



DIELS-ALDER REACTIONS OF ORGANOTIN ACETYLIDES  
AND THE CHEMISTRY OF THE ADDUCTS

by

ANTHONY BASIL EVNIN

A.B., Princeton University

(1962)

SUBMITTED IN PARTIAL FULFILLMENT

OF THE REQUIREMENTS FOR THE

DEGREE OF DOCTOR OF

PHILOSOPHY

at the

MASSACHUSETTS INSTITUTE OF

TECHNOLOGY

July, 1966

Signature redacted

Signature of Author

Department of Chemistry, July 26, 1966

Certified by

Signature redacted

Thesis Supervisor

Accepted by

Signature redacted

Chairman, Departmental Committee on Graduate Students



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Anthony B. Evnin

Submitted to the Department of Chemistry  
in Partial Fulfillment of the Requirements  
for the Degree of  
Doctor of Philosophy

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ABSTRACT

Chapter I. Diels-Alder Reactions of Organotin Acetylides with  
Highly Chlorinated Cyclopentadienes and the Chemistry  
of the Adducts

The Diels-Alder reaction of organotin acetylides  $[RC \equiv CSn(CH_3)_3]$ ,  $R = (CH_3)_3Sn-$ ,  $\phi-$ ,  $CH_3-$  gives bicyclo[2.2.1]hepta-2,5-dienes, typically in 50-70% yields. The carbon-tin bonds in the adducts are readily cleaved by electrophiles, without rearrangement of the carbon skeleton, to give novel, highly halogenated bicyclo[2.2.1]hepta-2,5-dienes. One of these, 2,3-dibromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene, was converted by bromine-metal exchange, to its 2-lithio derivative, which exhibits unusual stability for a  $\beta$ -halolithium system. The Diels-Alder reaction of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene and bis(trimethyltin)acetylene, which yields 1,2-bis(trimethyltin)tetrachlorobenzene, was also examined.

Chapter II. Diels-Alder Reactions of  $\alpha$ -Pyrone and Bis(trimethyltin)acetylene and the Chemistry of the Adducts

The Diels-Alder reaction of  $\alpha$ -pyrone and several of its analogs (5-carbomethoxy-, 5-methyl- and 4,6-dimethyl- $\alpha$ -pyrone) with bis(trimethyltin)acetylene to produce *o*-bis(trimethyltin)benzenes in good yields is described. The reaction affords a route to novel tin-substituted aromatic compounds. The utility of  $\alpha$ -pyrones in a general, one-step synthesis of benzenoid systems is discussed. The enhanced reactivity towards bis(trimethyltin)acetylene of  $\alpha$ -pyrones substituted with electron withdrawing groups is established



and discussed in terms of current theories of the Diels-Alder reaction.

### Chapter III. Photochemistry of Unsaturated Organotin Compounds

Irradiation of 2,3-bis(trimethyltin)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene and of 2-(trimethyltin)-1,4,5,6,7,7-hexachloro-3-methylbicyclo[2.2.1]hepta-2,5-diene converts them to the corresponding quadricyclenes. This constitutes one of the first examples of photoisomerization of a main group organometallic compound. Protodestannation of these tin-substituted quadricyclenes occurs without rearrangement or carbon-carbon bond cleavage. Bromodestannation was found to be more complex and evidence is presented for the involvement of free radical intermediates in this case. Irradiation of o-bis(trimethyltin)benzene leads only to dissociation of the carbon-tin bond; no isomerization of the aromatic nucleus was observed.

### Chapter IV. Thermal Decomposition of 2-Metallo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-dienes and o-Halo(trimethyltin)aromatics

Thermal decomposition of 2-metallo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-dienes (M = Sn, Hg) in the melt at 230° yielded the mixture of products expected from homolytic scission of the carbon-metal bond and subsequent reactions of the fragments. The mechanism is discussed in detail. Similar heating of o-halo-(trimethyltin)benzene systems does not result in carbon-tin homolysis; instead, coupling reactions to form (2-halo-2'-biphenyl)trimethyltin derivatives or disproportionation of the tin compound occur. Evidence is presented that similar intermediates are involved in the formation of these two types of products.

Thesis Supervisor: Dietmar Seyferth

Title: Professor of Chemistry

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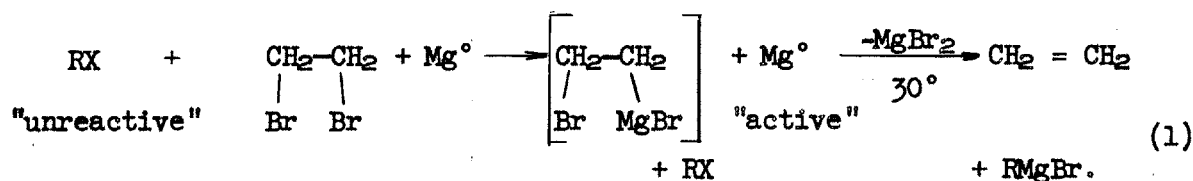
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## INTRODUCTION

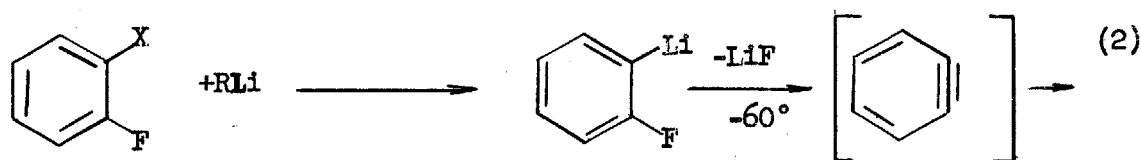
Reactions in which a metal halide is eliminated from a halogen-substituted organometallic compound with concomitant formation of a new carbon-carbon bond are of synthetic and mechanistic significance in organic chemistry. The entrainment method of initiating Grignard reaction, the formation of benzyne from *o*-lithiohalobenzenes and the initial synthesis of tetraphenylcyclobutadiene are all examples of this reaction:




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(1) D. E. Pearson, D. Cowan and J. D. Beckler, *J. Org. Chem.*, **24**, 504 (1959).

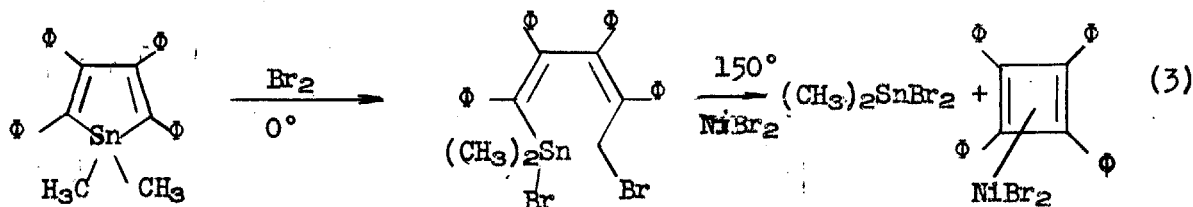
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(2) G. Wittig and H. Harle, *Ann. Chem.*, **623**, 17 (1959), and references contained therein.

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- 
- (3) H. H. Freedman, J. Am. Chem. Soc., 83, 2194 (1961).
- 

We were particularly intrigued by the possibility of synthesizing, or generating and trapping, novel organic molecules by this route. Organotin compounds seemed to possess the desired balance of stability to the atmosphere and facile thermal decomposition at moderate temperature for this study (The synthesis of tetraphenylbutadiene illustrated this nicely). The necessary organotin intermediates are relatively easy to obtain and the cleavage of the C-Sn bond by halogens is a well known reaction.<sup>4</sup>

- 
- (4) See, for example, J. G. A. Luitjens and G. J. M. Van der Kerk, "Investigations in the Field of Organotin Chemistry," Tin Research Council, Middlesex, England, 1955.
- 

Diels-Alder reactions of bis(trimethyltin)acetylene followed by monohalodestannylation of the adducts seemed to be an attractive route to some of the systems of interest to us. The synthesis of tin acetylides was documented in the work of Hartmann<sup>5</sup>, and Diels-

- 
- (5) H. Hartmann and H. Honig, Angew. Chem., 69, 614 (1957).
- 

Alder reactions with organometallic dienophiles had been previously reported, Becker's study of the reaction of tetraphenylcyclopentadienone(cyclone) and a vinyltin compound<sup>6</sup> and Abramov's study of



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(6) L. A. Rothman and E. I. Becker, J. Org. Chem., 24, 294 (1959).

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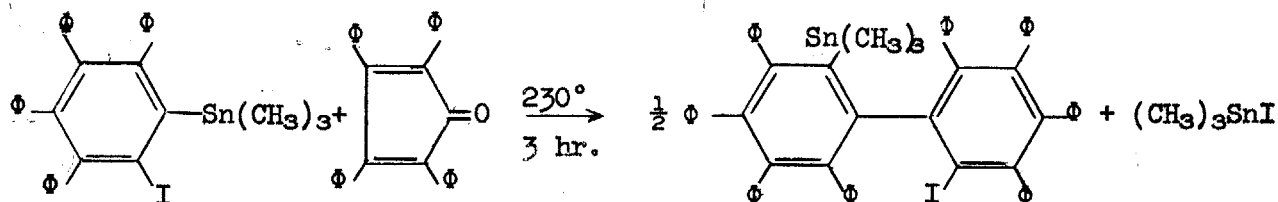
cyclone and bis(organomercuri)acetylenes<sup>7</sup> being the most relevant.

---

(7) V. S. Abramov and L. A. Shapskinskaya, Dokl. Akad. Nauk, S.S.S.R., Otdel Khim. Nauk, 59, 1291 (1948); C. A., 43, 2614 (1949).

---

Initial investigations of the Diels-Alder reaction of bis-(trimethyltin)acetylene with various standard dienes were fruitless, however, reaction with cyclone resulted in the formation of the decarbonylated adduct, 1,2-bis(trimethyltin)tetraphenylbenzene (I), in high yield. Reaction of I with one equivalent of iodine yielded 1-iodo-2-(trimethyltin)tetraphenylbenzene (II). When II was thermally decomposed in the presence of a diene trapping agent, tetraphenylbenzyne was not formed; instead, a coupling reaction occurred<sup>8</sup> (It was subsequently demonstrated that tetraphenylbenzyne




---

(8) D. Seyferth, C. Sarafidis, and A. B. Evin, J. Organometal. Chem., 2, 437 (1964).

---

could be generated from other precursors.<sup>9</sup> Although our initial

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(9) D. Seyferth and H. Menzel, J. Org. Chem., 30, 649 (1965).

---

expectations had not been realized, the coupling reaction is novel in the area of organotin chemistry<sup>10</sup> and is of considerable mech-

- 
- (10) There is an analogy in organolithium chemistry in the formation of 2,2'-dibromobiphenyl from o-dibromobenzene and n-butyllithium at -75° in THF: H. Gilman and B. J. Gaj, *J. Org. Chem.*, 22, 449 (1957). The Ullmann reaction is also somewhat analogous as intermediates with some sort of carbon-copper bond are involved: P. Fanta, *Chem. Revs.*, 64, 613 (1964).
- 

anistic interest. Accordingly, it was decided to prepare other systems with  $\beta$ -halo(trimethyltin) functionality.

In the course of these syntheses, a number of extremely interesting bistrimethyltin organic compounds were prepared, for example, 2,3-bis(trimethyltin)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene and o-bis(trimethyltin)benzene, and a considerable amount of time was devoted to an examination of their chemistry. In particular, a study was made of their photochemistry, in the course of which one of the first examples of photoisomerization of an organometallic compound was observed, and of the cleavage of their C-Sn bonds by electrophiles. The Diels-Alder reactions of the organotin acetylide turned out to be of considerable interest themselves. What appears to be a general, one-step benzene synthesis utilizing  $\alpha$ -pyrones as dienes<sup>11</sup> emerged from this study. Also, the relative reactivity

- 
- (11) The system is not novel (O. Diels and K. Alder, *Ann. Chem.*, 490, 257 [1931]) but its synthetic possibilities do not seem to have been realized.
-

of bis(trimethyltin)acetylene and related acetylenes with various dienes is not that generally observed for dienophiles in the classical Diels-Alder reaction<sup>12</sup> (see Chapter 1 for a discussion) and

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(12) Reaction appears to be most facile with electron deficient dienes. This phenomenon has previously been observed by Sauer, among others: J. Sauer and H. Wiest, *Angew. Chem.*, 74, 353 (1962).

---

this has some bearing on both the mechanism and synthetic utility of the Diels-Alder reaction.

CHAPTER I

DIELS-ALDER REACTIONS OF ORGANOTIN ACETYLIDES  
WITH HIGHLY CHLORINATED CYCLOPENTADIENES  
AND THE CHEMISTRY OF THE ADDUCTS

## DISCUSSION

The Diels-Alder reaction as elaborated in the classical papers of O. Diels and K. Alder, which start in 1928, involves reaction of a 1,3-diene with an olefin or acetylene (the dienophile) which is typically conjugated with an electron withdrawing group.<sup>1</sup> A wide

- 
- (1) For reviews see: (a) M. C. Kloetzel, *Organic Reactions*, Vol. IV, J. Wiley and Sons, New York, p. 1; M. L. Holmes, *ibid*, p. 60
- 

range of dienes and dienophiles may be used, and it has been demonstrated that electron-donating substituents on the diene and electron-withdrawing substituents on the dienophile facilitate the reaction.<sup>2</sup>

- 
- (2) (a) E. J. Dewitt, C. T. Rester and G. A. Ropp, *J. Am. Chem. Soc.*, **78**, 2101 (1956); (b) T. Benghiat and E. J. Becker, *J. Org. Chem.*, **23**, 885 (1958).
- 

When one evaluates bis(trimethyltin)acetylene as a dienophile it is readily apparent that it should be a poor one. The triple bond is not electron-deficient, if anything, it is electron-rich since it appears that the inductive flow of electrons from tin to carbon is the predominant electronic interaction in (trimethyltin)acetylene.<sup>3</sup> Also, the trimethyltin group is extremely bulky,

- 
- (3) R. West and C. S. Kraihanzel, *Inorg. Chem.*, **1**, 967 (1962).
- 

although the long C<sub>sp</sub>-Sn bond, ~ 2.0Å<sup>4</sup> tends to remove the group

- 
- (4) Estimated from values in "Tables of Interatomic Distances,"  
The Chemical Society, London, 1958.
- 

somewhat from the triple bond, and steric inhibition of the Diels-Alder reaction by large substituents is pronounced.<sup>5</sup>

---

- (5) J. G. Martin and R. K. Hill, Chem. Revs., 61, 537 (1961).
- 

In view of this, it is not surprising that bis(trimethyltin)-acetylene fails to undergo the Diels-Alder reaction with "classical" dienes such as furan, cyclopentadiene, 1,4-diphenylbutadiene and 2,5-diphenylisobenzofuran.<sup>6</sup> However, as was mentioned above, an

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- (6) C. S. Sarafidis, unpublished data.
- 

adduct was formed, in good yield, with tetraphenylcyclopentadienone.<sup>7</sup>

---

- (7) D. Seyferth, C. S. Sarafidis and A. B. Evin, J. Organometal. Chem., 2, 437 (1964).
- 

The reaction of number of electron rich and unsubstituted olefins with hexachlorocyclopentadiene has been reported by Sauer and Wiest.<sup>8</sup> They interpret their data in terms of a Diels-Alder

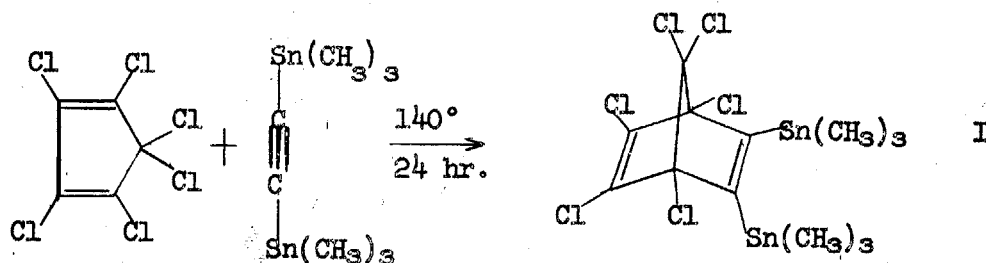
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- (8) J. Sauer and H. Wiest, Angew. Chem., 74, 353 (1962).
-

reaction with "inverse electron demand" with hexachlorocyclopentadiene acting as an electron acceptor. Therefore, it was of interest to evaluate the reactivity of hexachlorocyclopentadiene with bis(trimethyltin)acetylene. The thermal stability of this diene, its availability and the extensive literature on its Diels-Alder reactions (due largely to the importance of many of the adducts as biocides)<sup>9</sup> were additional attractive features.

- 
- (9) Leading references are (a) E. A. Pritt, J. Am. Chem. Soc., 69, 62 (1947); (b) E. K. Fields, *ibid.*, 76, 2709 (1954); (c) H. E. Ungnade and E. T. McBee, Chem. Revs., 58, 249 (1958).
- 

Reaction of equimolar amounts 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. Identification of the adduct, although



complicated by the absence of skeletal protons, was made by elemental analysis, by molecular weight determination and by the correlation of the ultraviolet and infrared spectra with those of other norbornadiene systems (see Table 1).

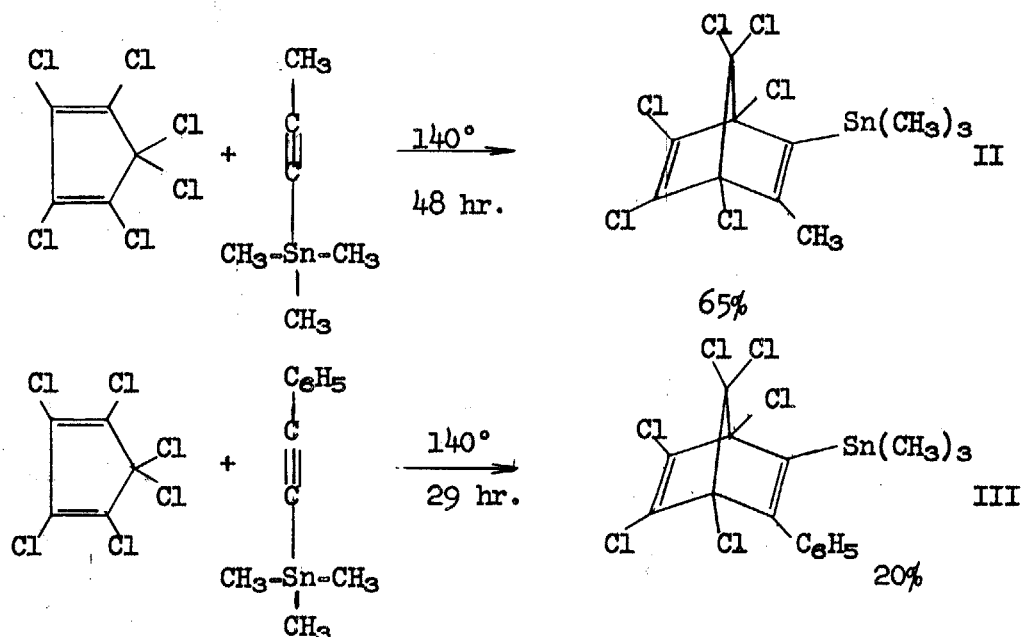
TABLE I

<u>Compound</u>	<u>UV</u>	<u>IR</u> ( $\text{C}=\text{C}$ str. region)
(1) norbornadiene (bicyclo[2.2.1]- hepta-2,5-diene)	$\lambda_{\text{max}}$ 205m $\mu$ ( $\epsilon$ 2100), $\lambda_{\text{max}}$ 214 m $\mu$ ( $\epsilon$ 14,800), $\lambda_{\text{max}}$ 220m $\mu$ ( $\epsilon$ 870), $\lambda_{\text{sh}}$ 230m $\mu$ ( $\epsilon$ 200).	1635cm $^{-1}$ , 1543cm $^{-1}$ (a)
I	$\lambda_{\text{max}}$ 236m $\mu$ ( $\epsilon$ 5600), $\lambda_{\text{sh}}$ 257m $\mu$ - ( $\epsilon$ 1600), $\lambda_{\text{sh}}$ 285m $\mu$ ( $\epsilon$ 360)	1605cm $^{-1}$
II	$\lambda_{\text{max}}$ 227m $\mu$ ( $\epsilon$ 4000), $\lambda_{\text{sh}}$ 276m $\mu$ - ( $\epsilon$ 280)	1605cm $^{-1}$ , 1585cm $^{-1}$
III	$\lambda_{\text{max}}$ 255m $\mu$ ( $\epsilon$ 3800), $\lambda_{\text{sh}}$ 297m $\mu$ - ( $\epsilon$ 1300)	1605cm $^{-1}$ , 1555 cm $^{-1}$
IV	$\lambda_{\text{max}}$ 233m $\mu$ ( $\epsilon$ 4430), $\lambda_{\text{sh}}$ 239m $\mu$ - ( $\epsilon$ 3630), $\lambda_{\text{sh}}$ 265m $\mu$ ( $\epsilon$ 300)	1610cm $^{-1}$ , 1585cm $^{-1}$
1,2,3,4,5,6,7,7-octa- chlorobicyclo[2.2.1]- hept-2-ene	$\lambda_{\text{max}}$ 212m $\mu$ ( $\epsilon$ 6300)	(b)
hexachlorocyclopentadiene		1606cm $^{-1}$ , 1572cm $^{-1}$ (c)
1,2,3,4,7,7-hexachloro-5- phenylbicyclo[2.2.1]- hepta-2,5-diene	$\lambda_{\text{max}}$ 223m $\mu$ ( $\epsilon$ 11,500), $\lambda_{\text{max}}$ 254 m $\mu$ ( $\epsilon$ 8920), $\lambda_{\text{sh}}$ 285 m $\mu$ ( $\epsilon$ 3300)	(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 1600cm $^{-1}$  is interpreted as a coupled oscillator phenomenon.
- b) J. D. Idol, C. W. Roberts and E. T. McBee, J. Org. Chem., 20, 1743 (1955).
- c) H. Gerding, H. J. Prins and H. Van Brederode, Rec. Trav. Chim., 65, 168 (1946).
- d) A. J. Fry, J. Org. Chem., 31, 1863 (1966); apparently steric interactions have reduced the conjugation in III, as is reasonable.



