-hr irradiation). Removal of solvent under vacuum left a yellow oil whose nmr spectrum showed singlets at 2.0 ppm (C–CH_3 of II) and at 1.33 ppm in the ratio of 1:5.5, as well as absorption around 0.35 ppm. Tlc (silica gel–pentane) indicated a single major product had been formed with an R_f slightly lower than that of II. Column chromatography (silica gel–pentane) yielded a total of 2.815 g (85%) of oils and solids. II was concentrated into the first fraction (0.2839 g). Crystallization of the remaining fractions from pentane–methanol gave colorless crystals of 2-(trimethyltin)-1,4,5,6,7,7-hexachloro-3-methylquadricyclo[2.2.1.0^{2,6}.0^{3,5}] heptane, 2.105 g, mp 60–68°, free of II (by tlc). An analytical sample obtained after two further recrystallizations had mp 64–67.5°.

Anal. Calcd for $C_{11}H_{12}Cl_6Sn$: C, 27.78; H, 2.54; Cl, 44.73. Found: C, 28.08; H, 2.77; Cl, 44.82.

Ultraviolet and nmr spectral data are given in Table II. The infrared spectrum (CCl_4) showed absorptions at 2980 (m), 2925 (m), 2860 (w), 1550 (w), 1445 (m), 1380 (w), 1360 (w), 1290 (w), 1275 (w), 1215 (sh), 1200 (s), 1190 (s), 1175 (m), 1150 (m), 1110 (m), 1065 (m), 1025 (w), 940 (w), 905 (w), 845 (s), 725 (s), 700 (m), 600 (m), and 530 (m) cm^{-1}.

Irradiation of 2-Bromo-1,4,5,6,7,7-hexachloro-3-methylbicyclo-[2.2.1]hepta-2,5-diene (XII). Under conditions identical with those described above 1.212 g (3.09 mmoles) of XII in 100 ml of diethyl ether was irradiated for 35 hr. The residue from an aliquot withdrawn after 17 hr had an nmr spectrum (CCl_4) showing singlets at 1.96 ppm (C–CH_3 of XII) and 1.42 ppm in a ratio of 1.8:1. The irradiation was continued for an additional 18 hr. Examination of an aliquot by nmr spectroscopy showed the ratio of the 1.96- and 1.42-ppm absorption intensities to be 1.4:1. Since the system appeared to be near photoequilibrium, the irradiation was discontinued. Attempts to resolve the mixture by column chromatography (silica gel G or Woelm alumina, neutral, activity 1) were unsuccessful, as were attempts to fractionally crystallize portions of the chromatography residues from pentane–methanol. Strong circumstantial evidence that the photoproduct was 2-bromo-1,4,5,6,7,7-hexachloro-3-methylquadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptane was given by the absorption at 1.42 ppm in the nmr spectrum of the reaction mixture (*cf.* Table II), by infrared spectral data of the reaction mixture, and by the fact that thermal conversion of the product mixture to pure XII occurred during attempted glpc at 200°.

The infrared spectrum of the product mixture showed absorptions (among others) at 1445, 1435, 1380, 1365, 1330, 1310, 1225, 1190, and 1155 cm^{-1}. The infrared spectrum of XII has bands at 1435, 1380, 1220, and 1155 cm^{-1} in common. The infrared spectrum of the quadricyclane XVI (Table II) showed bands at 1445, 1390, 1330, 1305, 1210, 1195, and 1150 cm^{-1}. Furthermore, the ultraviolet spectrum of a sample of the reaction mixture in which the absorptions at 1.96 and 1.42 ppm had relative areas of 1.3:1 (*i.e.*, 60% XII and 40% quadricyclane isomer) was measured. The mixture ultraviolet spectrum showed λ_{max} 224 mμ (ϵ 3100) and λ_{sh} 277 mμ (ϵ 206); in comparison, the ultraviolet spectrum of pure XII showed these absorptions with ϵ 4090 and 344, respectively.

Cleavage Reactions of 2-(Trimethyltin)-1,4,5,6,7,7-hexachloro-3-methylquadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptane (XV). a. With Bromine. A solution of 0.6234 g (1.31 mmoles) of XV in 50 ml of 1:1 ether–methanol was cooled to −20° and 0.225 g (1.41 mmoles) of bromine in 40 ml of methanol was added dropwise. The persistence of the bromine color after addition indicated a slow reaction, and the temperature was raised gradually to 30°. The reaction mixture was stirred for 15 hr after completion of the addition. Removal of volatiles at 0.3 mm (pot temperature to 40°) left an oily, brown residue which was chromatographed on a silica gel column using pentane as eluent. The final fractions of the chromatography consisted of a single compound. Distillation of these fractions gave a colorless liquid, bp *ca.* 55° (0.12 mm); this was identified as the quadricyclane XVI.