Propynyltrimethyltin and (phenylethynyl)trimethyltin were also reacted with hexachlorocyclopentadiene. Both gave Diels-Alder adducts, the (phenylethynyl)trimethyltin system in rather low yield, however. The adducts II and III were identified as described above,



but in these cases N.M.R. spectra were useful as well. The spectrum of 2-(trimethyltin)-1,4,5,6,7,7-hexachloro-3-phenyl-bicyclo[2.2.1]-hepta-2,5-diene (II) is interesting in that the trimethyltin absorbs at unusually high field, 0.10 p.p.m. (in I and II it occurs at 0.35 p.p.m.), due to its lying above the phenyl group which must be skewed to the plane of the 2,3-double bond.

The three Diels-Alder adducts are stable, crystalline compounds. On extended standing (several weeks), however, a slow decomposition occurs, with formation of methyltin chlorides. This type of behavior is typical of many organometallic systems with a halogen proximate

to the metal.<sup>10</sup>

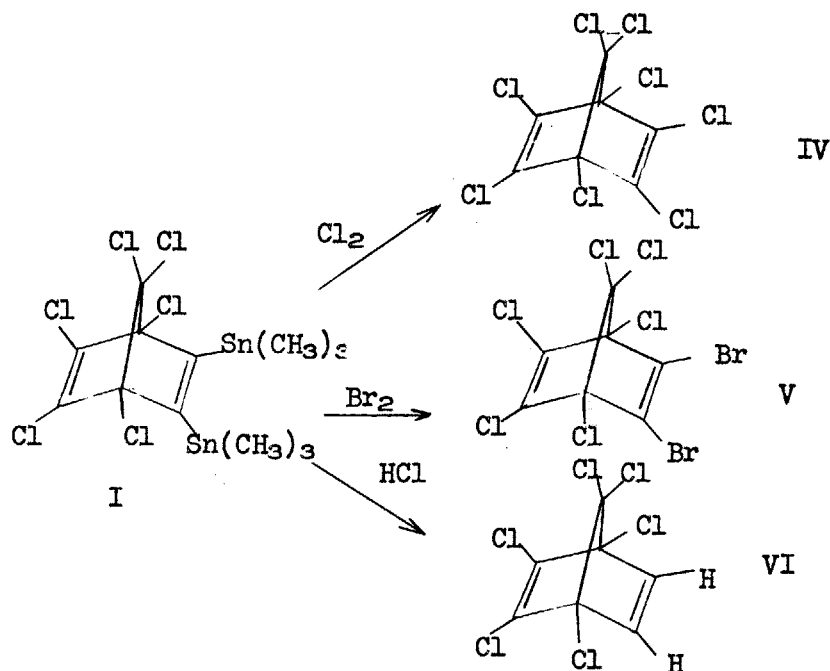
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- (10) (a) A. N. Nesmeyanov and A. E. Borisov, *Izv. Akad. Nauk, S.S.S.R., Otdel Khim. Nauk* (146) (1945); (b) F. M. Rabel and R. West, *J. Am. Chem. Soc.*, **84**, 4169 (1962); (c) D. Seyferth, unpublished data.
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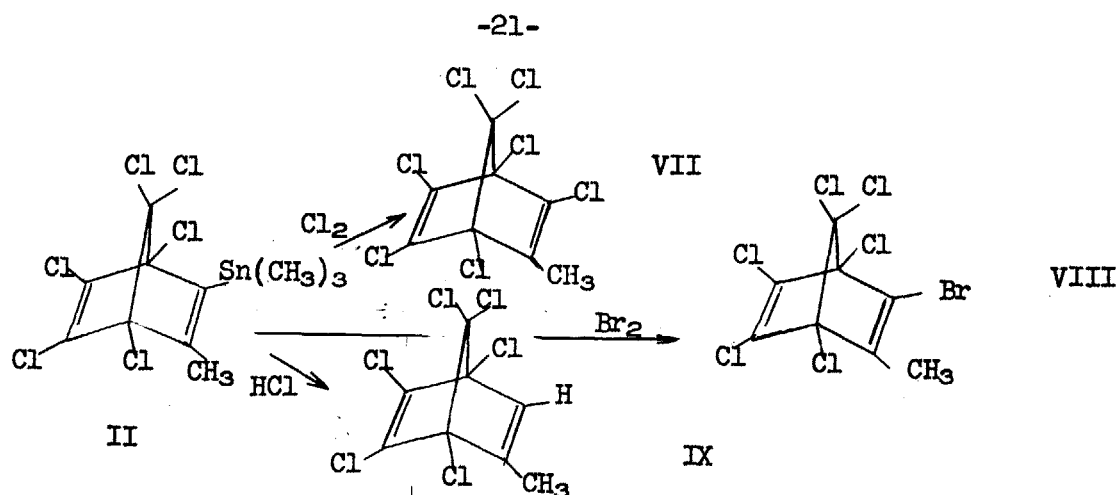
Cleavage of the C-Sn bonds in I and II by electrophiles such as halogens and halogen acids is a very facile reaction occurring in high yield under mild conditions.<sup>11</sup>

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- (11) D. Seyferth, *J. Am. Chem. Soc.*, **79**, 2133 (1957).
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FIGURE I





Compounds IV-IX have not been reported in the literature, with the exception of VI, and were characterized by their spectral properties and elemental analyses. All of the destannated norbornadienes IV-IX are stable to further attack by electrophiles, unlike norbornadiene itself,<sup>12</sup> which indicates a significant withdrawal of electron den-

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(12) S. Winstein and M. Shabatsky, Chem. and Ind. (London), 56 (1956).

sity by the chlorines. It must also be stressed that no rearrangement of the carbon skeleton occurred during the C-Sn cleavage reactions, which almost certainly involve an electrophilic attack at C-2 (see discussion in Chapter 3); this can be attributed either to electron withdrawal by the chlorines or to the absence of carbonium intermediates in C-Sn cleavage reaction or to both, since rearrangements of unhalogenated norbornenes involving a transannular positive charge are exhaustively documented.<sup>13, 14</sup>

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(13) J. A. Berson "Molecular Rearrangements" (ed. P. de Mayo), Interscience, New York, 1963.

- (14) Nesmeyanov has observed the electrophilic cleavage of the C-Hg bond in  $\beta$ -chlorovinylmercury systems occurs with retention of configuration which speaks against carbonium ion intermediates: A. N. Nesmeyanov and A. E. Borisov, *Tetrahedron*, 1, 158 (1957).
- 

The products which contain vinylic hydrogens, VI and IX, discolor and polymerize rapidly in the atmosphere even at  $-20^\circ$ . No electrophiles other than the above noted halogens and halogen acids were utilized, although a wide variety of other derivatives are certainly available by C-Sn cleavages.

Attempts to cleave only one of the vinyl-tin bonds in I by use of one equivalent of bromine or iodine were not successful, although several modes of addition and temperatures were examined. This is in contrast to the highly selective cleavage of one C-Sn bond by iodine ( $30^\circ$ ) and bromine ( $-75^\circ$ ) in several *o*-bis(trimethyltin)benzene systems discussed subsequently. The mechanistic implications of this are not clear, but the availability of systems such as 2-(trimethyltin)-3-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene by an alternate route led to discontinuation of efforts in this direction.

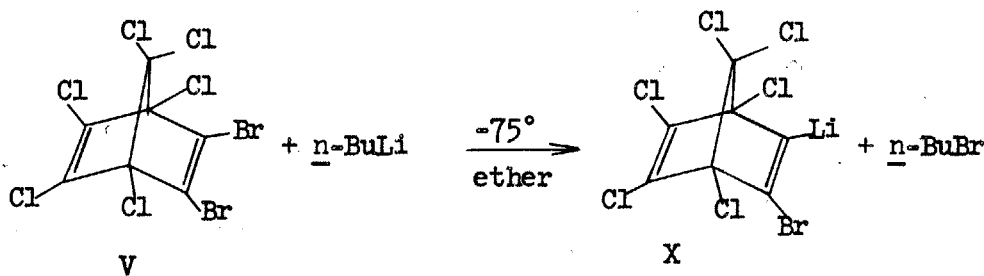
The perhalogenated norbornadiene systems IV and V offer intriguing possibilities for the study of halogen-metal exchange reactions. In particular, the recent work of Wittig<sup>15</sup> in which 1-bromo-2-chloro-

- 
- (15) For example, see, G. Wittig and H. Heyn, *Chem. Ber.*, 97, 1609 (1964).
- 

cycloalkenes were converted to the corresponding  $\beta$ -chlorolithium

compounds at low temperatures and then, by raising the temperature, to the cycloalkynes, suggested the application of a similar sequence to 2,3-dibromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (V).

It has been found that treatment of V with one equivalent of n-butyllithium in ether at  $-75^{\circ}$  gives a virtually quantitative yield of 2-lithio-3-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (X).<sup>18</sup> The lithium reagent was not isolated but its structure was

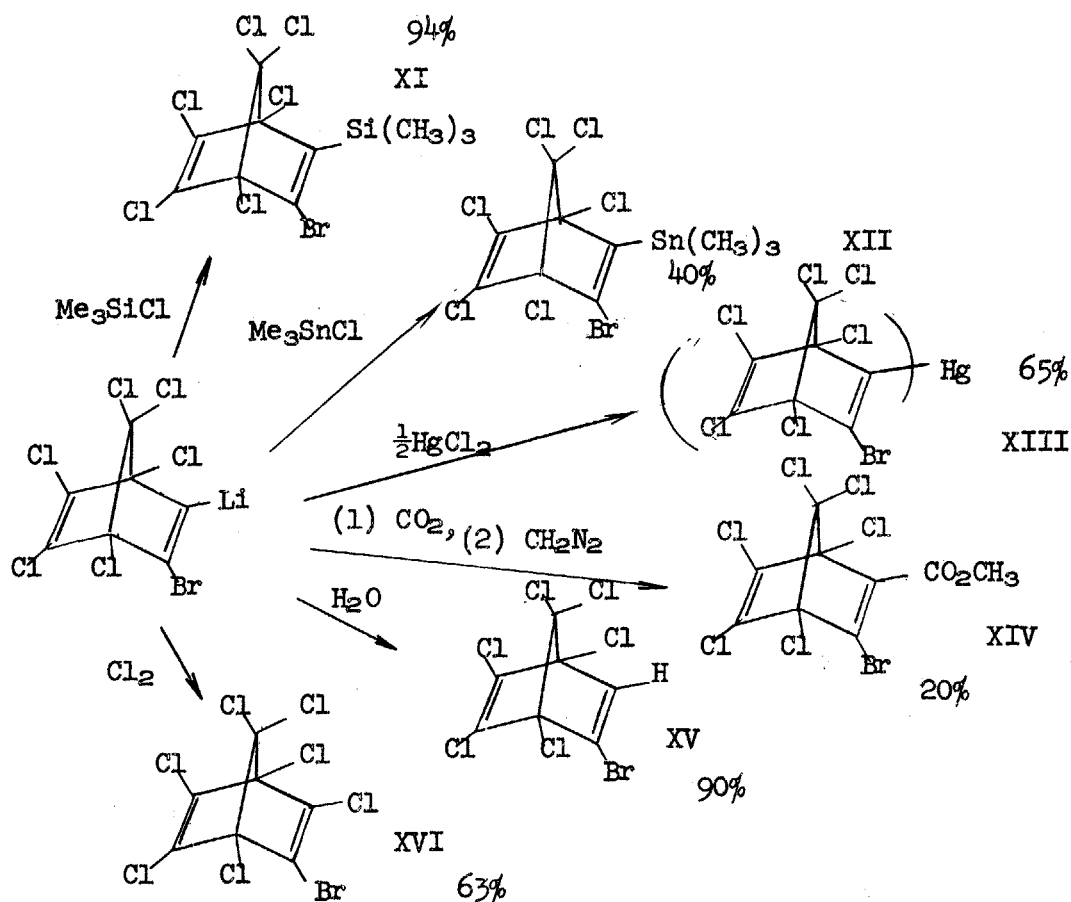


(16) These are the conditions of choice; the use of higher temperatures or of ether-pentane or ether-tetrahydrofuran solutions gave less satisfactory results.

established by quenching with a number of reagents known to react with organolithium compounds (see Figure 2). In addition, the yield of n-butylbromide (The n-butyllithium was prepared from n-butylchloride) was determined both to establish the course of the halogen-metal exchange and to check on the yields in the quenching experiments.

Optimum results were obtained with trimethylchlorosilane; the yield of 2-(trimethylsilyl)-3-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene(XI) was 94.5% and of n-butylbromide 93.5% (yields were calculated by quantitative g.l.p.c.); less than 1% of n-butyl chloride was formed.

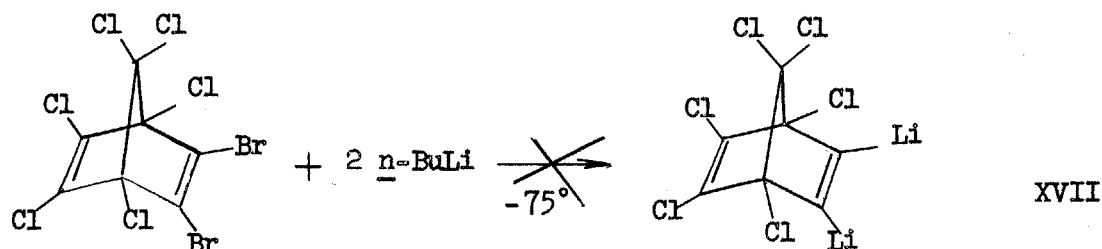
FIGURE 2



All of the compounds XI-XVI are new; XI, XII, XIV and XVI are stable, crystalline solids while XII, which is also crystalline, decomposes at a significant rate on standing and XV, a viscous liquid, polymerizes readily upon standing in the atmosphere. Attempts to react the lithium reagent (X) with one equivalent of mercuric halide to form 2-(halomercuri)-3-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene were unsuccessful as symmetrization reactions occur and unrectifiable mixtures are obtained.

Treatment of V with two equivalents of n-butyllithium at  $-75^\circ$

did not yield identifiable amounts (of derivatives) of 2,3-dilithio-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (XVII). Quench-



ing the reaction mixture at  $-75^{\circ}$  with trimethylchlorosilane yielded only 2-(trimethylsilyl)-3-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (49% crude yield). Examination of the volatile products of the reaction by quantitative g.l.p.c. indicated the presence of n-butylbromide (61.3%) and of n-butyl chloride (22.8%). The formation of n-butyl chloride (not observed in the 1:1 reaction) suggests that attack of a second equivalent of n-butyllithium on the bromine atom bonded to the charged, solvated 2,3-double bond of X is not favorable and attack at one of the chlorines occurs at at least a comparable rate. The formation of more than 50% of the theoretical amount of n-butyl bromide, however, suggests that some of the dilithio compound (XVII) might have formed, at least transiently.

Attempts to synthesize 2,3-dilithio-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene by metal-metal exchange between the 2,3-bis(trimethyltin compound (I) and two equivalents of n-butyllithium were entirely unsuccessful; tars were obtained from which only starting material could be isolated.

In evaluating the attempts to prepare XVII, it should be noted that there are no reports in the literature of  $\beta$ -dialkalimetal organic compounds with the exception of the acetylides which comprise a special class by virtue of the stability of the  $C_{sp}$  carbanion<sup>17</sup> and

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- (17) G. E. Coates, *Organo-Metallic Compounds*, Methuen and Co., London, 1956, p. 3.
- 

several aromatic systems<sup>18</sup>; none of which were prepared by consecu-

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- (18) (a) G. Wittig and F. Bickelhaupt, *Chem. Ber.*, 91, 883 (1958); (b) R. J. Harper, E. J. Soloski and C. Tamborski, *J. Org. Chem.*, 29, 2385 (1964); (c) o-bis(magnesiumhalo)benzene can, however, be prepared in low yield in this manner; H. Heaney, F. G. Mann and J. T. Millar, *J. Chem. Soc.*, 3930 (1957).
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tive metal-halogen exchanges. The reason that consecutive metal-halogen exchanges cannot be used is that the intermediate  $\beta$ -halometal compounds eliminate metal halide, even at low temperatures and even when the halogen is fluorine.<sup>19</sup>

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- (19) (a) H. Gilman and B. J. Gaj, *J. Org. Chem.*, 22, 449 (1957); (b) D. Seyferth, D. E. Welch and G. Raab, *J. Am. Chem. Soc.*, 84, 4266 (1962); (c) P. L. Coe, R. Stephens and J. C. Tatlow, *J. Chem. Soc.*, 3227 (1962); (d) H. E. Zieger and G. Wittig, *J. Org. Chem.*, 27, 3270 (1962).
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Exceptions to the above statement which are very relevant to the properties of X appear in systems in which elimination of the metal halide and formation of a new C-C  $\pi$  bond is very unfavorable due to steric limitations on the abilities of the carbons to rehy-



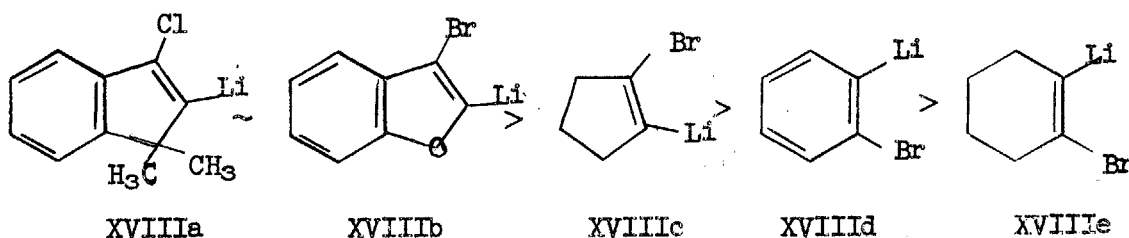
bridize. In particular, Wittig's<sup>15,20</sup> and Roberts'<sup>21</sup> studies of

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- (20) (a) G. Wittig and A. Pohmer, Chem. Ber., 89, 334 (1956);  
 (b) G. Wittig and R. Pohlke, *ibid.*, 94, 3276 (1961); (c) G. Wittig and U. Mayer, Angew. Chem., 74, 479 (1962); (d) G. Wittig and F. Winkler, Chem. Ber., 97, 2139 (1964); (e) G. Wittig, J. Weinlich and E. R. Wilson, *ibid.*, 98, 458 (1965).
- (21) L. K. Montgomery, F. Scardaglia and J. D. Roberts, J. Am. Chem. Soc., 87, 1917 (1965).
- 

the generation of small ring acetylenes (Cyclooctyne is the smallest stable cycloalkyne and it is highly strained),<sup>22</sup> indicate that the 1-

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- (22) A. T. Blomquist and L. H. Liu, *ibid.*, 78, 2153 (1953).
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lithio-2-halocycloalk-1-enes will be relatively stable in cases where formation of the corresponding acetylene is unfavorable.



Considered in this light, 2-lithio-3-bromo-1,4,5,6,7,7-hexa-

chlorobicyclo[2.2.1]hepta-2,5-diene (X) should be stable, since the acetylene that would be obtained by elimination of lithium bromide, hexachlorobicyclo[2.2.1]hept-2-ene-5-yne, is considerably more strained than cyclopentyne. Some idea of the increased strain is obtained by an estimate of the strain in norbornadiene itself,<sup>23</sup> taken with

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- (23) A strain of 20-30 kcal. is indicated by the data of P. R. Schleyer, *ibid.*, 80, 1700 (1958) and R. B. Turner, W. R. Meador and R. E. Winkler, *ibid.*, 79, 411 (1957).
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the fact that the significant distortions necessary to accommodate a linear acetylene unit are virtually impossible for the rigid bicyclo-[2.2.1]heptane skeleton. The possibility of X decomposing by an alternate route with lithium chloride elimination must also be considered.

Experimentally, X is found to be quite stable in ether at room temperature. Quenching aliquots of the lithium reagent with trimethylchlorosilane at various time intervals indicates that some of the compound ( $< 15\%$ ) is still present after 48 hr. at  $28 \pm 2^\circ$ . Decomposition is complete within 72 hr., however. In comparison, 1-lithio-2-bromocyclopent-1-ene is entirely decomposed, after 20 hr. at  $20^\circ$ .<sup>20c</sup> Specific data on XVIIIa and XVIIIb are not available except that Wittig and Heyn<sup>15</sup> note that a 50% yield methyl esters was obtained by treating a solution of XVIIIa that had stood at room temperature for 14 hr. with carbon dioxide and then diazomethane. (It should be noted that treatment of 2-bromo-3-chloro-1,1-dimethylindene with *n*-butyllithium at  $-75^\circ$  actually gives a 9:1 mixture of XVIIIa and 3-lithio-2-bromo-1,1-dimethylindene.<sup>15</sup>) The stability of X is, thus, roughly in line with expectations based on Wittig's data. It must be reiterated that the possibility of X's decomposition by lithium chloride elimination cannot be rigorously excluded since

all experiments were carried out with n-butyllithium containing complexed lithium chloride.

The short-lived acetylenes formed from XVIIIc,d, and e by elimination of lithium bromide were successfully trapped with dienes;<sup>19</sup> the acetylene from XVIIIb could not be generated in this way but was generated by an alternate route and trapped. Attempts to generate cyclobutyne have not been successful.<sup>24</sup> A bicyclo[3.2.1]oct-2-yne

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- (24) (a) J. D. Roberts and L. K. Montgomery, J. Am. Chem. Soc., 82, 4750(1960); (b) G. Wittig and E. R. Wilson, Chem. Ber., 98, 451 (1965).
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has been generated and trapped, in high yield.<sup>25</sup>

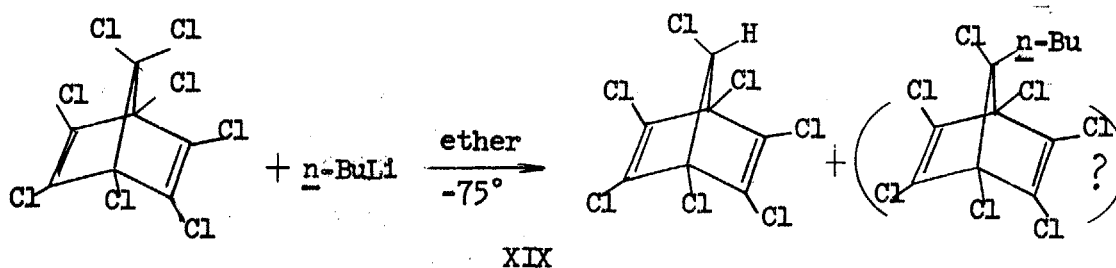
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- (25) K. L. Erickson and J. Wolinsky, J. Am. Chem. Soc., 87, 1142 (1965).
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Wittig's results indicate clearly that the stability of the cycloalkynes (and the ability to trap them) decreases rapidly with increased strain (decreasing size of the ring); this is dramatically indicated by the decreasing yields of cycloheptyne, cyclohexyne and cyclopentyne adducts with isobenzofuran under identical conditions.<sup>20b</sup> With cyclopentyne the yields are already very low (12% was optimum and 1-6% was typical), and it is reasonable that more strained acetylenes will be even more elusive.

Attempts to generate and trap bicyclo[2.2.1]hept-2-ene-5-yne by allowing X to decompose in the presence of excess 2,5-diphenyl-

isobenzofuran or furan were without success. None of the adduct could be isolated nor was there any evidence of its formation from spectral (NMR) and t.l.c. examination of crude reaction mixtures. The only organic products isolable from these reaction mixtures were small amounts of the starting dibromide and some of the product of hydrolysis of the lithium reagent; there were also considerable amounts of black tars.

The reaction of one equivalent of *n*-butyllithium with octachlorobicyclo [2.2.1]hepta-2,5-diene (IV) has also been examined but only in a cursory manner. The course of the reaction is quite different than with V; a considerable amount of starting material, >30%, is recovered and the major product, when the reaction mixture was quenched with ethanol, was 1,2,3,4,5,6,7-heptachlorobicyclo[2.2.1]hepta-2,5-diene (XIX).



Other, higher boiling products appeared to contain the same bicyclic carbon skeleton (on the basis of infrared and NMR spectral analysis) but to have a 7-butyl substituent; insufficient amounts of these products were available for complete structure determinations. The recent observation that 7,7-dichloronorcarane reacts with *n*-butyllithium at low temperature to give a 7-chloro-7-norcaranyl radical by one

electron transfer<sup>26</sup>(The dibromo analog behaved "normally.")<sup>27</sup> might

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(26) D. B. Ledlie, PhD. Thesis, M.I.T., 1966.

(27) H. R. Ward, PhD. Thesis, M.I.T., 1961.

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be relevant to the behavior of octachlorobicyclo[2.2.1]hepta-2,5-diene.

The Diels-Alder reaction of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene and bis(trimethyltin)acetylene was also examined. It had been reported that adducts of this diene with acetylenes aromatize with loss of the bridgehead at moderate temperatures ( $\sim 100^\circ$ )<sup>28</sup>

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(28) Leading references are (a) H. Feichtinger and H. Linden, Ger. Pat. 1,105,862; C.A. 56, 2803 (1962); (b) J. Dieckman, J. Org. Chem., 28, 2880 (1963); (c) R. W. Hoffman and H. Hauser, Tetrahedron, 21, 891 (1965); (d) D. M. Lemal, E. P. Gosselink and S. D. McGregor, J. Am. Chem. Soc., 88, 583 (1966).

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and, accordingly, it seemed to offer a direct route to aromatic systems with chlorine and tin in the ortho positions. It should be noted that the behavior of the ketal bridgehead in 1,2,3,4-tetrachloro-7,7-dimethoxybicyclo[2.2.1]hepta-2,5-diene is quite different than that of a chlorine substituted bridgehead (stable to at least  $230^\circ$ )<sup>29</sup> or

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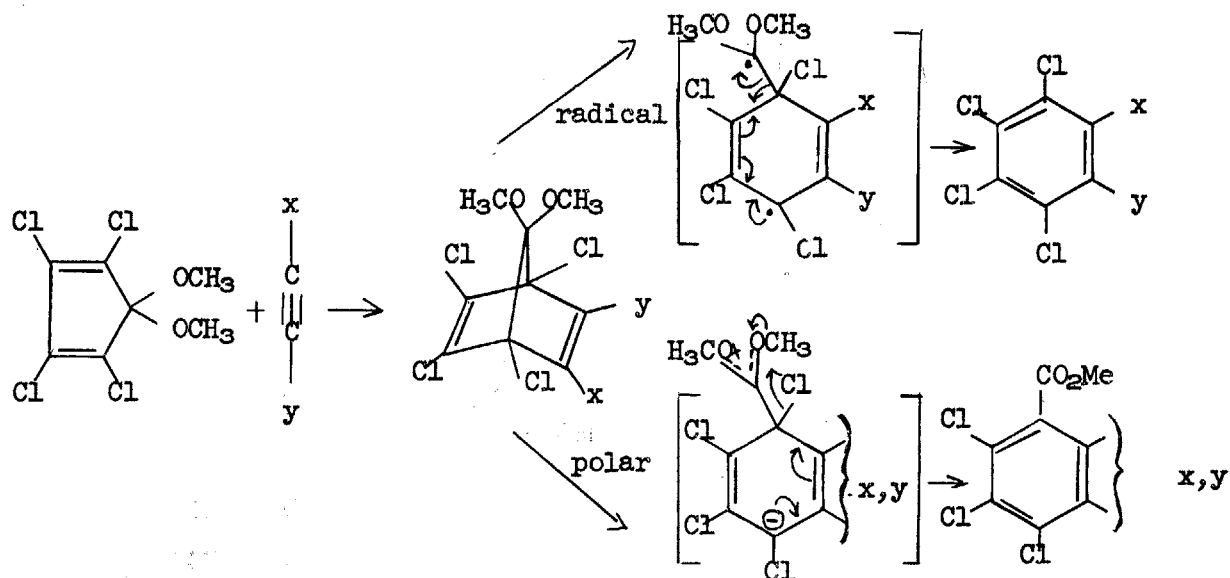
(29) (a) H. M. Molotsky, U. S. Pat. 2946817 (1960); C.A., 55, 5856 (1961); (b) Data obtained in this study.

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of a fluorine substituted bridgehead (eliminates at  $480^\circ$ ).<sup>30</sup> Loss

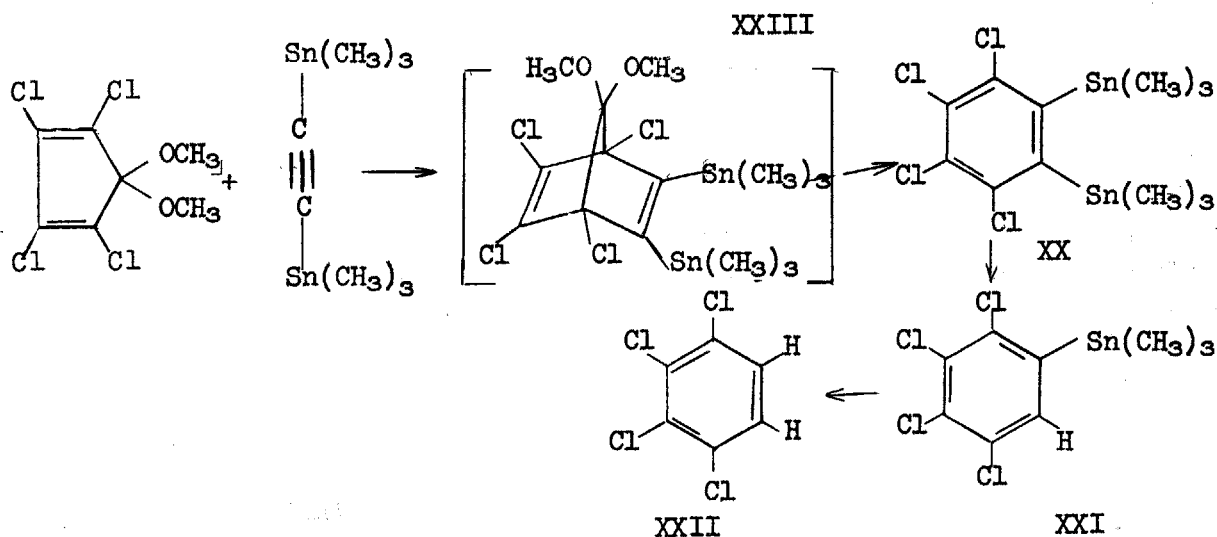
(30) E. T. McBee, D. K. Smith and H. E. Ungnade, J. Am. Chem. Soc., 77, 387 (1955).

of the bridgehead from the 1,2,3,4-tetrachloro-5,5-dimethoxy cyclopentadiene-acetylene adducts can apparently proceed by one of two paths depending on the polarity of the groups on the 5,6-double bond and on the polarity of the solvent.



The "radical" path is favored by non-polar substituents (X, Y) and solvents.<sup>28c,d</sup>

When 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene and bis-(trimethyltin)acetylene are heated in refluxing xylene or *n*-butyl ether for 24-48 hrs., the products obtained are 1,2-bis(trimethyltin)tetrachlorobenzene (XX), 1-(trimethyltin)-2,3,4,5-tetrachlorobenzene (XXI) and 1,2,3,4-tetrachlorobenzene (XXII).



The exact mixture of products obtained depends strongly on the work-up but yields of aromatic compounds are generally 40-60% (the highest yield of XX obtained was 38%). The occurrence of XXI and XXII has been shown to be due primarily to secondary reactions during the 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, show traces of absorption in the aryl region of the NMR spectrum.

The sensitivity of the C-Sn linkages in XX and XXI is due to the generally high reactivity of aryl-tin bonds (they are considerably more sensitive to electrophiles than vinyl-tin bonds)<sup>11</sup> which is enhanced in these cases by the considerable relief of strain resulting from destannation<sup>31</sup> and by the electron-withdrawing chlorine sub-

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- (31) Relief of strain has been shown to have a powerfully accelerating effect on electrophilic C-Sn cleavage; O. Buchman, M. Grosjean, J. Nasielski and B. Wilmet-Devos, *Helv. Chem. Acta*, 47, 1689 (1964).
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stituents.<sup>32</sup>

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- (32) R. D. Chambers and T. Chivers, *J. Chem. Soc.*, 4782 (1964), have found greatly enhanced susceptibility to nucleophilic cleavage in perfluoroaryltin compounds.
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None of the initial Diels-Alder adduct, 2,3-bis(trimethyltin)-1,4,5,6-tetrachloro-7,7-dimethoxybicyclo[2.2.1]hepta-2,5-diene (XXIII) is isolable under the reaction conditions. Examination of crude reaction mixtures, prior to work-up, indicated the presence of, at most, trace amounts.

The decomposition of XXIII appears to occur exclusively by the "radical path" since no compounds with the carbomethoxy moiety were isolable (an examination of crude reaction mixtures by NMR suggested that perhaps 1% might be present, but this could not be confirmed). This is as predicted by Lemal<sup>28d</sup> and Hoffmann<sup>28c</sup> since the reaction medium (xylene) is nonpolar and the 2,3-substituents have relatively weak interactions with the double bond.



## EXPERIMENTAL

Infrared spectra were recorded on either a Perkin Elmer Infra-cord 337 or 237 spectrophotometer. Absorptions at  $1603\text{ cm}^{-1}$  and  $1029\text{ cm}^{-1}$  from a polystyrene film were used to calibrate the spectra.

Ultraviolet spectra were recorded on a Cary 14 instrument by Mrs. Nancy Alvord of M.I.T.

NMR spectra were obtained with a Varian Associates A-60 spectrometer. Chemical shifts are given in p.p.m. downfield from tetramethylsilane (TMS) which was employed as an internal standard.

In some systems, the occurrence of absorptions due to the compound at about 0.0 p.p.m. necessitated the use of alternate internal standards. In these cases chloroform or cyclohexane was typically employed. The sweep calibration (chloroform, cyclohexane and TMS in carbon tetrachloride) was always checked concurrently.

Elemental analyses were performed by Dr. S. M. Nagy of M.I.T. (SMN), The Galbraith Laboratories of Knoxville, Tennessee (G), and the Schwarzkopf Microanalytical Laboratory of Woodside, N. Y. (S).

Melting points were taken with a Mel-temp or Büchi apparatus and are corrected.

Thin layer chromatograms were obtained using either 50 x 150 mm. glass plates or 25 x 75 mm. microscope slides coated with a uniform layer of Silica Gel G (Brinckman Instruments). Development was generally accomplished with iodine. In specific cases sodium sulfide or 50% sulfuric acid were utilized.

All reactions were carried out in dry flasks in an atmosphere of prepurified nitrogen using magnetic stirring, unless otherwise indicated.

References to the research notebooks are given immediately following the title of the experiments.

Bis(trimethyltin)acetylene- (I-AE-13).

Approximately 400 ml. of ammonia (National Ammonia Co.) was condensed in a 3 l., 3-necked flask equipped with mechanical stirring apparatus and a Dry Ice condenser and cooled to  $-75^{\circ}$  with a Dry Ice-acetone bath. Addition of 14.5 g. (0.63 g-atom) of sodium (J. T. Baker, purified) and 0.15 g. of ferric nitrate (Mallinckrodt anal. reagent) resulted in the formation of a very dark blue solution of sodamide; the sodium required approximately 30 min. to dissolve completely. After an additional 30 min., acetylene (Airco) was passed into the solution via a frittered glass gas dispersion tube. A vigorously exothermic reaction ensued which appeared to be over in about 15 min.; the flow of acetylene was continued for 1 hr. in all. The reaction mixture was grey and contained a large amount of suspended, white (?) solid. A solution of 98 g. (0.49 m.) of trimethyltin chloride in 500 ml. of ether (Mallinckrodt anhydrous) was added dropwise but rapidly to the reaction mixture (slow addition leads to clogging of the apparatus due to complexing of the tin halide by ammonia); the stannation was visibly exothermic. After stirring for an additional 1 hr. at  $-75^{\circ}$ , the cooling bath was re-

moved and the ammonia allowed to evaporate overnight.

An additional 700 ml. of ether was added to the reaction mixture and the solution was then filtered. The filtrate was distilled fractionally with a trap-to-trap apparatus. The first fraction (60°/0.4 mm.) contained ether, various low boiling side products and probably some(trimethyltin)acetylene. The second fraction, which distilled at ~100°/0.2 mm., consisted of a colorless, crystalline solid, m.p. 57-60° (Lit. m.p. 59-60°)<sup>7</sup>. The yield was 72 g. (83.5%).

Bis(trimethyltin)acetylene has a strong but not unpleasant odor; in view of its almost certain toxicity, this is beneficial since its presence in the atmosphere can be rapidly detected. The compound is moisture sensitive but has considerable thermal stability (It was recovered in high yields from unsuccessful Diels-Alder reactions after 7 days at 140°).

In some preparations, the product was a mixture of solids and an oil. Attempts at fractional distillation were not successful, but it was found that a product of satisfactory purity could be obtained by pumping on the sample at approximately .1 mm. (30°) for several days.

The procedure of Lappert<sup>33</sup> was also utilized in the preparation

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(33) K. Jones and M. F. Lappert, J. Chem. Soc., 1944 (1965).

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of bis(trimethyltin)acetylene and found to give an extremely pure

product, although in lower yield ( ~50%) than the sodium acetylide preparation. This procedure does have the advantage of eliminating the rather tedious trap-to-trap distillation.

(Phenylethynyl)trimethyltin- (V-AE-68).

(Phenylethynyl)trimethyltin was prepared by a slight modification of the procedure of L. Vaughan.<sup>34</sup> A solution of 0.085 m. of

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(34) L. Vaughan, these laboratories, unpublished data.

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n-butyllithium (Foote Mineral Co.) in 200 ml. of dry hexane (distilled from IAH) was added to a solution of 9.1 g. (0.089 m.) of phenylacetylene (Eastman practical grade, redistilled) in 100 ml. of hexane. The reaction was significantly exothermic and the lithium acetylide precipitated immediately. The reaction mixture was stirred vigorously for 8 hr. and, then, 22.0 g. (0.90 m.) of trimethyltin bromide in 30 ml. of hexane was added. The resultant solution was stirred for 14 hr. The reaction mixture was filtered and concentrated on a water aspirator. Distillation trap-to-trap at 90°/0.07 mm. gave 19.7 g. (86%) of colorless crystals, m.p. 58-63°. Extended pumping on the distillate raised the melting point to 60.5-66°. Prior to use, small portions were crystallized from hexane at -20° and filtered under nitrogen, m.p. 62-6°, (lit. m.p. 67°).<sup>35</sup>

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(35) H. Hartmann, B. Karbstein, B. Schaper, and W. Reiss, *Naturwissenschaften*, 50, 373 (1963).

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Propynyltrimethyltin- (VI-AE-1).

Propynyltrimethyltin was prepared by a slight modification of the method of Vaughan.<sup>34</sup> Propyne (Matheson gas) was passed into a well stirred solution of 0.148 m. of n-butyllithium in 150 ml. of pentane (freshly distilled from IAH), cooled at 0° with an ice-water bath. The reaction was visibly exothermic and a voluminous white precipitate (the acetylide) formed immediately. Addition of the propyne was discontinued after 3 hr., and the reaction mixture was stirred vigorously for another 10 hr. A solution of 35.0 g. (0.144 m.) of trimethyltin bromide in 30 ml. of pentane was added; the reaction was quite vigorous and it was necessary to cool the reaction vessel to 0°. After addition was complete, the reaction mixture was slowly warmed to room temperature and then heated at reflux for 12 hr. Filtration of the solution and concentration with a water aspirator left an evil-smelling, discolored liquid. Distillation with a Vigreux column equipped with a fraction cutter gave two fractions of relatively pure product: 17.15 g. (b.p. 135-139.5°) and 10.60 g. (139.5-41°). The crude yield is 95%. Examination of the distillate by g.l.p.c. indicated that the first fraction contained approximately 3% of a low boiling impurity but that the second fraction consisted of a single compound. Redistillation of the first fraction gave 13.2 g., b.p. 138-9° (lit. b.p. 76-8°/100 mm.<sup>36</sup>). An NMR spectrum of this ma-

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(36) M. L. Quan and P. Cadiot, *Compt. Rend.*, 254, 133 (1962).