Anal. Calcd for $C_8H_4Cl_6$: C, 30.71; H, 1.29. Found: C, 30.48; H, 1.42.

For nmr and ultraviolet spectral data see Table II. The compound showed absorption at 1.655 μ in the near infrared region, which is characteristic of the 6-quadricyclic hydrogen. (The isomeric norbornadiene, XIII, absorbs at 1.645 μ, and the quadricyclane is expected to absorb at slightly higher frequency.[21]) The infrared spectrum (liquid film) showed bands at 3080 (w), 2980 (w), 2930 (m), 2865 (w), 1445 (m), 1380 (w), 1325 (m), 1305 (m), 1200 (s), 1185 (m), 1150 (m), 1110 (s), 1075 (sh), 1060 (m), 965 (w), 920 (w), 890 (m), 845 (s), 830 (m), 810 (m), 770 (m), 695 (m), 675 (w), 655 (w), and 590 (w) cm^{-1}.

The remainder of the chromatography residues, 0.2999 g, was examined by glpc (7.5% SE-50 on Chromosorb P, 222°) and nmr spectroscopy. The nmr spectrum (CCl_4) had absorptions at 6.19 (4X, J = 2.2 cps), 2.81 (1X), 2.0 (2X, J = 2.2 cps), 1.95, 1.42, and 1.35 ppm; the four highest field (methyl) absorptions were in the approximate ratio 1:1:1:1. The multiplets at 6.19 and 2.0 ppm were assigned to the vinyl and methyl protons, respectively, of the norbornadiene XIII. The component of shortest retention time (glpc) had an infrared spectrum identical with that of XIII. The absorption at 1.95 ppm could be assigned to the methyl group of the bromodestannated norbornadiene XII. The major component of the gas chromatogram and that with the longest retention time had the correct melting point, 98–100°, infrared spectrum, and analysis (found: C, 24.24; H, 0.75) for XII.

The absorptions at 2.81 and 1.35 ppm were assignable to the cyclopropyl and methyl hydrogens, respectively, of XVI. The only unassigned absorption was the one at 1.42 ppm; this, however, was exactly the position of the absorption of the photoproduct of the brominated norbornadiene XII and so the presence of the quadricyclane XVIII was indicated. The yields of XII, XIII, XVI, and XVIII were approximately 15, 15, 35, and 15%.

The brominolysis of XV was also carried out under rigorously air-free and anhydrous conditions with starting material of ~96% purity. The reaction vessel was covered with aluminum foil. After the completion of the bromine addition, the reaction mixture was

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[21] P. G. Gassman and W. M. Hooker, *J. Am. Chem. Soc.*, **87**, 1079 (1965).

stirred for 85 hr. Examination of the reaction products by nmr spectroscopy revealed the presence of XII, XVIII, and XIII in the ratio of 2:1:1; only a trace of XVI was present (very weak signal at 2.81 ppm), and there was absorption at 1.22 ppm that could not be assigned.

In another experiment, 1.95 mmoles of XV (no C=C visible *via* infrared spectroscopy) in anhydrous chloroform (50 ml) was treated with 2.07 mmoles of bromine in 25 ml of chloroform, and the reaction mixture was stirred for 48 hr. Analysis of the reaction residue by nmr spectroscopy revealed that only brominolysis products and starting materials were present. The nmr spectrum had absorptions at 1.95 (C–CH_3 of XII), 1.43 (C–CH_3 of XVIII), 1.32 (C–CH_3 of XV), and 0.36 ppm (Sn–CH_3 of XV); the ratio of XII:XVIII:XV was 3.5:1:1. Filtration of the residue through a short silica gel column using pentane as eluent gave 0.448 g of oil (corresponds to an 11% recovery of XV and 46% yield of brominolysis products using the ratios obtained in the nmr analysis).