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terial was identical with that reported for propynyltrimethyltin.<sup>37</sup>

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(37) M. P. Simonin, J. Organometal. Chem., 5, 155 (1966).

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Diels-Alder Reaction of Bis(trimethyltin)acetylene and Hexachlorocyclopentadiene: 2,3-Bis(trimethyltin)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (I) - (IV-AE-11; I-AE-15; I-AE-46).

A solution of 19.10 g. (56.7 mmole ) of bis(trimethyltin)acetylene, 14.56 g. (53.4 mmole ) of hexachlorocyclopentadiene (Hooker Chem. Co., redistilled,  $n_D^{25}$  1.5622; lit.  $n_D^{25}$  1.5614<sup>38</sup>) and 0.5 g.

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(38) H. Gerding, H. J. Prins and H. Van Bredewode, Rec. Trav. Chim., 65, 168 (1946).

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of hydroquinone in 300 ml. of n-butyl ether (Union Carbide pure, distilled from sodium) were heated for 25 hr. The solution darkened and was black after 1 hr.

Removal of volatile material by trap-to-trap distillation (30°/0.3 mm.) and then direct distillation (70°/0.05 mm.) left a black, solid residue. The residue was washed with 200 ml. of cold methanol and, then, was dissolved in pentane and decolorized with charcoal. Concentration, addition of methanol and cooling yielded two crops, 20.63 g., of off-white crystals (m.p. 84-8°); an additional 1.46 g. (m.p. 82-7°) was obtained from the methanol washings. The yield was 22.1 g. (66%). One recrystallization from pentane-methanol gave colorless crystals, m.p. 89-90°.

All analytical data were in agreement with the structure I. The NMR( $\text{CCl}_4$ ) was a singlet at 0.35 p.p.m. with satellites,  $J_{\text{Sn}^{117}\text{-H}}$  54 c.p.s. and  $J_{\text{Sn}^{119}\text{-H}}$  56 c.p.s. The infrared spectrum ( $\text{CCl}_4$ ,  $\text{CS}_2$ ) consisted of absorptions at 2980(m), 2920 (m), 1605( $\text{V}_{\text{C}=\text{C}}$ ; m), 1260 (w), 1195 (  $\text{Sn-CH}_3$  sym; w), 1160 (w), 1135(m), 1098(m), 1020(m), 863(s), 835(m), 775(  $\text{Sn-CH}_3$  rock; v.s.), 720(m), 685(m), 650(w), and  $520\text{ cm}^{-1}$ ( $\text{H}_3\text{C-Sn}$  str.; s).

Anal. Calcd. for  $\text{C}_{13}\text{H}_{18}\text{Cl}_6\text{Sn}_2$  (M. W. 624.4): C, 25.01; H, 2.91; Cl, 34.07. Found (G) (M. W. 640):<sup>39</sup> C, 24.95; H, 2.78; Cl, 33.76.

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(39) Determined osmometrically in benzene by Mrs. N. Alvord of M.I.T.

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

In some cases, especially when slightly impure acetylide was employed, the residue from distillation of the volatiles was an oil. Work-ups involving chromatographic filtration through alumina (Woelm, neutral, activity 1) or silica gel (Brinckman G) columns using pentane as the eluent were most satisfactory in these instances. Removal of the eluent gave crystalline material directly.

Diels-Alder Reaction of Propynyltrimethyltin and Hexachloro-  
cyclopentadiene: 2-(Trimethyltin)-1,4,5,6,7,7-hexachloro-3-methyl-  
bicyclo[2.2.1]hepta-2,5-diene (II) - (II-AE-66).

A solution of 6.639 g. (32.7 mmole ) of propynyltrimethyltin, 10.868 g. (40.0 mmole ) of hexachlorocyclopentadiene and 0.2 g. of hydroquinone in 50 ml. of xylene (Fisher Scientific Co., freshly distilled from sodium) was heated at reflux for 44 hr. The solution was black after 1 hr.

Removal of the solvent and starting materials by trap-to-trap distillation (80°/0.3 mm.) left an oily, black residue. This was adsorbed on a few grams of silica gel and filtered through a (7in. x 7/8in) column of silica gel using pentane (500 ml.) as the eluent. Removal of the pentane left 10.42 g. of oil from which 9.72 g. of off-white crystals, m.p. 80.5-83.5° were obtained by crystallization from ethereal-methanol at 0°. Recrystallization from the same solvent gave colorless prisms, m.p. 83-5°.

Analytical data indicated the structure II for the product. The compound had absorptions in the NMR at 2.03 p.p.m. (singlet, C-CH<sub>3</sub>) and 0.36 p.p.m. (singlet, Sn-CH<sub>3</sub>) with relative areas of 1:3. The Sn-CH<sub>3</sub> absorption had satellites  $J_{\text{Sn}^{117}\text{-H}}$  55 c.p.s.;  $J_{\text{Sn}^{119}\text{-H}}$  57 c.p.s. The infrared spectrum (CCl<sub>4</sub>) had bands at 2985(w), 2910(w), 1605( $\text{Y}_{\text{C}=\text{C}}$ ; m), 1585( $\text{Y}_{\text{C}=\text{C}}$ ; w), 1550(w), 1435(m), 1385(w), 1193( $\text{Y}_{\text{Sn-CH}_3}$  sym.; 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 cm<sup>-1</sup> ( $\text{Y}_{\text{Sn-C}}$ ; s).



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

Diels-Alder Reaction of (Phenylethynyl)trimethyltin and Hexachlorocyclopentadiene: 2-(Trimethyltin)-1,4,5,6,7,7-hexachloro-3-phenylbicyclo[2.2.1]hepta-2,5-diene (III) - (V-AE-69; I-AE-59).

A solution of 2.59 g. (9.84 mmole) of (phenylethynyl)trimethyltin, 2.85 g. (10.83 mmole) of hexachlorocyclopentadiene, and 0.1 g. of hydroquinone in 50 ml. of xylene (freshly distilled from sodium) was heated at reflux for 29 hr.

After removal of the solvent and unreacted starting materials in vacuo, the oily, black residue was dissolved in pentane and decolorized with charcoal. Attempts to induce crystals to form from pentane-methanol solutions were unsuccessful. The reaction mixture was filtered through a short silica gel column using pentane as the eluent. Concentration of the chromatographed solution, addition of methanol and cooling (several days) led to the formation of 1.10 g. (21%) of off-white crystals, m.p. 97-102°. Recrystallization from pentane-methanol or ether-methanol solution gave colorless crystals, m.p. 101.5-102.5°.

The NMR spectrum of the adduct ( $CCl_4$ ) had a broad complex multiplet at 7.0-7.52 p.p.m. (Ar-H) and a singlet ( $Sn-CH_3$ ) at 0.10 p.p.m. ( $J_{Sn^{117}-H}$  56 c.p.s.;  $J_{Sn^{119}-H}$  58 c.p.s.), with relative areas of 6:9 (should be 5:9). The infrared spectrum ( $CCl_4$ ) had bands at 3070(w), 3330(w), 2980(w), 2920(w), 1605( $\nu_{C=C}$ ; m), 1555( $\nu_{C=C}$ ; m),

$\begin{array}{c} Cl \\ | \\ Cl \end{array}$

$\begin{array}{c} C=C \\ | \quad | \\ \phi \quad Sn \end{array}$

1485(m), 1450(m), 1250(w), 1190( $\gamma_{\text{Sn-CH}_3}$  sym.; w), 1145(m), 1130(m), 1085( $\gamma_{\text{Sn-ar}}$ ; 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  $\text{cm}^{-1}$ ( $\gamma_{\text{Sn-C str.}}$ ; w).

Anal. Calcd. for  $\text{C}_{16}\text{H}_{14}\text{Cl}_6\text{Sn}$ : C, 35.74; H, 2.62; Cl, 39.56.  
Found (G): C, 35.73; H, 2.75; Cl, 39.76.

2,3-Bis(trimethyltin)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]-hepta-2,5-diene (I), Chlorinolysis: Octachlorobicyclo[2.2.1]hepta-2,5-diene (IV) - (V-AE-41; I-AE-48).

A solution of 5.04 g. (8.08 mmole ) of I in 50 ml. of chloroform (Fisher reagent) was treated in dropwise fashion with 1.19 g. (16.76 mmole ) of chlorine (Matheson; gas) in 30 ml. of chloroform (Fisher reagent). Reaction was instantaneous as evidenced by disappearance of the chlorine color. The solvent and trimethyltin chloride were removed in vacuo (30°/0.05 mm.). The residue, a yellow oil, was dissolved in pentane, filtered and concentrated. Addition of methanol and cooling yielded three crops of colorless crystals: 1.84 g. (m.p. 86-88.3°), 0.33 g. (m.p. 83-88°) and 0.27 g. (m.p. 82-6°). The crude yield was quantitative. One recrystallization from pentane-methanol gave analytically pure material, m.p. 87.5-88.5°.

Absorption spectra and elemental analysis were in agreement with the structure IV. The ultraviolet spectrum (n-heptane) had  $\lambda_{\text{max}}$  233  $\text{m}\mu$  ( $\epsilon$  4430),  $\lambda_{\text{sh}}$  239  $\text{m}\mu$  ( $\epsilon$  3630), and  $\lambda_{\text{sh}}$  265  $\text{m}\mu$  ( $\epsilon$  320).

The infrared spectrum ( $\text{CCl}_4$  and  $\text{CS}_2$ ) had absorptions at 1610 ( $\gamma_{\text{C}=\text{C}}$ ; m),  
 $\text{Cl}$   $\text{Cl}$   
 1585 ( $\gamma_{\text{C}=\text{C}}$ ; m), 1145(s), 1095(s), 1055(w), 1000(m), 920(w), 905(w),  
 $\text{Cl}$   $\text{Cl}$   
 865(w), 760(s), 700(s), 685(s), and 675  $\text{cm}^{-1}$ (s).

Anal. Calcd. for  $\text{C}_7\text{Cl}_8$ : C, 22.86; Cl, 77.14. Found (G):  
 C, 22.87; Cl, 77.30.

Brominolysis of I: 2,3-Dibromo-1,4,5,6,7,7-hexachlorobicyclo-  
[2.2.1]hepta-2,5-diene (V) - (I-AE-74; IV-AE-10).

A solution of 5.60 g. (8.97 mmoles) of III in 100 ml. of chloro-  
 form was treated in a dropwise manner with 3.00 g. (18.76 mmole )  
 of bromine (Mallinckrodt analytical reagent) in methanol (Fisher  
 reagent). Cleavage was instantaneous. Removal of the solvent in  
vacuo (60°/0.04 mm.) left a yellow, crystalline residue. This was  
 dissolved in pentane, filtered, concentrated and, then, induced to crystal-  
 lize by addition of methanol and cooling. Three crops of crystals  
 were obtained: 2.94 g. (m.p. 96.5-100°), 0.34 g. (m.p. 94-8°) and  
 0.57 g. (m.p. 91-6°); the yield was 3.85 g. (94%). One recrystal-  
 lization gave analytically pure material, m.p. 98.5-100.5°.

The ultraviolet spectrum (n-heptane) had  $\lambda_{\text{max}}$  237  $\text{m}\mu$  ( $\epsilon$  6780),  
 $\lambda_{\text{sh}}$  244  $\text{m}\mu$  ( $\epsilon$  6190) and  $\lambda_{\text{max}}$  271  $\text{m}\mu$  ( $\epsilon$  701). The infrared spectrum  
 ( $\text{CCl}_4$ ) had absorptions at 1605 ( $\gamma_{\text{C}=\text{C}}$ ; m), 1575 ( $\gamma_{\text{C}=\text{C}}$ ; m), 1230(w),  
 $\text{Cl}$   $\text{Cl}$   $\text{Br}$   $\text{Br}$   
 1120(s), 1083(s), 1075(s), 1045(w), 1005(w), 920(w), 900(s), 700(s),  
 670(m), 640(s), and 620  $\text{cm}^{-1}$ (m).

Anal. Calcd. for  $C_7Br_2Cl_8$ : C, 18.41; Hal., 81.58; Br, 35.00.  
Found (SMN, G): C, 18.58; Hal., 81.40; Br, 34.76.

Protolysis of I: 1,2,3,4,7,7-Hexachlorobicyclo[2.2.1]hepta-2,5-diene (VI) - (I-AE-67).

A solution of 2.46 g. (3.94 mmole) of I in 50 ml. of ether (Mallincrodt anhydrous) was treated in a dropwise manner, with 4.8 mmole of HCl (0.40 ml. of conc. HCl [duPont] diluted to 30 ml. with Fisher reagent methanol). Addition of saturated potassium fluoride (ethanol [1]:water[1]) converted the trimethyltin chloride to the insoluble fluoride. Filtration and separation of the ethereal layer gave a yellow solution. This was dried (anhydrous  $MgSO_4$ ) and concentrated. Column filtration (Woelm alumina) gave 0.905 g. (82%) of a colorless oil,  $n_D^{28}$  1.5469, which darkened rapidly on standing in the atmosphere. An analytical sample was obtained by distillation with a Hickman Still (b.p.  $\sim 80^\circ/0.20$  mm.;  $n_D^{25}$  1.5520).<sup>40</sup>

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(40) A. F. Plate and G. A. Tarasova, Izv. Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk, 873 (1957); C. A., 56, 7166c (1962).

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The compound was further characterized by its NMR spectrum ( $CCl_4$ ) which consisted of a singlet at 6.68 p.p.m.,<sup>41</sup> and infrared spectrum

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(41) The vinyl hydrogens in norbornadiene absorb at 6.75 p.p.m.: Varian Associates, Palo Alto, California, vol. 2, spectrum #487.

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(film) which showed peaks at 3120(w), 3080(w), 2925(imp.), 1615 ( $\gamma_{C=C}$ ; s), 1275(s), 1150(s), 1090(s), 1030(m), 1000(s), 900(s), 858(s), 790(s), 750(v.s.), 678(w), and  $640\text{ cm}^{-1}$ (m).

Anal. Calcd. for  $C_7H_2Cl_6$ : C, 21.14; H, 0.67. Found (SMN): C, 28.34; H, 0.77.

2-(Trimethyltin)-1,4,5,6,7,7-hexachloro-3-methyl(bicyclo[2.2.1]-hepta-2,5-diene (II), Chlorinolysis: 1,2,3,4,5,6,7-heptachloro-6-methylbicyclo-[2.2.1]hepta-2,5-diene (VII) - (VI-AE-30).

To an ethereal solution of 0.60 g. of IV was added a solution of chlorine (g.) in methanol until a yellow color persisted in the reaction mixture. Removal of the solvents and trimethyltin chloride in vacuo left a yellow oil. This was dissolved in pentane, filtered, concentrated, treated with methanol and cooled. Two crops of crystals, 0.305 g. (82.5%), m.p.  $91.5-93^\circ$ , were obtained. One recrystallization from the same solvent gave analytical material, m.p.  $92.3-93.3^\circ$ .

The properties of the material were in agreement with the structure IX. The NMR ( $CCl_4$ ) was a singlet at 1.95 p.p.m. The ultraviolet spectrum (EtOH) had  $\lambda_{max}$  228  $m\mu$  ( $\epsilon$  3900),  $\lambda_{sh}$  270  $m\mu$  ( $\epsilon$  285), and  $\lambda_{sh}$  270  $m\mu$  ( $\epsilon$  285). The infrared spectrum ( $CCl_4$ ) had absorptions at 2980(w), 2950(w), 2915(w), 2850(imp.), 1645( $\gamma_{C=C}$ ), 1605 ( $\gamma_{C=C}$ ), 1435(m), 1375(w), 1260(w), 1230(m), 1150(s), 1110(s), 1070(m), 1065(m), 1030(sh), 1010(s), 955(m), 910(m), 900(s), 700(s), 690(s), 635(m), and  $550\text{ cm}^{-1}$ (w).

Brominolysis of II: 2-bromo-1,4,5,6,7,7-hexachloro-3-methyl-bicyclo[2.2.1]hepta-2,5-diene (VIII) - (V-AE-49).

An ethereal solution of 0.127 g. (0.266 mmole) of II was treated in a dropwise manner with a solution of bromine in methanol until a bromine color persisted in the reaction mixture. After stirring for an additional 20 min., the volatiles were removed in vacuo. The resultant residue was dissolved in pentane, filtered and crystallized by addition of methanol and cooling. A second recrystallization (pentane-methanol) gave colorless crystals, m.p. 98.5-100.5°.

The analytical data for the product was in accord with the expected structure, VIII. The NMR ( $\text{CCl}_4$ ) was a singlet at 1.95 p.p.m. The ultraviolet spectrum (EtOH) had  $\lambda_{\text{max}}$  224  $\text{m}\mu$  ( $\epsilon$  4100) and  $\lambda_{\text{sh}}$  277  $\text{m}\mu$  ( $\epsilon$  340). The compound absorbed in the infrared ( $\text{CCl}_4$ ) at 2980(w), 2950(w), 2920(w), 2850(w; imp.), 1640( $\gamma_{\text{C}=\text{C}}$ ; m), 1600( $\gamma_{\text{C}=\text{C}}$ ; s), 1435 (m), 1380(w), 1220(m), 1150(s), 1110(s), 1060(s), 1030(sh), 1010(s), 955(s), 910(s), 905(sh), 895(sh), 885(s), 710(w), 700(w), 700(s), 690(s), 660(s), and 610  $\text{cm}^{-1}$ (s).

Anal. Calcd. for  $\text{C}_8\text{H}_3\text{BrCl}_6$ : C, 24.53; H, 0.77. Found (SMN): C, 24.13, H, 1.01.

Protolysis of II: 1,2,3,4,7,7-hexachloro-5-methylbicyclo-[2.2.1]hepta-2,5-diene (IX) - (V-AE-49).

A solution of 0.170 g. (0.36 mmole) of II in 5 ml. of ether was treated with 0.42 mmole of methanolic-HCl. The solution was

stirred overnight and, then, the solvent removed using a water aspirator. The residue, a light yellow oil, was collected by g.l.p.c. (F and M isothermal at 205° using a 6 ft. x 5 mm. column of 7.5% of General Electric's silicone SE 30 on Chromosorb P). An analytical sample was colorless and had  $n_D^{25.5}$  1.5440.

The compound had the properties expected for XI. The NMR spectrum ( $\text{CCl}_4$ ) consisted of a quartet ( $J = 2.2$  c.p.s.) at 6.20 p.p.m. and a doublet at 1.97 p.p.m. with relative areas of 1:3. The ultraviolet spectrum (EtOH) had  $\lambda_{\text{max}}$  222  $m\mu$  ( $\epsilon$  3150) and  $\lambda_{\text{max}}$  265  $m\mu$  ( $\epsilon$  550). The near infrared ( $\text{CCl}_4$ ) showed an absorption at 1.645  $\mu$  ( $6078 \text{ cm}^{-1}$ ).<sup>42</sup> The infrared spectrum (film) showed bands

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(42) The vinyl proton in 1,2,3,4-tetrachloro-7,7-dimethoxybicyclo-[2.2.1]hepta-2,5-diene absorbs at 1.644  $\mu$ : P. Gassman and H. M. Hooker, J. Am. Chem. Soc., 87, 1079 (1966).

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at 3100(w), 2980(w), 2950(w), 2920(w), 1635(w), 1600(m), 1430(m), 1380(w), 1265(sh), 1250(m), 1200(m), 1170(w), 1155(s), 1115(s), 1060(m), 1045(s), 1010(s), 999(m), 955(m), 905(s), 850(s), 710(m), 690(s), 660(s), and 630  $\text{cm}^{-1}$ (m).

Anal. Calcd. for  $\text{C}_8\text{H}_4\text{Cl}_8$ : C, 30.71; H, 1.29. Found (SMN): C, 30.74; H, 1.46.

Attempted Preparation of 2-(Trimethyltin)-1,4,5,6,7,7-hexachloro-3-iodobicyclo[2.2.1]hepta-2,5-diene - (V-AE-16).

A solution of 1.3509 g. (2.163 mmole) of I in 60 ml. of ether (1):

methanol (2) was treated dropwise with a solution of 0.5863 g. (2.31 mmole) of iodine (Mallincrodt analytical) in 50 ml. of methanol. The rate of addition was controlled so that the concentration of iodine in the reaction mixture (coloration) was always low; addition in this manner required 12 hr. Removal of solvent and trimethyltin iodide in vacuo (25°/0.05 mm.) left a yellow oil. T.l.c. analysis (silica gel-pentane) showed a single spot with the same  $R_f$  as I. An infrared spectrum (film) had absorptions at  $1605\text{cm}^{-1}(\text{m})$ ,  $1535\text{cm}^{-1}(\text{w})$ , and  $1520\text{cm}^{-1}(\text{w})$ , among others; the last two bands are at the frequencies expected for the  $\begin{array}{c} \text{I} \quad \text{I} \quad \text{I} \quad \text{Sn}(\text{CH}_3)_3 \\ | \quad | \quad | \\ \text{C}=\text{C} \quad \text{and} \quad \text{C}=\text{C} \end{array}$ , respectively, by analogy to other compounds in this series. Addition of ether to the residue resulted in the formation of a colorless precipitate (m.p.  $>250^\circ$ ). The filtrate, after long standing in the dark at  $-20^\circ$ , deposited an oily, yellow solid, 0.30 g., melting broadly around  $90^\circ$ . Recrystallization from a pentane-methanol mixture yielded faintly yellow crystals, m.p.  $99^\circ$  (dec.). The infrared spectrum (KBr) had bands at  $2975(\text{w})$ ,  $2920(\text{w})$ ,  $1605(\text{m})$ ,  $1525(\text{m})$ ,  $1195(\text{w})$ , and  $785\text{cm}^{-1}(\text{s})$ , among others. Satisfactory analytical data could not, however, be obtained for a moniodinolysis product of I.

Attempted Monobrominolysis of I: (II-AE-71).

A solution of 2.0784 g. (3.33 mmole) of I in 50 ml. of ethereal-methanol (1:1) was cooled to  $-75^\circ$  with a Dry Ice-acetone bath and treated in a dripwise manner, over 5 hr., with 0.5463 g. (3.42 mmole) of bromine in 50 ml. of the same solvent. At the end of the addition, the color of the reaction mixture indicated that bromine was still present; accordingly, the solution was warmed up slowly (5 hr.)



to room temperature. Removal of the solvent and trimethyltin bromide in vacuo left a mixture of oil and solids. The infrared spectrum (KBr) showed absorptions at  $1605\text{ cm}^{-1}(\text{s})$ ,  $1575\text{ cm}^{-1}(\text{m})$  and  $1535\text{ cm}^{-1}$ ; the latter two absorptions are due to the  $\begin{array}{c} \text{Br} \quad \text{Br} \\ | \quad | \\ \text{C}=\text{C} \end{array}$  and  $\begin{array}{c} \text{Br} \quad \text{Sn} \\ | \quad | \\ \text{C}=\text{C} \end{array}$  moieties, respectively, and the strength of the  $1605\text{ cm}^{-1}$  absorption indicated that starting material (III) was still present. The mixture could not be separated by either column chromatography (silica gel-pentane), fractional crystallization or fractional sublimation.

In another experiment, high speed stirring and a Morton flask were utilized in an attempt to effect selective cleavage of I with one equivalent of bromine. The reaction, carried out at  $30^\circ$ , involved slow addition of 0.3076 g. (1.90 mmole) of bromine in 40 ml. of methanol to 1.1795 g. (1.90 mmole) of I in 70 ml. of ether. Removal of solvents and tin halide left an oily reaction mixture from which no crystalline components could be obtained.

Halogen-metal Exchange Between 2,3-dibromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene IV and one equivalent of n-Butyllithium. Quenching with Trimethylchlorosilane - (IV-AE-15; III-AE-18).

A solution of 1.414 g. (2.50 mmole) of IV in 50 ml. of ethyl ether (Mallinckrodt anhydrous, freshly distilled from calcium hydride) was cooled to  $-75^\circ$  with a Dry Ice-acetone bath. Then 2.07 ml. of 1.20N n-butyllithium<sup>43</sup> in pentane diluted to 20 ml. with ether was

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- (43) Prepared from n-butyl chloride by halogen-metal exchange. The normality of the solution was determined by the double titration method using ethylene bromide: H. Gilman and F. K. Cartledge, J. Organometal. Chem., 2, 447 (1964).
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added dropwise over 1 hr. The reaction mixture became light brown and then deep green. Stirring at  $-75^{\circ}$  was continued for an additional 3 hr. The reaction was quenched with 1.90 ml. (15.0 mmole) of trimethylchlorosilane (Dow Corning, freshly distilled), and after an additional 30 min. allowed to warm up to room temperature.

The solvent and low boiling products were separated by distillation (trap-to-trap at  $45^{\circ}/0.45$  mm.). Analysis of the distillate by g.l.p.c. (M.I.T. isothermal at  $71.5^{\circ}$  and 14 p.s.i. of helium using an 8 ft. x 6 mm. column of 25% SE 30 on Chromosorb P.) using toluene as an internal standard and correcting for the molar responses, indicated the presence of 2.34 mmole (93.5%) of n-butyl bromide, identified by comparison of its retention time and infrared spectrum with those of an authentic sample. Less than 1% of n-butyl chloride was present.

The residue from the distillation, which consisted of black solids and an oil, was sublimed ( $25-65^{\circ}/0.03$  mm.) onto a cold finger inserted directly into the reaction vessel via a vacuum adapter. The cold finger was carefully washed with 50 ml. of carbon tetrachloride and the resultant solution analyzed by g.l.p.c. (F and M programmed run from  $150^{\circ}$ - $222^{\circ}$  at  $10^{\circ}/\text{min.}$  using a 6 ft. x 5 mm.

column of 7.5% SE 30 on Chromosorb P) using 1-chloronaphthalene as an internal standard and correcting for molar responses, indicated the presence of 2.36 mmole (94%) of 2-(trimethylsilyl)-3-bromo-1, 4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (XI) and 0.12 mmole (4.8%) of starting dibromide (V), identified by comparison of retention times and infrared spectra (of collected samples) with those of authentic materials.

An authentic sample of XI had previously been obtained by a reaction carried out in the same manner but worked up by column chromatography (Silica Gel G-pentane) and crystallization from ether-methanol mixtures (yield 66%). The sample, m.p. 97-8.5°, had a singlet in the NMR spectrum ( $\text{CCl}_4$ ) at 0.34 p.p.m. and absorbed in the ultraviolet at  $\lambda_{\text{sh}}$  225 $\mu$ ( $\epsilon$  4250),  $\lambda_{\text{max}}$  237 $\mu$ ( $\epsilon$  4250) and  $\lambda_{\text{sh}}$  275  $\mu$ ( $\epsilon$  310). The infrared spectrum contained bands at 2985(w), 2965(m), 2905(w), 1610( $\gamma_{\text{C}=\text{C}}$ ; s), 1540( $\gamma_{\text{C}=\text{C}}$ ; s), 1415(m), 1265(m), 1258( $\gamma_{\text{Si}(\text{CH}_3)_3}$  sym.; s), 1110(s), 1068(s), 1025(m), 975(m), 905( $\gamma_{\text{Si}-\text{CH}_3}$  rock; m), 890(s), 877(s), 845(s), 700(s), 690(s), 667(m), 662(m), 645(m), 615(m), and 595  $\text{cm}^{-1}$ (m).

Anal. Calcd. for  $\text{C}_{10}\text{H}_9\text{BrCl}_6\text{Si}$ : C, 26.92; H, 2.02; Br, 17.76. Found (SMN, G): C, 26.78; H, 2.11; Br, 17.95.

2-Lithio-3-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene, Protonation -(II-AE-56).

Under conditions identical to those described above, an ethereal solution of 3.46 g. (7.60 mmole) of V was treated, over the course of 1.3 hr., with 7.60 mmole of n-butyllithium (5.17ml. of 1.47 N n-butyllithium in hexane; Foote Mineral Co.). After completion of addition, the solution was stirred for 4 hr. at -75° and then quenched by addition of 15 ml. of saturated, aqueous ammonium chloride and allowed to warm up to room temperature. Separation of the aqueous and ethereal layers and washing of the aqueous layer with ether gave a black solution which was dried over MgSO<sub>4</sub>, concentrated, and chromatographed on alumina (Woelm, neutral, activity I) using pentane as solvent. The chromatography residue was 2.534 g. (crude yield is 90%) of light yellow oil which was homogeneous by t.l.c., and contained small amounts of solvent residues, on the basis of infrared and NMR spectra. Short-path distillation (Hickman apparatus) yielded a colorless liquid, b.p. ~60°/0.05 mm. which discolored rapidly on standing in the atmosphere. The compound was identified as 2-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene by its spectra and elemental analysis. The NMR spectrum (CCl<sub>4</sub>) consisted of a single peak at 6.80 p.p.m. The infrared spectrum (film) had absorptions at 3.25(w), 3090(w), 2920(imp; w), 1605( $\gamma_{\text{C}=\text{C}}$ ; s), 1565( $\gamma_{\text{C}=\text{C}}$ ; s), 1225(s), 1155(s), 1097(s), 1043(m), 1023(m), 1002(s),

$$\begin{array}{c} \text{C}=\text{C} \\ | \quad | \\ \text{H} \quad \text{Br} \end{array}$$

908(s), 900(s), 892(s), 823(s), 792(s), 702(s), 669(m), 658(m), and 597  $\text{cm}^{-1}$ (s).

Anal. Calcd. for  $\text{C}_7\text{HBRCl}_6$  (377.8): C, 22.26; H, 0.27; Cl, 56.32; BR, 21.15. Found (SMN, G) (408):<sup>44</sup> C, 22.42; H, 0.42; Cl, 56.09; BR, 20.74.

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(44) By osmometry in benzene: Galbraith Laboratories.

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2-Lithio-3-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene, Quench with Trimethyltin Bromide - (II-AE-55; V-AE-27).

Under conditions identical to those described above, a solution of 2.278 g. (5.00 mmole) of V in 40 ml. of ether (freshly distilled from  $\text{CaH}_2$ ) was cooled to  $-75^\circ$  and, then, treated in a dropwise fashion with 3.25 ml. of 1.695 N (5.51 mmole) n-butyllithium in hexane (Foote Mineral Co.) diluted to 20 ml. with dry ether. The solution was stirred for 30 min. after the completion of addition and quenched with an ethereal solution of 1.67 g. (6.87 mmole) of trimethyltin bromide. The reaction mixture was gradually warmed to room temperature, and after a few hours of stirring, stored in the dark at  $0^\circ$ . (Precautions were taken because in a previous experiment the crystalline product was observed to decompose to a brown oil with the smell of methyltin halide on standing in the atmosphere.)

After removal of the solvent on a rotary evaporator, the black residue was adsorbed on a small amount of Silica Gel G and chro-

matographed on a  $5\frac{1}{2}$  in. x  $7/8$  in. Silica Gel G column using pentane as the eluent. The residue from the chromatography (2.121 g.) was examined in the infrared ( $\text{CCl}_4$ ) and found to contain some starting material ( $\gamma_{\text{C}=\text{C}}$  at  $1575 \text{ cm}^{-1}$ ) but to consist mainly ( $\sim 75\%$ ) of a new compound with  $\gamma_{\text{C}=\text{C}}$  at  $1535 \text{ cm}^{-1}$ . Crystallization of the chromatography residue from pentane-methanol yielded three crops of crystals: 0.323 g. (m.p.  $84.3-6.3^\circ$ ), 0.480 g. (m.p.  $82-5^\circ$ ) and 0.290 g. (m.p.  $81-6^\circ$ ); the total was 1.093 g. (40% crude yield). Recrystallization of the last two crops (same solvents) yielded 0.650 g., m.p.  $83-6^\circ$ . The yield is 0.973 g. (36.3%). One additional recrystallization gave an analytical sample, m.p.  $85-86.5^\circ$ .

The compound was identified as 2-(trimethyltin)-3-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene by its infrared spectrum and elemental analysis. The infrared spectrum ( $\text{CCl}_4$ ) had absorptions at 2980(w), 2915(w), 1605( $\gamma_{\text{C}=\text{C}}$ ; m), 1535( $\gamma_{\text{C}=\text{C}}$ ; m), 1400(w), 1300(w), 1211(w), 1190( $\gamma_{\text{Sn}-\text{CH}_3 \text{ sym.}}$ ; w), 1145(m), 1090(m), 1060(s), 1020(m), 900(w), 885(m), 845(m), 775( $\gamma_{\text{Sn}-\text{CH}_3 \text{ rock.}}$ ; s)<sup>45</sup>,

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(45) From spectrum of KBr pellet.

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700(m), 685(m), 660(m), 612(m), and  $530 \text{ cm}^{-1}$  ( $\gamma_{\text{Sn}-\text{CH}_3 \text{ str.}}$ ; m).

Anal. Calcd. for  $\text{C}_{10}\text{H}_9\text{BrCl}_6\text{Sn}$ : C, 22.22; H, 1.68; Hal., 54.13. Found (SMN): C, 21.97; H, 1.73; Hal., 54.06.

2-Lithio-3-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (X); Chlorination - (IV-AE-34).

Under conditions identical to those described above, a solution of X was prepared from 4.837 g. (10.60 mmole) of 2,3-dibromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene and 8.85 ml. of 1.20 N n-butyllithium (10.60 mmole) in 200 ml. of dry ether. Then, 20 ml. (1.06 mmole) was withdrawn, with a dry, nitrogen-flushed syringe and transferred to a second flask. Gaseous chlorine (Matheson), was then passed into the solution for 10 min.

Low boiling components were removed with a water aspirator and the oily yellow residue sublimed (30-50°/0.03 mm.). The sublimation yielded colorless crystals and an oil. These were crystallized from ether-methanol, three crops being obtained: 0.183 g. (m.p. 93-4.7°), 0.105 g. (m.p. 90-2°) and 0.046 g. (m.p. 88-93°). Examination of the various fractions by g.l.p.c. (F and M isothermal at 218° and 55 ml./min of He using a 6 ft. x 5 mm. column of 7.5% SE-30 on Chromosorb P) indicated the presence of three components. The lowest boiling was present in minor amounts and was not examined further. The highest boiling component had the same retention time (comparison with an authentic sample) as the starting dibromide. The compound of intermediate retention time was the major component; its yield was estimated (all R.F.'s were assumed to be 1.00, as is not unreasonable for such similar compounds) as 0.67 mmole (63%). Collection of this component by g.l.p.c. gave colorless crystals, m.p. 92.5-5°.

The compound was identified as 2-bromoheptachlorobicyclo[2.2.1]-hepta-2,5-diene by its infrared spectrum and elemental analysis.

The infrared spectrum ( $\text{CCl}_4$ ) consisted of absorptions at 1605(s), 1585( $\text{C}=\text{C}$ ; s), 1265(w), 1175(w), 1150(s), 1130(s), 1100(s), 1055(s), 1010(s), <sup>Cl Br</sup>925(m), 910(s), 905(s), 880(m), 700(s), 685(s), 660(s), 635(s), and  $550\text{ cm}^{-1}$ (w).

Anal. Calcd. for  $\text{C}_7\text{BrCl}_7$ : C, 20.40; Br, 19.39; Cl, 60.21.

Found (G): C, 20.52; Br, 19.62; Cl, 60.10.

2-Lithio-3-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (X), Reaction with Mercuric Bromide: Bis(2-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-dienyl)mercury (XIII) - (III-AE-70; V-AE-7).

Under conditions identical to those described above, a solution of X was prepared from 1.5987 g. (3.50 mmole) of 2,3-dibromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (V) and 3.57 mmole of n-butyllithium. After stirring for 6 hr. at Dry Ice-acetone temperatures, the lithium reagent was quenched with 0.625 g. (1.74 mmole) of mercuric bromide (Mallinckrodt reagent) in 15 ml. of tetrahydrofuran (Fisher reagent, freshly distilled from calcium hydride). The reaction mixture was warmed to  $25^\circ$  and stirred overnight.

Removal of the volatiles by distillation in vacuo left a green-black residue. This was chromatographed on a  $4\frac{1}{2}$  in. x  $7\frac{7}{8}$  in. silica gel column. The first few fractions contained a yellow



oil but all successive fractions contained a single mercury compound (on the basis of the t.l.c. employing iodine and sodium sulfide developers), total 1.226 g. (72%). Repeated recrystallizations from ether-pentane mixtures yielded 1.084 g. (65.2%), m.p. 185-95°(dec.). An analytical sample had m.p. 195-8° (dec.).

The analytical data for the compound was in accord with structure XIII. The ultraviolet spectrum (EtOH) consisted of absorptions at  $\lambda_{\max}$  238 m $\mu$  ( $\epsilon$  11,400), and  $\lambda_{\max}$  285 m $\mu$  ( $\epsilon$  930); the maxima are typical of the compounds in this series and the extinction coefficients are roughly double those of the others as expected for the bis structure. The infrared spectrum (CCl<sub>4</sub>) consisted of absorptions at 1605(m), 1550( $\gamma_{\text{C}=\text{C}}$ ; m), 1260(s), 1150(m), 1105(m), 1080(s), 1035(w), 1005(m), 895(s), 885(w), 700(s), 665(m), and 630 cm<sup>-1</sup>(m).

Anal. Calcd. for C<sub>14</sub>Br<sub>2</sub>Cl<sub>12</sub>Hg: C, 17.62; Hal, 61.35; Br, 16.75. Found (SMN, G): C, 17.25; Br, 16.47.

An earlier attempt to prepare (2-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-dienyl) mercuric chloride by reaction of the lithium compound with an equivalent amount of mercuric halide yielded a mixture of products from which only traces of a compound, later identified as bis(2-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-dienyl)mercury by its infrared spectrum, could be obtained. The inability to obtain the vinylmercuric halide in good yield is believed to be due to the occurrence of symmetrization reactions. The tendency of perhalovinyl mercuric halides to undergo such reactions

is known.<sup>48</sup>

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(46) D. Seyferth and R. Towe, *Inorg. Chem.*, 1, 185 (1962).

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2-Lithio-3-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-  
2,5-diene (X), Carboxylation - (III-44).

The lithium reagent (X) was prepared as described above from 1.533 g. (2.52 mmole) of V and 2.55 mmole of *n*-butyllithium. After addition of the lithium reagent was complete, the reaction mixture was stirred for three hours at  $-75^{\circ}$  and then poured via glass and short tygon connectors onto an excess of crushed Dry Ice in a 3-necked flask equipped with magnetic stirring bar and maintained under a positive nitrogen pressure. After warming up to room temperature and stirring for 1 hr., the reaction mixture was hydrolyzed with 50 ml. of distilled water.

The ether and water layers were separated, the aqueous layer washed twice with 200 ml. of ether and the ether solutions combined and dried over sodium sulfate (Mallinckrodt anhydrous reagent). Removal of the ether left a black oil which was dissolved in carbon tetrachloride and filtered. On standing, 0.60 g. (42.5%) of brown crystals, m.p.  $116^{\circ}$  (dec.), were deposited. These did not redissolve and could not be purified.

A suspension of 0.200 g. of the black powder in ether was treated in a dropwise manner with ethereal diazomethane until the

yellow color of diazomethane persisted in the reaction mixture. Removal of the volatiles left a brown oil which was dissolved in ether and crystallized by addition of methanol and cooling; 0.105 g. (corresponds to a 20% yield) of colorless crystals, m.p. 83-7°, were obtained. An analytical sample was obtained by sublimation (45°/0.05 mm.), m.p. 85-7°.

The compound was identified as 2-carbomethoxy-3-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene by spectral data and by elemental analysis. The NMR spectrum (CCl<sub>4</sub>) consisted of a singlet at 3.85 p.p.m. The infrared spectrum (CCl<sub>4</sub>) had absorptions at 3010(imp., w), 2950(w), 1735( $\nu_{C=O}$ ; s), 1605(m), 1590( $\nu_{C=C}$  ; m),  
 $\begin{array}{c} \text{Br} \quad \text{CO}_2\text{Me} \\ | \quad | \end{array}$   
 1550(sh), 1440(m), 1305(s), 1270(s), 1195(w), 1150(s), 1130(s), 1100(s), 1045(w), 1010(m), 975(w), 905(m), 700(s), and 670 cm<sup>-1</sup>(m).

Anal. Calcd. for C<sub>9</sub>H<sub>3</sub>O<sub>2</sub>BrCl<sub>6</sub>: C, 24.84; H, 0.70. Found (SMN): C, 25.09; H, 1.08.

Attempted Preparation of 2,3-dilithio-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene from V - (III-AE-65).

Under conditions identical to those described above, a solution of 1.1424 g. (2.50 mmole) of V in 60 ml. of ether (freshly distilled from calcium hydride) was treated during 1.8 hr. with 5.20 mmole of n-butyllithium (4.23 ml. of 1.23 N n-butyllithium in hexane; Foote Mineral Co.). The reaction mixture was stirred at -75° for 4 hr. after the completion of addition, and quenched with

1.90 ml. (14.16 mmole) of trimethylchlorosilane.