b. With Hydrochloric Acid. A solution of 0.696 mmole of XV (shown by its nmr spectrum to contain 4 ± 1% of the corresponding norbornadiene as impurity) in 30 ml of ether was treated with 6 ml of 0.6 *N* (3.6 mmoles) methanolic HCl (prepared from aqueous 12 *M* HCl). The reaction mixture was stirred at room temperature for 41 hr. Removal of volatiles at 0.5 mm left a yellow oil which was neutralized with solid sodium carbonate, dissolved in carbon tetrachloride, and filtered. An nmr spectrum of this solution showed singlets at 2.81 and 1.34 ppm with relative areas of 1:3. A doublet was discernible at 1.97 ppm (J = 2.2 cps) with an area of 0.04 relative to that of the absorption at 1.34; this absorption is due to XIII, the protolysis product of the norbornadiene impurity in the starting material. Distillation of the residue obtained by evaporation of the carbon tetrachloride solution with a micro Hickman still gave 0.153 g (70%) of colorless liquid, bp ~55° (0.08 mm), the infrared spectrum of which was identical with that of the quadricyclane XVI.

In another experiment, a sample of XV containing 18% of the isomeric norbornadiene II was treated, under conditions identical with those described above, with 1 equiv of hydrochloric acid. Examination of the mixture by tlc (silica gel–pentane) after 8 hr indicated that all of the norbornadiene had been consumed, but that most of the quadricyclane remained. After 71 hr, the ratio of XV to XVI was 7:3.

A sample of the quadricyclane XVI (containing *ca.* 4% of the isomeric norbornadiene) was injected onto a glpc column heated to 200° (SE-30 on Chromosorb P); with a helium carrier gas flow of 60 cc/min a single product (retention time 18 min) was eluted which had an infrared spectrum identical with that of XIII.

Cleavage of 2,3-Bis(trimethyltin)-1,4,5,6,7,7-hexachloroquadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptane (XIV) with Hydrochloric Acid. A solution of 0.298 g (0.477 mmole) of XIV (no C=C visible in the infrared spectrum) in 50 ml of 1:1 ether–methanol was treated with 6 mmoles of HCl (concentrated acid diluted with 10 ml of methanol). The resulting solution was stirred at room temperature for 66 hr. Removal of volatiles under vacuum left an oily residue. The nmr spectrum of the latter (CCl_4) had absorptions at 3.23, 2.93, and 0.31 ppm, with relative areas of 1:3:8. There was no absorption in the region 5–7 ppm. Two distillations with a micro Hickman still gave 0.085 g (60%) of colorless liquid, bp ~65° (0.1 mm). The nmr spectrum of the distillate ($CDCl_3$) showed a singlet at 2.97 and at 0.38 ppm with relative areas of 3:2. The latter absorption is due to either XIV or to the product of a single Sn–C cleavage. The absorption at 2.97 ppm is believed to be due to the cyclopropane hydrogens of 1,2,3,4,7,7-hexachloroquadricyclo[2.2.1.0^{2,6}.0^{3,5}]heptane, and the purity of the distilled sample is estimated at 90%, assuming that the 0.38-ppm absorption represents at least nine protons. The infrared spectrum was in agreement with the quadricyclic structure showing bands (pure liquid) at 3080 (m), 2980 (w), (impurity), 2945 (w) (impurity), 1325 (m), 1305 (m), 1250 (m), 1220 (s), 1205 (m), 1165 (m), 1115 (s), 1080 (w), 1050 (m), 990 (m), 965 (m), 945 (m), 900 (m), 875 (m), 835 (s), 825 (s), 770 (sh), 765 (s), 720 (w), 650 (w), 590 (s), and 560 (m) cm^{-1}. The absorptions between 1325 and 1165 cm^{-1} appear to be characteristic of the highly chlorinated quadricyclanes. A mass spectrum, obtained with a Hitachi RMU-6D mass spectrometer, although showing peaks above M^+ 300, had the molecular ion, M^+ 298 ($C_7H_2Cl_5{}^{35}Cl^{37}$), for the hexachloroquadricyclane and the expected peak of maximum intensity at M^+ 263 ($C_7H_2Cl_4{}^{35}Cl^{37}$) owing to loss of the 7-Cl substituent and formation of the relatively stable 7-quadricyclic carbonium ion.[22]

Thermal Decomposition of 2-(Trimethyltin)-1,4,5,6,7,7-hexachloro-3-methylbicyclo[2.2.1]hepta-2,5-diene (II). A 25-ml flask was charged with 1.4453 g (3.03 mmoles) of II; the flask was attached *via* glass connections to a trap maintained at −78° which led to a vacuum pump. The system was evacuated three times and filled with nitrogen. With the system under a positive pressure of nitrogen, the pot was heated gradually to 230° and maintained at this temperature for 4 hr. The reaction mixture then was distilled at 30° (0.07 mm). Analysis of the distillate (SE-30 on Chromosorb P, 110°) showed that trimethyltin chloride (51%) had been formed. The distillation residue was chromatographed on silica gel (hexane and 2:1 hexane–benzene) to give 0.51 g of yellow oil. The nmr spectrum of the latter showed it to contain XIII (characteristic quartet at 6.2 and doublet at 2.0 ppm), as well as a compound showing a singlet at 1.95 ppm and smaller amounts of materials absorbing at 2.59 and 4.1 ppm. The two major components were identified by comparison of their infrared spectra and glpc retention times as XIII and XI. Their yields, determined by quantitative glpc using 1-chloronaphthalene as internal standard, were 13 and 6%, respectively.

Reaction of 1-(Trimethyltin)-2,3,4,5-tetrachlorobenzene with *p*-Iodotoluene. A solution of 0.745 g (1.97 mmoles) of the tin compound in 7 g of *p*-iodotoluene was heated at reflux under nitrogen for 19 hr (*ca.* 210°). Colorless solids sublimed into the inside of the reflux condenser during this time. Most of the iodotoluene was removed by distillation at 0.13 mm. The residue, approximately 0.5 ml of oily liquid, was evacuated overnight at 0.03 mm and then sublimed at 80° (0.04 mm) to give 0.430 g of fibrous, colorless crystals, mp 87.5–89.5°.

Anal. Calcd for $C_{13}H_8Cl_4$: C, 51.02; H, 2.63; Cl, 46.35. Found: C, 50.71; H, 2.58; Cl, 46.05.

The nmr spectrum (CCl_4) showed absorptions at 2.38, 7.19, and 7.30 ppm with relative areas of 3:4:1, in agreement with the structure 2,3,4,5-tetrachloro-4′-methylbiphenyl.

Thermal Decomposition of 1-(Trimethyltin)-2,3,4,5-tetrachlorobenzene. In an apparatus identical with that used in the thermolysis of II, 0.9682 g (2.60 mmoles) of the tin compound was heated at 230° for 3 hr. During the heating period a few microliters of a colorless liquid collected in the −78° trap; subsequent glpc analysis showed this to consist of tetramethyltin and trimethyltin chloride. Sublimation of the material remaining in the reaction flask at 60° (0.03 mm) gave 0.4728 g (1.28 mmoles) of starting material, mp 62.5–67°. The sublimation residue was dissolved in hexane and crystallization was induced by additions of methanol and chilling. A total of 0.189 g of solid, mp 130–140°, was obtained. Two recrystallizations from ether–methanol gave colorless crystals, mp 140–141.5°.

Anal. Calcd for $C_{14}H_8Cl_8Sn$: C, 29.06; H, 1.39; Cl, 49.01. Found: C, 28.81; H, 1.42; Cl, 48.66.

Spectral data confirmed its structure as being dimethylbis(2,3,4,5-tetrachlorophenyl)tin. The nmr spectrum (CCl_4) consisted of singlets at 7.30 ppm (Ar–H) and 0.75 ppm with relative areas of 1:3. The infrared spectrum (CCl_4) showed bands at 2965 (w), 2940 (w), 1600 (w), 1510 (w), 1380 (s), 1320 (s), 1295 (w), 1240 (w), 1190 (m), 1175 (w), 1150 (m), 1070 (m), 880 (w), 845 (m), 710 (w), 635 (m), and 530 (w) cm^{-1}. The ultraviolet spectrum (in ethanol) consisted of λ_{max} 211 mμ (ϵ 115,000), λ_{max} 238 (30,000), λ_{sh} 275 (700), λ_{max} 284 (830), and λ_{max} 293 (230). The maxima are essentially identical with those of the starting material, but the extinction coefficients are, as expected, about twice as great.

Acknowledgment. The authors are grateful to the National Science Foundation (Grant NSF-GP 2511) and to the National Lead Foundation for generous support of this work, and to M & T Chemicals, Inc., for gifts of organotin chemicals. This work was supported in part by Public Health Service Fellowship 5-F1-GM-20,099 (to A. B. E.).

(22) Quadricyclane itself shows a weak molecular ion peak and a very strong ion at $C_7H_7^+$: Z. Dolejsek, V. Hanus, and H. Prinzbach, *Angew. Chem.*, 74, 902 (1962).