The volatiles were removed by trap-to-trap distillation (25°/0.1 mm.) and analyzed, as above, for n-butyl bromide and n-butyl chloride. The yield of n-butyl bromide was 61.3% and of n-butyl chloride 22.8%. The distillation residue was sublimed (25-60°/0.05 mm.) and yielded 0.551 g. (49% crude yield) of tan crystals, m.p. 92-7°. Examination of the infrared spectrum (CCl<sub>4</sub>) of this material indicated that it was slightly impure 2-(trimethylsilyl)-3-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene. Re-sublimed material had the correct analysis for this structure.

Analysis of the residue from the sublimation, a brown powder, by NMR (CCl<sub>4</sub>) and IR (CCl<sub>4</sub>) suggest the presence of the  $\begin{array}{c} \text{Si}(\text{CH}_3)_3 \\ || \\ \text{X} \end{array}$  moiety (absorption at 0.06 p.p.m. in the NMR spectrum and 1595 cm<sup>-1</sup> in the infrared) but no pure compounds were isolable by column chromatography or crystallization.

Anal. Calcd. for C<sub>10</sub>HgBrCl<sub>6</sub>Si: C, 26.69; H, 2.02. Found (SMN): C, 27.09; H, 2.18.

Stability of 2-lithio-3-bromo-1,4,5,6,7,7-hexachlorobicyclo-[2.2.1]hepta-2,5-diene(X) - (V-AE-64).

Under conditions described above, a solution of X was prepared from 2.27 g. (5.00 mmole) of V and 5.12 mmole of n-butyllithium in 100 ml. of ether. After the n-butyllithium had been added, the solution was stirred for 2 hr. and then warmed to room temperature.

A 15 ml. aliquot was then withdrawn (after 45 min. at room temperature) with a dry, nitrogen-flushed syringe and added to a solution of 8 mmole of trimethylchlorosilane (freshly distilled) in 10 ml. of ether. After stirring for 1 hr., the volatiles were removed by trap-to-trap distillation (45°/0.6 mm.) and the residue sublimed (30-70°/0.07 mm.). Analyses of the n-butyl bromide, starting dibromide (V) and the silane XI were made by quantitative g.l.p.c. under conditions described above. Aliquots were similarly withdrawn after 25, 49, and 70 hr. at room temperature (28<sup>±</sup> 2°).

<u>Sample</u>	<u>hr.</u>	<u>mmole butyl bromide</u>	$  \begin{array}{c}  \text{Si(CH}_3\text{)}_3\text{---Br} \\  \parallel \qquad \qquad \parallel \\  \text{Br} \qquad \qquad \text{Br} \\  \text{XI} : \text{V}  \end{array}  $
1	1	0.720	17.5 : 1
2	25		1.41 : 1
3	49		.135: 1
4	70	0.737	- 1

The ratio of XI:V is considered to be the most accurate measure of the concentration of XI due to the small size of the samples and the low accuracy inherent in measurement of small amounts of a standard. The data do give a straight line plot of log[XI]-vs-time (from which  $t_{\frac{1}{2}} = 11$  hr.) may be estimated), which suggests a first order decomposition process for XI. Their accuracy is considered sufficient only to indicate the considerable stability of XI, however.

Decomposition of 2-lithio-3-bromo-1,4,5,6,7,7-hexachlorobicyclo-  
[2.2.1]hepta-2,5-diene in the Presence of 2,5-diphenyl-3,4-benzofu-  
ran-(III-AE-66).

A solution of 2.248 g. (4.92 mmole) of V and 3.167 g. (11.72 mmole) of 2,5-diphenyl-3,4-benzofuran (Columbia Organic Chemicals Co., recrystallized from ethanol, m.p. 125-9°; lit. m.p. 131-3°<sup>47</sup>) in

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(47) A. Guyot and J. Catel, Bull. Soc. Chim. France, 35, 1124 (1906).

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60 ml. of n-butyl ether (freshly distilled from sodium) at -75° was treated over 4 hr. with 5.06 mmole of n-butyllithium in 20 ml. of a 1:5 pentane:butyl ether mixture. After the completion of the addition, the solution was stirred at -75° for 4 hr. and, then, gradually warmed to 65°, at which temperature it was maintained for 10 hr. Finally, 1.90 ml. (15 mmole) of trimethylchlorosilane was added.

The volatiles were removed fractionally in vacuo by trap-to-trap distillation. Analysis of the fractions by g.l.p.c. (using conditions described above) indicated that the first fraction contained 3.62 mmole (73.6%) of n-butyl bromide and that the second fraction contained additional traces of this compound.

The residue from the distillations was sublimed (70°/0.08 mm.) and 0.5489 g. of solids and oils were obtained.

Examination of the crude sublimate by NMR (CCl<sub>4</sub>) and IR (CCl<sub>4</sub>) indicated that it was a mixture of starting dibromo compound V, and

2-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene(XVI).

Crystallization of the sublimate from a mixture of pentane and methanol yielded 0.5027 g. (~20%) of still impure V.

Column chromatography of the residue from sublimation on alumina (Woelm, neutral, activity 1) using pentane (2):benzene (1) and carbon tetrachloride yielded 3.141 g. of a mixture of 2,5-diphenyl-3,4-benzofuran and o-dibenzoylbenzene. Examination of the fractions by t.l.c. failed to indicate the presence of any other components. The infrared spectrum also indicated the absence of any halogenated bicyclo[2.2.1] moiety.

X and Furan - (VI-AE-14).

A solution of X was prepared at  $-75^{\circ}$  in 50 ml. of ether (distilled directly from IAH) from 2.370 g. (5.20 mmole) of V and 5.43 mmole of n-butyllithium. The solution was stirred for 1 hr. after the completion of addition and, then, 10 ml. of furan (Eastman Kodak reagent grade, distilled freshly from IAH, b.p.  $31.3^{\circ}$ ) was added via a dry, nitrogen-flushed syringe. The reaction mixture was warmed to room temperature ( $28 \pm 2^{\circ}$ ) and stirred for 2 days. After 50 hr., 0.4 ml. (3.5 mmole) of trimethylchlorosilane was added and the solution stirred for an additional 30 min. The volatiles were then removed by trap-to-trap distillation ( $29^{\circ}/0.03$  mm.). The distillation residue, a black oil, was dissolved in carbon tetrachloride and its NMR spectrum examined; there was absorption at 0.35 p.p.m.

( $\text{H}-\text{Si}(\text{CH}_3)_3$ ) and 6.75 p.p.m. ( $\text{H}-\text{Br}$ ) as well as some absorption

between 1-4 p.p.m. due to incomplete removal of the volatiles. The region in which the vinylic hydrogens of the 2,5-dihydrofuran moiety absorb<sup>48</sup> contained only a trace of absorption. Filtration of the

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(48) 5.3 p.p.m. and 6.5 p.p.m. in a related Diels-Alder adduct of furan: S. F. Campbell, R. Stephens and J. C. Tatlow, *Tetrahedron*, 21, 2997 (1965).

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residue through a short, silica gel column using hexane as the eluent yielded 1.340 g. of a light yellow oil. Examination of the NMR spectrum of the oil revealed the presence of absorptions at 6.75 p.p.m. and 0.37 p.p.m. only. Quantitative g.l.p.c. (under conditions described above) indicated a 17% recovery of V and the formation of 2-(trimethylsilyl)-3-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (XI) and of 2-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene(XV) in 15% and 9% yields, respectively.

Reaction of Octachlorobicyclo[2.2.1]hepta-2,5-diene (IV) and One Equivalent of n-butyllithium - (V-AE-43).

Under conditions identical to those described above, a solution of 0.915 g. (2.49 mmole) of IV in 50 ml. of ether (freshly distilled from calcium hydride) was cooled to -75° and treated with 2.53 mmole of n-butyllithium in 15 ml. of ether (10:hexane(1)). The solution became bright green during the course of the addition. After stirring for an additional 3.5 hr. at -75°, the reaction was quenched with 1 ml. of absolute ethanol (U. S. Industrial Chemicals



Co., absolute reagent).

Distillation of the mixture trap-to-trap ( $30^{\circ}/0.3$  mm.) effected removal of the solvent and volatile products. The distillation residue was then distilled directly ( $80^{\circ}/0.07$  mm.) into a trap at  $-75^{\circ}$ . The distillate consisted of solids, 0.203 g., and an oil. The solids were washed with cold methanol and dried, m.p.  $75-8^{\circ}$ . Examination by g.l.p.c. (F and M isothermal at  $200^{\circ}$  and 60 ml./min. of He using a 7.5% SE 30 on Chromosorb P column that was 6 ft. x 5 mm.) indicated that the crystals were composed of > 95% of starting material. The distillation residue and the remaining distillate were then combined and examined by g.l.p.c. (same conditions). The major component was starting material, identified by its retention time and by the infrared spectrum of a collected sample. There was also one lower boiling compound (the major product) and smaller amounts of at least 2 high boilers.

The low boiler was collected by g.l.p.c. and identified as 1,2,3,4,5,6,7-heptachlorobicyclo[2.2.1]hepta-2,5-diene. The infrared spectrum ( $\text{CCl}_4$ ) was nearly identical to that of starting material and consisted of absorptions at 1605(s), 1585(m), 1280(m), 1265(s), 1145(s), 1100(w), 1055(s), 1015(m), 920(m), 860(s), 695(s), 660(w), and  $595\text{ cm}^{-1}$ (m).

The NMR spectrum ( $\text{CCl}_4$ ) had a single absorption at 4.85 p.p.m. (IX).<sup>49</sup> The mass spectrum had a fairly weak molecular ion,  $M^{+}_{232}$

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(49) The 7H in 7-chlorobicyclo[2.2.1]hepta-2,5-diene occurs at 4.22 p.p.m.: E. I. Snyder and B. Franzus, J. Am. Chem. Soc., 86, 1166 (1964).

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( $C_7Cl_6^{35}Cl_1^{37}H$ ) and, then, a very strong ion at  $^+C_7Cl_6H$ , corresponding to loss of a chlorine and formation of the stable quadricyclic (or tropylium) ion.<sup>50</sup> Other favorable ions are  $^+C_7Cl_5H$ ,  $^+C_5Cl_5$ ,

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(50) This behavior is analogous to that of norbornadiene itself: Z. Dolejšek, V. Hanus, and H. Prinzbach, Angew. Chem., 24, 902 (1962).

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and  $^+C_5Cl_4$ .

The two high boilers were present in insufficient amounts to identify and had boiling points too close together to separate satisfactorily by g.l.p.c. A collected sample of the two had NMR and IR spectra which indicated the presence of a butyl substituent. The NMR ( $CCl_4$ ) contained complex absorption between 0.8-1.8 p.p.m. and the infrared spectrum ( $CCl_4$ ) had bands at 3030(w), 2965(s), 2940(s), 2880(m), 1610(s), and 1585  $cm^{-1}$ (s), among others.

Diels-Alder Reaction of 1,2,3,4-Tetrachloro-5,5-dimethoxycyclopentadiene and bis(trimethyltin)acetylene - (III-AE-1; IV-AE-65; V-AE-56).

A solution of 5.700 g. (2.16 mmole) of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene, prepared by the method of McBee,<sup>51</sup>

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(51) J. S. Newcomer and E. T. McBee, J. Am. Chem. Soc., 71, 949 (1949).

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(b.p.  $56^{\circ}/0.06$  mm.;  $n_D^{25}$  1.5240; lit., b.p.  $108-10^{\circ}/11$  mm.  $n_D^{20}$  1.5288), 7.125 g. (20.2 mmole) of bis(trimethyltin)acetylene and 0.1 g. of hydroquinone in 50 ml. of xylene, (distilled from sodium directly into the reaction vessel) were heated at reflux for 26 hr. The reaction flask was wrapped with aluminum foil to minimize exposure to light.

Removal of the solvent and other volatiles in vacuo ( $70^{\circ}/0.1$  mm.) left a black oil and some solids. The NMR spectrum ( $CCl_4$ ) of the crude residue had absorptions at 7.27 p.p.m. (Ar-H) and in the Sn-CH<sub>3</sub> region at 0.43 p.p.m. and 0.40 p.p.m. with relative areas (Ar-H to Sn-CH<sub>3</sub>) of 1:116. The absorption at 7.27 may be due to either 1-(trimethyltin)-2,3,4,5-tetrachlorobenzene or to 1,2,3,4-tetrachlorobenzene. There was also absorption at 3.36 p.p.m. corresponding to the methoxyl groups of the starting diene and minor absorptions at 3.90 p.p.m. (-CO<sub>2</sub>CH<sub>3</sub>?) and 3.43 p.p.m. (-OCH<sub>3</sub> of bridgehead ketal?) with areas relative to that of SnCH<sub>3</sub> of 0.017 and 0.027 respectively.

The reaction residue was dissolved in pentane; the extracts were concentrated, and diluted with methanol and cooled. Three crops of crystals, total 3.50 g., were obtained, m.p.  $113-7^{\circ}$ . Recrystallization from pentane-methanol mixtures gave 3.15 g. (28%) of colorless crystals, m.p.  $118-20^{\circ}$ .

The properties of this compound were consistent with the structure 1,2-bis(trimethyltin)tetrachlorobenzene. The NMR spectrum ( $\text{CCl}_4$ ) contained a singlet at 0.43 p.p.m. ( $J_{\text{Sn}^{117}\text{-H}}$  52 c.p.s. and  $J_{\text{Sn}^{119}\text{-H}}$  54 c.p.s.). The ultraviolet spectrum had  $\lambda_{\text{max}}$  217  $\text{m}\mu$  ( $\epsilon$  51,000) and  $\lambda_{\text{max}}$  294  $\text{m}\mu$  ( $\epsilon$  400). The infrared spectrum ( $\text{CCl}_4$  and  $\text{CS}_2$ ) had bands at 2980(m), 2915(m), 1550(m), 1390(w), 1325(m), 1265(s), 1200(w), 1190( $\gamma_{\text{Sn-CH}_3}$  sym.; m), 1135(s), 1095(w), 1155( $\gamma_{\text{Sn-aryl}}$ ; m), 1015(w), 835(m), 810(s), 775( $\gamma_{\text{Sn-CH}_3}$  rock; s), 715(m), 630(w), 580(w), and 515  $\text{cm}^{-1}$  ( $\gamma_{\text{Sn-CH}_3}$  str.; s).

Anal. Calcd. for  $\text{C}_{12}\text{H}_{18}\text{Cl}_4\text{Sn}_2$ : C, 26.62; H, 3.35; Cl, 26.19. Found (SMN): C, 26.51, 26.94; H, 3.39, 3.39; Cl, 25.89.

The discolored mother liquors from the crystallization were adsorbed on 5 g. of alumina (Woelm, neutral, actively 1) and chromatographed on 16 in. x 7/8 in. column using pentane as the eluent. Removal of the solvent gave 0.95 g. of aromatic, white needles which were found by NMR ( $\text{CCl}_4$ ) and IR ( $\text{CCl}_4$ ) spectroscopy to be an approximately 10:1 mixture of 1,2,3,4-tetrachlorobenzene and 1-(trimethyltin)-2,3,4,5-tetrachlorobenzene, by comparison with spectra of authentic sample. Recrystallization from ether-methanol-water gave 0.60 g. of colorless crystals, m.p. 44-6° (lit. m.p. 47.5° for 1,2,3,4-tetrachlorobenzene).<sup>52</sup>

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(52) Handbook of Chemistry and Physics, The Chemical Rubber Publishing Company, Cleveland, 1961.

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In another experiment, a solution of 7.8 g. (22.2 mmole) of bis(trimethyltin)acetylene and 5.50 g. (20.8 mmole) of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene in 120 ml. of *n*-butyl ether was refluxed for 36 hr. A 30 ml. aliquot was withdrawn after 12 hr but attempts to analyze it were not satisfactory. Removal of the solvent from the remainder of the reaction mixture led to formation of crystals. Thorough washing with cold methanol gave 2.93 g. (38.4%) of slightly tan crystals, m.p. 117-120°. Refrigeration of the mother liquors at -20° yielded two additional crops of crystals: 0.623 g. (m.p. 60-80°) and 0.285 g. (m.p. 55-62°).

Sublimation of the last two crops (40°/0.05 mm.) yielded colorless crystals, m.p. 64-8°. Recrystallization of the sublimate from an ether-methanol-water mixture gave fluffy needles, m.p. 65.5-68.3°. The spectra and elemental analysis indicate a structure, 1-(trimethyltin)-2,3,4,5-tetrachlorobenzene (XXI) for the compound. The NMR spectrum had absorptions at 7.27 p.p.m. (Ar-H) and 0.40 p.p.m. (Sn-CH<sub>3</sub>) with relative areas of 1:9. The trimethyltin absorption had satellites,  $J_{\text{Sn}^{117}\text{-H}} = 52$  c.p.s. and  $J_{\text{Sn}^{119}\text{-H}} = 54$  c.p.s. The ultra-violet spectrum (EtOH) had  $\lambda_{\text{max}} = 210 \text{ m}\mu$  ( $\epsilon = 86,500$ ),  $\lambda_{\text{sh}} = 237 \text{ m}\mu$  ( $\epsilon = 11,200$ ),  $\lambda_{\text{sh}} = 274 \text{ m}\mu$  ( $\epsilon = 231$ ),  $\lambda_{\text{max}} = 283 \text{ m}\mu$  ( $\epsilon = 317$ ), and  $\lambda_{\text{max}} = 292 \text{ m}\mu$  ( $\epsilon = 264$ ).<sup>53</sup>

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(53) The model system, 1,2,3,4-tetrachlorobenzene, has a similar pattern for the long wavelength absorption:  $\lambda = 294 \text{ m}\mu$  ( $\epsilon = 260$ ),  $\lambda = 280 \text{ m}\mu$  ( $\epsilon = 330$ ), and  $\lambda = 291 \text{ m}\mu$  ( $\epsilon = 290$ ): W. R. Jondorf, D. V. Park and R. T. Williams, *J. Biochem.*, **69**, 181 (1958).

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The infrared spectrum ( $\text{CCl}_4$ ) had absorptions at 3075(w), 2980(m), 2920(m), 1550(m), 1520(m), 1395(s), 1320(s), 1290(w), 1260(s), 1235(m), 1205(w), 1190( $\gamma_{\text{Sn-CH}_3}$  sym.; s), 1165(w), 1145(m), 1095(w), 1070( $\gamma_{\text{Sn-aryl}}$ ; s), 1010(w), 880(m), 845(s), 630(m), and  $530\text{ cm}^{-1}$  ( $\gamma_{\text{Sn-CH}_3}$  str.; s).

Anal. Calcd. for  $\text{C}_9\text{H}_{10}\text{Cl}_4\text{Sn}$  (M. W. 378.7): C, 28.55; H, 2.66; Cl, 37.42. Found (SMN) (M. W. 400):<sup>54</sup> C, 28.73; H, 2.79; Cl, 37.67.

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(54) Determined osmotically in benzene by the Galbraith Laboratories.

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A solution of 0.450 g (1.2 mmole) of XXI and 1.5 mmole of HCl, in 10 ml. of an ether-methanol mixture, were stirred for 48 hr. Removal of the trimethyltin chloride by conversion to the fluoride (addition of potassium fluoride), concentration and addition of water led to formation of fibrous crystals, 0.160 g. (0.74 mmole), m.p.  $41-2^\circ$ . Two recrystallizations from methanol-water yielded material, m.p.  $46.5-48^\circ$  (lit. m.p. of 1,2,3,4-tetrachlorobenzene is  $47.5^\circ$ ). The infrared spectrum ( $\text{CCl}_4$ ) was identical to that of 1,2,3,4-tetrachlorobenzene except for weak absorptions at  $2950\text{ cm}^{-1}$  and  $1260\text{ cm}^{-1}$ . The NMR spectrum ( $\text{CCl}_4$ ) was a singlet at 7.31 p.p.m.

Anal. Calcd. for  $\text{C}_6\text{H}_2\text{Cl}_4$ : C, 33.37; H, 0.94; Cl, 65.69. Found (G): C, 33.41; H, 0.71; Cl, 65.67.

In order to establish the occurrence of C-Sn cleavage during column chromatography a sample of pure 1,2-bis(trimethyltin)tetrachlorobenzene was dissolved in ether and adsorbed on some of the same

alumina used in the chromatography described above. After standing for 10 hr., the alumina was extracted with ether, the ether removed and the residue's NMR spectrum examined ( $\text{CCl}_4$ ). The ratio of Ar-H (7.3 p.p.m.) to Sn-CH<sub>3</sub> (0.4 p.p.m.) was 3:2 indicating >90% destannation had occurred.

## CHAPTER II

### DIELS-ALDER REACTIONS OF $\alpha$ -PYRONES WITH BIS(TRIMETHYLTIN)ACETYLENE AND THE CHEMISTRY OF THE ADDUCTS



The Diels-Alder reactions of cyclone, hexachlorocyclopentadiene and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene with bis(trimethyltin)-acetylene, which have been described above, all yield highly substituted adducts. The substitution pattern of the dienes cannot, moreover, be readily varied because less highly stabilized cyclopentadienones and their ketals are unstable to dimerization and exceedingly difficult to work with.<sup>1</sup>

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- (1) (a) C. F. H. Allen, J. Van Allen, J. Am. Chem. Soc., 72, 5165 (1958);  
(b) C. H. DePuy, M. Isaks and R. L. Eilers, J. Org. Chem., 29, 3503 (1964); (c) P. E. Eaton and R. A. Hudson, J. Am. Chem. Soc., 87, 2769 (1965).

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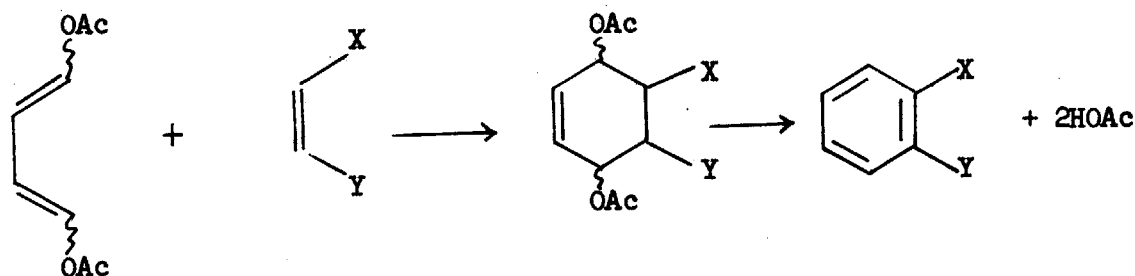
Since an examination of the properties of  $\beta$ -dimetallic systems should be more facile in less highly substituted systems, we again turned our attention to finding a simple diene that would react with bis(trimethyltin)acetylene. Particular attention was paid to diene systems that might yield aromatic compounds directly, as do cyclone and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene, in view of our especial interest in the o-bis(trimethyltin)-benzene series.

Hill and Carlson have reported that reaction of 1,4-diacetoxybutadiene and conjugated olefins and 1-acetoxybutadiene and conjugated acetylenes affords a direct route to benzene derivatives.<sup>2</sup> Their system has several

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- (2) R. K. Hill and R. M. Carlson, Tetrahedron Letters, 1157 (1964).

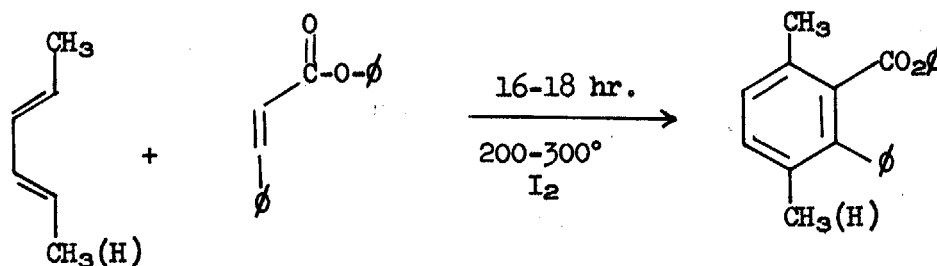
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disadvantages, however, in particular, the difficulty of preparing 1,4-diacetoxybutadiene, the rather low reactivity of both dienes and the fact that the system cannot be used with acid sensitive groups.



A recent article in the Russian literature describes a direct benzene synthesis which may have general applicability but requires pressure apparatus and rather severe conditions,<sup>3</sup> too severe for our purposes.

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- (3) D. T. Tsybikova, V. R. Skvarchenko, R. Y. Levina, Tr. Vost-Sibrosk, Tekhnol. Inst., 1, 67-73 (1962); *CA*, 62, 3957 (1965).
- 



The  $\alpha$ -pyrones, however, appeared to offer interesting possibilities. Their excellent properties as Diels-Alder dienes with classical dienophiles were noted in the earliest studies of the reaction<sup>4</sup> and the fact that the

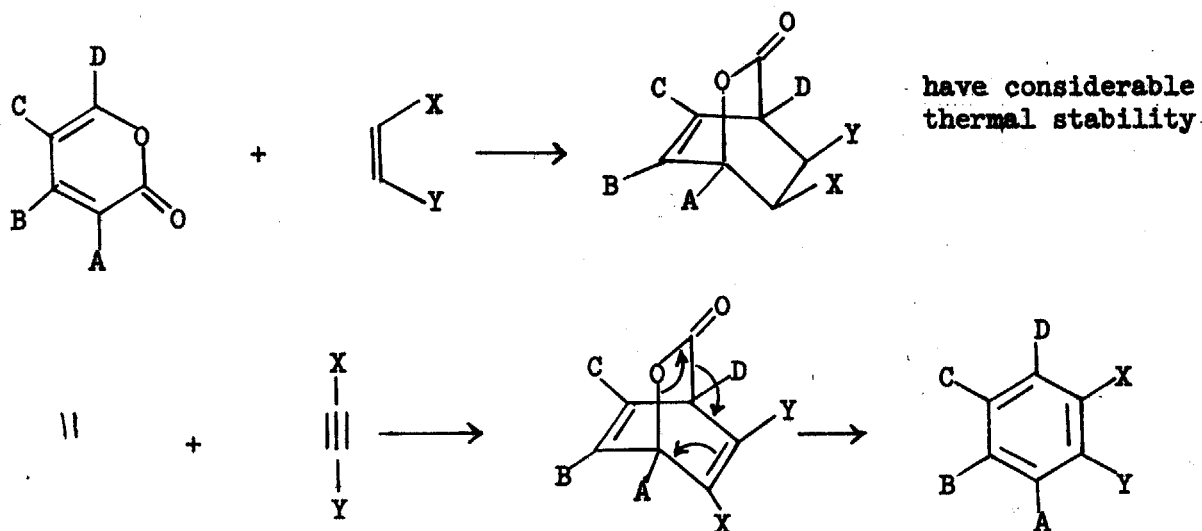
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- (4) O. Diels and K. Alder, Ann. Chem., 490, 257 (1931).
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systems contain both an electron-donating and an electron-withdrawing substituent suggests that they might be usefully reactive with the whole range of dienophiles: from electron-deficient to electron-rich. It is,

moreover, apparent from the work of Alder and Rickert and others that the Diels-Alder adducts of  $\alpha$ -pyrones with acetylenes decarboxylate under mild conditions to yield aromatic compounds.<sup>5,6</sup>

(5) K. Alder and H. F. Rickert, Chem. Ber., 70, 1354 (1937).

(6) G. Wittig and R. W. Hoffman, Angew. Chem., 73, 435 (1961).



Furthermore, the parent compound,  $\alpha$ -pyrone itself, is available in two steps from malic acid (although one involves a hot tube reaction) and many of its derivatives are well known and readily preparable.<sup>7</sup> In view

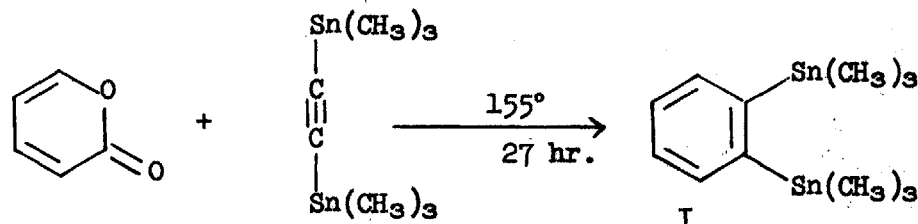
(7) J. Fried, Heterocyclic Chemistry, Vol. I (ed., R. C. Elderfield), J. Wiley and Sons, 1950, p. 354-70, and more recent references too numerous to record here.

of these properties it is surprising that the literature indicates little recognition of the synthetic possibilities of these systems outside of Zimmerman's synthesis of barralene,<sup>8</sup> a few papers in the Russian literature<sup>9</sup>

and a paper by Maerkerl.<sup>10</sup>

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- (8) H. Zimmerman and R. M. Paufler, J. Am. Chem. Soc., 82, 1514 (1960).
- (9) (a) N. P. Shusherina, R. Ya. Levina, T. S. Trubnikov, Zhurnal. Obshchei. Khim., 29, 294 (1959); CA., 54, 520 (1960). (b) N. P. Shusherina, R. Ya. Levina, Z. S. Sidenko and M. Ya. Lur'e, *ibid.*, 29, 403 (1959); CA., 54, 1510 (1960). (c) N. P. Levina, R. Ya. Levina and V. M. Shostakovskii, *ibid.*, 29, 3237 (1959); CA., 54, 12127a (1960).
- (10) G. Maerkerl, Chem. Ber., 96, 1441 (1963).
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Reaction of one equivalent of  $\alpha$ -pyrone and of bis(trimethyltin)acetylene in refluxing bromobenzene resulted in formation of o-bis(trimethyltin)benzene (I) in approximately 50% yield. The yield is considered quite satisfactory



in view of the steric hindrance of the dieneophile and the low yields in which the group IV analogs of I, o-di-t-butylbenzene<sup>11</sup> and o-bis-(trimethylsilyl)benzene,<sup>12</sup> have been synthesized by other routes.

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- (11) A. W. Burgstahler, and M. O. Abdul-Rahman, J. Am. Chem. Soc., 85, 173 (1963). (b) L. R. C. Barclay, C. E. Milligan and N. D. Hall, Can. J. Chem., 40, 1664 (1962).
- (12) H. A. Clark, A. F. Gordon, G. W. Young and M. J. Hunter, J. Am. Chem. Soc., 73, 3798 (1951) and H. A. Cook, Brit. Pat. 671,551 (1952); CA, 47, 4909 (1953).
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o-Bis(trimethyltin)benzene (I) was identified by its elemental analysis, spectral properties and by brominolysis to o-dibromobenzene which was

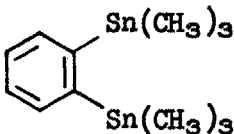
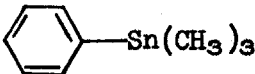
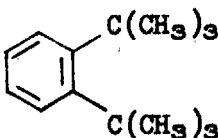
identical to an authentic sample. The NMR spectrum ( $\text{CCl}_4$ ) of I consists of a complex multiplet at 6.91-7.53 p.p.m., which is approximately an  $A_2B_2$  pattern, and a singlet at 0.31 p.p.m. ( $J_{\text{Sn}^{117} - \text{H}} = 51$  c.p.s. and  $J_{\text{Sn}^{119} - \text{H}} = 53$  c.p.s.), with relative areas of 1:4.5. The ultraviolet spectrum of I (EtOH) (see Table I) has no vibrational structure in its longest wavelength absorption, a feature that appears to be characteristic of distorted benzene rings.<sup>13</sup> Distortion of the benzene ring of I might be expected as a means

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- (13) R. T. Ingraham, "Steric Effects in Organic Chemistry" (ed., M. S. Newman), J. Wiley and Sons, New York, 1956, p. 500.
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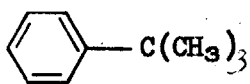
of relieving the severe interactions of the methyl groups on adjacent tin atoms. Models<sup>14</sup> suggest that the interaction of the methyl groups in I is as severe as it is in o-di-t-butylbenzene, for which a strain

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- (14) Framework Molecular Models, Prentice-Hall Inc., Englewood, N.J.
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Table I

Compound	Absorption in U.V.
	$\lambda_{\text{sh}} 217 \text{ m}\mu$ ( $\epsilon 16,700$ ) (EtOH) $\lambda_{\text{sh}} 240 \text{ m}\mu$ ( $\epsilon 2,700$ ) $\lambda_{\text{sh}} 265 \text{ m}\mu$ ( $\epsilon 430$ ); no fine structure
	$\lambda_{\text{sh}} 247 \text{ m}\mu$ ( $\epsilon 140$ ); $\lambda_{\text{max}} 253 \text{ m}\mu$ ( $\epsilon 210$ ) (EtOH) $\lambda_{\text{max}} 285 \text{ m}\mu$ ( $\epsilon 255$ ); $\lambda_{\text{max}} 264 \text{ m}\mu$ ( $\epsilon 210$ )
	$\lambda_{\text{max}} 261 \text{ m}\mu$ ( $\epsilon 189$ ); no fine structure <sup>a</sup> (solvent not given)

continued--



$\lambda_{\max}$  207  $m\mu$  ( $\epsilon$  8000)

$\lambda_{\max}$  253  $m\mu$  ( $\epsilon$  160);

$\lambda_{\max}$  257  $m\mu$  ( $\epsilon$  200) ( )

$\lambda_{sh}$  264  $m\mu$  ( $\epsilon$  160);  $\lambda_{\max}$  267  $m\mu$  ( $\epsilon$  120)

(a) E. M. Arnett and M. E. Strem, Chem. and Ind., 2008 (1961).

(b) Y. Thaya, Bull. Chem. Soc. Japan, 28, 369 (1955).

energy of at least 17 kcal. can be estimated.<sup>15</sup> The reason for

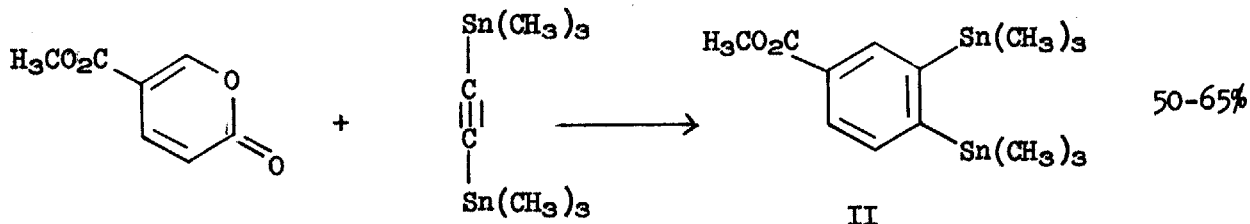
(15) See C. Hoogzand and W. Hübel, Tetrahedron Letters, 637 (1961).

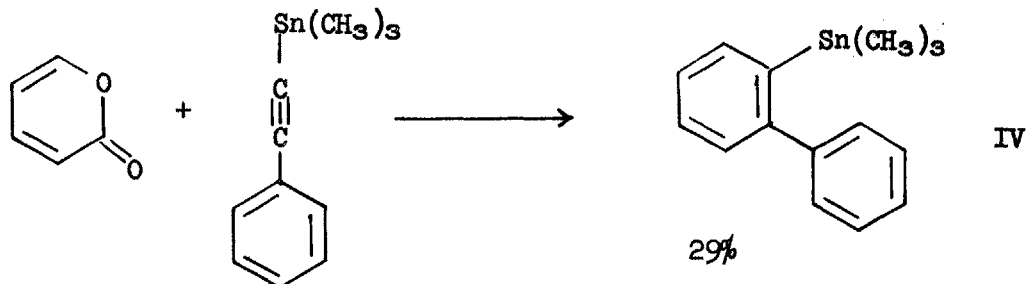
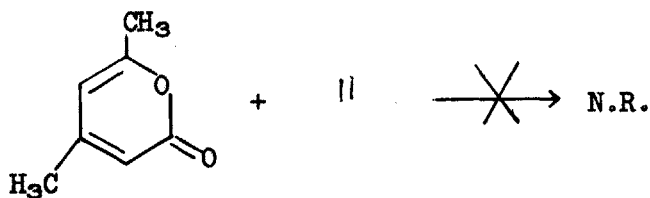
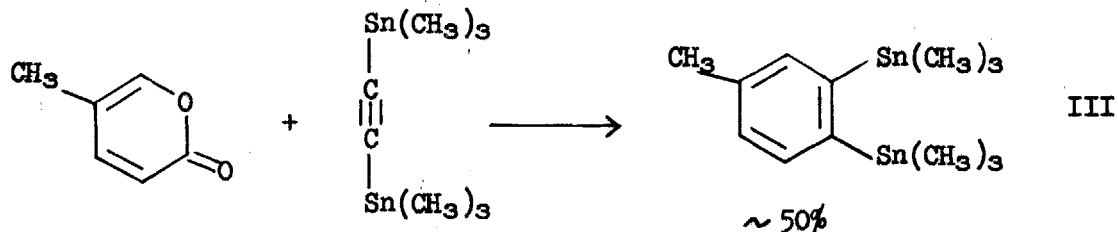
this is that the long Sn-CH<sub>3</sub> bonds, 2.17Å,<sup>16</sup> compensate for the long Ar-Sn bonds, (estimate 2.07Å) and bring the methyl groups quite close together. One other aspect of the absorption spectrum of I is noteworthy;

(16) Table of Interatomic Distances, The Chemical Society, London, 1958.

it is the occurrence of a band,  $\lambda_{sh}$  240  $m\mu$  ( $\epsilon$  2700), which has no counterpart in the spectra of either phenyltrimethyltin or o-di-t-butylbenzene. The absorption is clearly of too low an intensity to be a benzene primary band and no satisfactory explanation can be offered.

The scope and limitations of the reaction of  $\gamma$ -pyrones with organotin acetylides were examined, to some extent.





The failure of 4,6-dimethyl- $\alpha$ -pyrone to react must be due to steric effects since models<sup>14</sup> indicate severe interactions between the 6-methyl group and trimethyltin group long before the two molecules are within bonding distance. This system serves to define a limitation on the reaction of  $\alpha$ -pyrones with bis(trimethyltin)acetylene, although 6-substituents do not create such problems with less hindered dienophiles.<sup>9</sup> The fact that  $\alpha$ -pyrones react as readily as they do with these extremely hindered dienophiles is a powerful recommendation for their utility as a general tool for the synthesis of specifically substituted benzene derivatives.

Methyl 3,4-bis(trimethyltin)benzoate (II), 3,4-bis(trimethyltin)toluene (III) and 2-biphenyl(trimethyltin) (IV) are all new compounds and were characterized by their elemental analyses and spectra; IV was also converted to the known

2-iodobiphenyl by treatment with iodine. Several features of the spectra of these systems are noteworthy. III, similarly to I and to 1,2-bis-(trimethyltin)tetrachlorobenzene (see Chapter 1, experimental section), has no fine structure in its longest wavelength absorption in the ultraviolet region. (In II, interaction of the ester and benzene chromophores complicates observation of this phenomenon.) In the NMR spectrum of IV, the  $(\text{CH}_3)_3\text{Sn}$  group appears at 0.03 p.p.m. above TMS due to shielding by the ring current of the skewed, ortho-phenyl group; this is typical of other compounds in this study which have a phenyl group  $\beta$ - to a trimethyltin.

The availability of the variously substituted  $\alpha$ -pyrones made possible the evaluation of electronic effects on the Diels-Alder reactions of bis(trimethyltin)acetylene. If it behaves as a classical dienophile (see Chapter 1, discussion), a methyl substituent should enhance and a carbomethoxy lower the reactivity of an  $\alpha$ -pyrone towards it. If, as has been suggested earlier, Diels-Alder reactions of this acetylide are examples of the reaction with "inverse electron demand"<sup>17</sup> then the substituents

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(17) J. Sauer and H. Wiest, *Angew. Chem.*, 74, 353 (1962).

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should have the opposite effect. The term "inverse electron demand" was coined by Sauer to reflect his observation that hexachlorocyclopentadiene, an electron-deficient diene, reacted more readily with electron-rich and simple olefins than with classical, electron-deficient systems such as maleic anhydride. This phenomenon had previously been observed, although differently interpreted, in the reaction of acrolein with various dienophiles<sup>18</sup>

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(18) C. W. Smith, D. G. Norton and S. A. Ballard, *J. Am. Chem. Soc.*, 73, 5267 (1951).



and additional examples have been found recently in the reactions of 1,2,4,5-tetrazines<sup>19,20</sup> and tetrachloro-o-quinone.<sup>21</sup> Although the mechanistic

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(19) J. Sauer and D. Lang, *Angew. Chem.*, 76, 603 (1964).

(20) J. Sauer, A. Mielert, D. Lang and D. Peters, *Chem. Ber.*, 98, 1435 (1965).

(21) M. G. Ettlinger and C. S. Lewis, *Texas J. Sci.*, 14, 58 (1962).

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implications of these observations are not entirely clear, it seems that they lend support to the "one step mechanism" for the Diels-Alder Reaction,<sup>22</sup>

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(22) For a recent review of the subject see A. Wasserman, "Diels-Alder Reactions," Elsevier, Amsterdam, 1965.

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at least for these and closely related systems. In this mechanism, the transition state is represented as a "complex" of diene and dienophile, set one above the other with endwise overlap of the  $\pi$  orbitals. The extent of bond formation in the transition state depends on the specific characteristics of the reactants, and any factor which enhances the movement of electrons between diene and dienophile stabilizes the transition state. If this is an accurate picture of events in the Diels-Alder reaction, it is reasonable that factors encouraging the movement of electrons between the reactants in either direction should similarly lower the energy of the transition states, and this is exactly what the observation of an "inverse electron demand"<sup>17-21</sup> seems to suggest.

There is a problem inherent in the use of substituted  $\alpha$ -pyrones to examine electronic effects on Diels-Alder reactions. Fried has noted that phenyl and carbomethoxy substituents stabilize the  $\alpha$ -pyrone nucleus<sup>7</sup>,

and our experience suggests that even methyl groups have this effect. It is, therefore, possible that small electronic effects of substituents might be swamped out by their stabilization of the  $\alpha$ -pyrone nucleus.



Competition reactions were run between  $\alpha$ -pyrone and 5-carbomethoxy- $\alpha$ -pyrone(methyl coumalate) and  $\alpha$ -pyrone and 5-methyl- $\alpha$ -pyrone. The reactions were carried out in refluxing bromobenzene and were analyzed by both NMR spectroscopy and quantitative g.l.p.c.

Table 2

<u>Reactants</u>	<u>Yields</u>	<u>Relative Reactivity</u>
$\alpha$ -pyrone (1.00)	I 0%	1
5-carbomethoxy- $\alpha$ -pyrone (0.80)	II 64.5%	80>
bis(trimethyltin)acetylene (0.86)		
$\alpha$ -pyrone (1.00)	I 26%	1
5-methyl- $\alpha$ -pyrone (0.94)	III 35%	1.23
bis(trimethyltin)acetylene (0.97)		

Although it would be extremely desirable to extend the series, the greatly increased reactivity of the electron-deficient 5-carbomethoxy- $\alpha$ -pyrone can only be due to an electronic effect [ $\alpha$ -pyrone and bis(trimethyltin)acetylene give 50% yields of I under these conditions] and strongly suggests that this is a case of a Diels-Alder reaction with "inverse electron demand." The slight rate enhancement obtained with the electron-donating 5-methyl substituent does not contradict this, since the electronic effect of a methyl group is apparently small in these cases<sup>19</sup> and may easily be compensated for by its stabilization of the  $\alpha$ -pyrone nucleus. The qualitative observation that (phenylethynyl)trimethyltin reacts less readily with  $\alpha$ -pyrone than does bis(trimethyltin)acetylene,

despite a decrease in the steric hindrance, is in accordance with the results of the competition if the  $(\text{CH}_3)_3\text{Sn}$  group is assumed to be significantly electron-donating inductively (see discussion in Chapter 1).

The results of the competitions correlate closely with Sauer and Lang's study of the Diels-Alder reaction of 1,2,4,5-tetrazines with styrene<sup>19</sup> where it was found that the tetrazine's reactivity increased as the 3,6-substituents were varied as follows:  $\text{CO}_2\text{CH}_3 \gg \text{p-NO}_2$    $>$    
 $\approx \text{CH}_3$ . The dienophiles used in both these studies are similar in that they are electron-rich relative to a classical system such as maleic anhydride. These data suggest the empirical rule that simple and electron-rich olefins will undergo the Diels-Alder reaction most readily with electron-deficient dienes. This may have important synthetic implications in the use of such hitherto little employed dienophiles in the diene synthesis. When one considers both these data and the results obtained with  $\alpha$ -pyrones and classical dienophiles,<sup>5,10</sup> it seems that if one studied the Diels-Alder reactions of this diene with the entire spectrum of olefins (electron-rich to electron-deficient), or of certain olefins with a spectrum of substituted dienes, one might observe high reactivity at both ends of the scale where the diene and dienophile form a good electron donor-acceptor pair and lower reactivity in the center of the scale where they do not. This would constitute a very nice confirmation of the "one step mechanism" for the Diels-Alder reaction.

Returning now to the specific system composed of  $\alpha$ -pyrones and organotin acetylides, it is apparent that the reaction is a useful route to unusual aromatic tin compounds. The availability of a broad spectrum

of functionally substituted organotin acetylides of the type  $R_3SnC\equiv C-X$  (where X may be aryl, alkyl,  $-CH_2OR$ , CN, to name only a few) from the work of Shostakovski and of Neuman<sup>23</sup> and the possibility of using Lappert's tin amide system<sup>24</sup> to stannate any terminal acetylene makes this route quite a practical one. The fact that the trialkyltin group in the Diels-Alder

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- (23) (a) W. P. Neuman and F. G. Kleiner, Tetrahedron Letters, 3779 (1964);  
(b) M. F. Shostakovski, V. M. Vlasov and R. G. Mirskov, Dokl. Akad. Nauk. S.S.S.R., 159, 869 (1964); CA, 62, 7788 (1965).
- (24) K. Jones and M. F. Lappert, J. Chem. Soc., 1944, 2157 (1964).

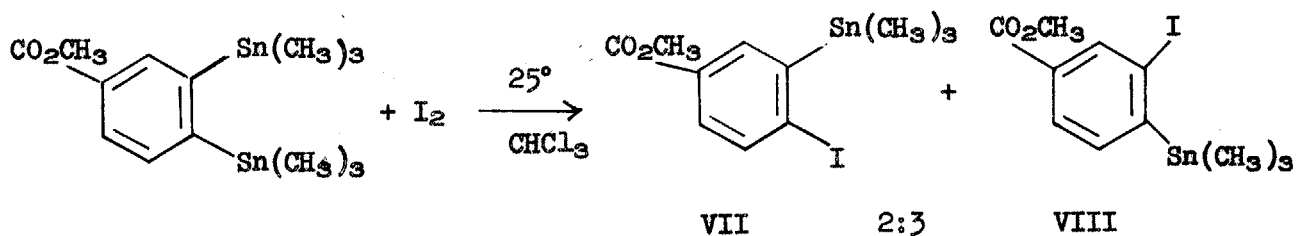
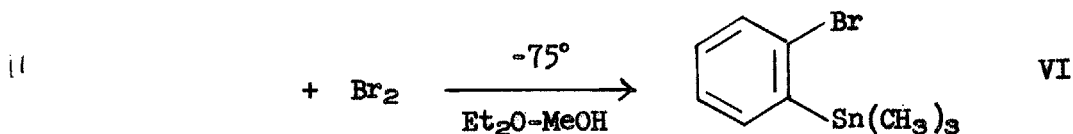
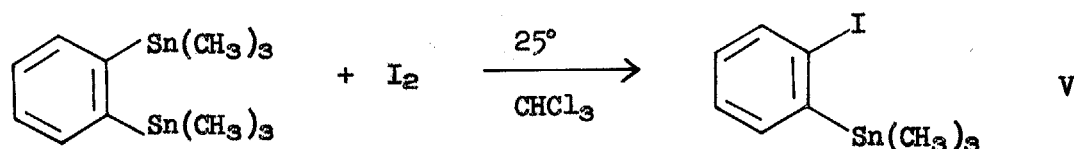
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adducts can be replaced under mild conditions by any of a large number of groups<sup>25</sup> increases the synthetic possibilities of the system still further.

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- (25) For example, H, Cl, Br, I,  $HgCl_2$ , Ag,  $SO_3$ ,  $PCl_2$ , etc.: R. K. Ingham, S. D. Rosenberg and H. Gilman, Chem. Revs., 60, 479 (1960).

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Some of the Chemistry of the adducts I-IV has been examined both in order to prepare the o-halo(trimethyltin)benzenes, which were of interest to us, and to determine their synthetic possibilities. Treatment of o-bis(trimethyltin)benzene with one equivalent of iodine at room temperature resulted in rapid formation of o-iodo(trimethyltin)benzene(V) in virtually quantitative yield. Monoiodinolysis of methyl 3,4-bis(trimethyltin)benzoate occurs analogously but yields a mixture of positional isomers. The reaction of one equivalent of bromine with I was not selective at room temperature, forming both mono- and dibromo compounds, but at  $-75^\circ$ , o-bromo(trimethyltin)-benzene was the only product (85%). The selectivity of these reactions must be due to a combination of steric effects which increase the reactivity of



the o-ditin compounds and electronic effects which reduce the reactivity of o-halo(organotin) compounds to electrophiles; the sensitivity of halodestannylation to both factors has been demonstrated by Nasielski and coworkers.<sup>26</sup>

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(26) O. Buchman, M. Grosjean and J. Nasielski, *Helv. Chem. Acta*, **47**, 1679 (1964).

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The compounds V-VIII, all of which have not been reported previously in the literature, were identified by their elemental analyses and spectral properties. It is interesting that both V and VI show fine structure in their longest wavelength absorption in the ultraviolet, suggesting that the benzene ring is no longer distorted from planarity by steric repulsions as it apparently is in I.<sup>13,14</sup> All four compounds are stable, pleasantly aromatic oils. A report on the preparation of

of o-chloro(tri-n-butyltin)benzene, by a rather questionable route, in which it is described as an unstable, evil smelling liquid is, thus, extremely curious.<sup>27</sup>

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- (27) T. Chao-lun, T. Shi-hua, C. Kuo-ming, Scientifica Sinica (Notes), XIII, 1170 (1964).

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Treatment of I with two equivalents of bromine in chloroform gave o-dibromobenzene in high yield, indicating that C-Sn cleavage in the o-halo(trimethyltin)benzenes presents no problems. Clearly, by taking advantage of the possibility for selective monocleavage and by varying the electrophilic reagent used<sup>25</sup> a wide variety of o-disubstituted aromatic systems can be prepared from I and its analogs.

We were particularly intrigued by the possibility of preparing o-dilithiobenzene from I by metal-metal exchange reactions.<sup>28</sup> o-Dilithio-

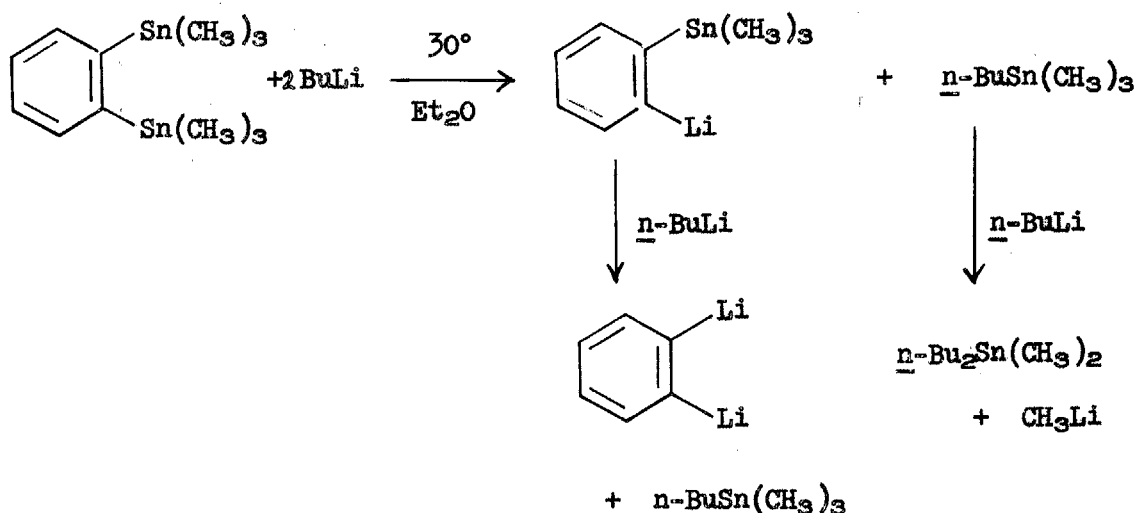
- 
- (28) D. Seyferth, M. A. Weiner, L. G. Vaughan, G. Raab, D. E. Welch, H. M. Cohen and D. Alleston, Bull. Soc. Chim. Fr., 1364 (1963).

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benzene is of interest from both synthetic and theoretical points of view, and, although it has been prepared by Wittig by a very elegant procedure,<sup>29</sup> it is not readily available.<sup>30</sup>

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- (29) G. Wittig and F. Bickelhaupt, Chem. Ber., 91, 883 (1958).
- (30) It cannot be prepared directly from o-dihalobenzene although low yields of the diGrignard can be obtained in this way: H. Heaney, F. G. Mann and I. T. Millar, J. Chem. Soc., 3930 (1957).
-

Preliminary investigations of the reaction of organolithium reagents with I were encouraging, but, on closer scrutiny, the system appears to be quite complex. When two equivalents of n-butyllithium in ether were utilized and the reaction mixture quenched with deuterium oxide, a low yield of benzene (8%), at least partially o-dideuterated, was obtained. The presence of di-n-butyldimethyltin in the reaction mixture and of 1,1-diphenylethylene when benzophenone quenching was utilized indicate the following reaction sequence. Apparently reaction of a second equivalent of n-butyllithium with the charged, solvated o-lithio(trimethyltin)benzene



is not favorable and the n-butyltrimethyltin is attacked instead. Investigation of this metal-metal exchange reaction in other solvents and with other reagents, in particular, methylolithium, is being continued by other workers in this laboratory. The possibility that o-lithio(trimethyltin)benzene might have limited stability at ambient temperatures has been raised. A synthetically useful system has not yet been obtained.

### Experimental

Comments on experimental and analytical techniques made in the first chapter are also true for this section. In particular, it is reiterated that all reactions were carried out in dry, nitrogen-flushed flasks under a positive pressure of prepurified nitrogen.

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#### Preparation of $\alpha$ -Pyrone<sup>31</sup> - (V-AE37,40).

(31) The preparation is based on one alluded to in ref. 8.

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Into a 50 ml. round bottomed flask was placed 14.47 g. (12.50 mmole) of coumalic acid (m.p. 209-14°; lit., m.p. 206-9° (dec.))<sup>32</sup> prepared

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(32) R. H. Wiley and N. R. Smith, Org. Syn., Coll. Vol. IV, J. Wiley and Sons, New York, 1963, p. 549,

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according to the method of Wiley and Smith.<sup>32</sup> The flask was connected by a Pyrex adapter (24/40 joints) wrapped with resistance wire to a vycor tube (20 mm. o.d. x 1 ft. in length) packed with copper gauze which was, in turn, connected to a trap and to a vacuum line. The vycor tube was enclosed in another vycor tube which was carefully wrapped with resistance wire and insulated from the atmosphere. The entire system was heated and evacuated (90°/0.02 mm.) prior to reaction. Then, the temperature in the vycor tube was raised to 625°  $\pm$  25° (measured by iron-constantan thermocouple) and the temperature of the pot and inlet system gradually brought up to 170°. The trap was cooled to -75° with a Dry Ice-acetone bath and kept open to the vacuum pump throughout. (The pressure rose to 0.3 mm.



during the course of the reaction.) After 5 hr., only a black residue remained in the pot and the trap contained 8.97 g. of golden liquid. Short path distillation yielded 8.20 g. (68.5%) of colorless, sweet-smelling oil, b.p.  $95^{\circ}/0.16$  mm.;  $n_D^{25}$  1.5251,  $d_4^{25}$  1.262 (lit. b.p.  $103-5^{\circ}/21$  mm;  $n_D^{22}$  1.5277)<sup>33</sup>

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(33) H. Von Pechman, Ann. Chem., 264, 272 (1891).

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The liquid was characterized as  $\alpha$ -pyrone by its spectral properties and elemental analysis. These are recorded below as they are not reported in previous preparations of the compound. The NMR spectrum ( $(CH_3)_2CO$ ) was the complicated pattern expected for an ABXY system with bands at 6.2-5 p.p.m. (2H :  $H_1$  and  $H_3$ ) and 7.35-7.85 p.p.m. (2H :  $H_2$ ,  $H_4$ ). The infrared spectrum had bands at  $3150\text{ cm}^{-1}$ ,  $3100$  (w),  $3025$  (2),  $1795$  (sh),  $1745$  ( $\nu_{C=O}$ ; s),  $1725$  ( $\nu_{C=O}$ ; s),  $1650$  ( $\nu_{C=C}$ ; m),  $1635$  (m),  $1550$  (s),  $1445$  (m),  $1380$  (w),  $1245$  (s),  $1175$  (w),  $1120$  (s),  $1085$  (s),  $1065$  (s),  $975$  (w),  $945$  (m),  $845$  (m),  $780$  (s),  $720$  (s) and  $605\text{ cm}^{-1}$  (m). The doublet for the carbonyl (Fermi resonance) and the C=C stretch at  $1650\text{ cm}^{-1}$  are highly characteristic of  $\alpha$ -pyrones.<sup>34</sup>

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(34) K. N. Nakanishi, "Practical Infrared Spectroscopy," Holden Day, San Francisco, 1961, p. 42.

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Calcd. for  $C_6H_4O_2$ : 62.50; H, 4.19.

Found (SMN): 62.31; H, 4.48.

5-Carbomethoxy- $\alpha$ -pyrone (Methyl Coumalate) - (V-AE-74).

This  $\alpha$ -pyrone was prepared by the method of Boyer and Schoen<sup>35</sup>

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- (35) J. H. Boyer and W. Schoen, Org. Syn., Coll. Vol. IV, J. Wiley and Sons, New York, 1963, p. 532.

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from coumalic acid.<sup>32</sup> The crude yield was 30%. Several recrystallizations from ethylacetate gave aromatic, colorless crystals, m.p. 69.5-71.5 (lit. m.p. 68-70°).<sup>35</sup>

4,6-Dimethyl- $\alpha$ -pyrone (3,5-Dimethylcoumalin).

A sample of this compound was obtained from Dr. A. Musco of M.I.T. Several recrystallizations from hexane-acetone yielded colorless crystals, m.p. 47.7-50.3° (lit. m.p. 50-1°).<sup>36</sup>

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- (36) N. R. Smith and R. H. Wiley, ibid., p. 337.

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5-Methyl- $\alpha$ -pyrone - (VI-AE21,24).

5-Methyl- $\alpha$ -pyrone was prepared by the method of Fried and Elderfield<sup>37</sup> starting from ethyl pent-2-enoate prepared according to von Auwers.<sup>38</sup>

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- (37) J. Fried and R. C. Elderfield, J. Org. Chem., 6, 566 (1941).  
(38) K. von Auwers, Ann. Chem., 422, 150 (1921).

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In our hands, the preparation of the 5-methyl- $\alpha$ -pyrone was, as reported, very straightforward with the exception of the conversion of 4-methyl-2-hexene-5-one-1,6 dioic acid to 5-methyl-6-carboxy- $\alpha$ -pyrone. This reaction generates considerable pressure, and one bomb tube exploded and a second

opened somewhat spectacularly; the reference mentions only that the bomb tube opened without pressure. The last step was done on a rather small scale and the product, a pleasant smelling oil, b.p.  $97^{\circ}/8.5$  mm.,  $n_{D}^{25.4}$  1.5227 (lit.  $n_{D}^{25}$  1.5210)<sup>37</sup>, was faintly yellow; purity was estimated by g.l.p.c. as at least 96%.

Diels-Alder Reaction of  $\alpha$ -Pyrone and Bis(trimethyltin)acetylene:

o-bis(trimethyltin)benzene (I) - (IV-AE-41).

A solution of 4.03 g (42.0 mmole) of  $\alpha$ -pyrone, 14.05 g (40.0 mmole) of bis(trimethyltin)acetylene and 0.3 g of hydroquinone in 250 ml. of bromobenzene (Fisher Reagent, freshly distilled from  $P_2O_5$ ) were heated at reflux for 31 hr. The solution turned yellow and then red, apparently due to some decomposition of the  $\alpha$ -pyrone.

Removal of the solvent by direct distillation at  $30^{\circ}/0.1$  mm. left an oily, red residue. The residue was extracted with 100 ml. of ether, filtered and the ether removed. Distillation with a short path apparatus gave 7.84 g. of faintly yellow oil, b.p.  $92-4/14.5$  mm.,  $n_{D}^{25}$  1.5623. A forerun of 2.29 g. was filtered through a short alumina column (9 in. of Woelm, neutral, activity 1) using hexane as the eluent and yielded 1.119 g. of colorless oil,  $n_{D}^{25}$  1.5573. Redistillation of the crude product gave 8.27 g.,  $n_{D}^{25}$  1.5629 (51.4%). An analytically pure sample had  $n_{D}^{25}$  1.5640.

If the crude reaction mixture was first filtered through a short alumina or silica gel column using pentane or hexane as the eluent and, then, distilled, analytically pure material was obtained directly; loss of material in this procedure is a function of scale but should be less than 5%.

The oil had the properties expected for o-bis(trimethyltin)benzene. The NMR and UV spectra have been discussed above. The infrared spectrum (film) had absorptions at 3125(w), 3100(w), 3045(m), 2970(m), 2915(m), 2000-1700(w), 1445(w), 1425(w), 1260(m), 1205(sh), 1190( $\gamma_{\text{Sn-CH}_3}$  sym.; m), 1095( $\gamma_{\text{Sn-aryl}}$ ; m), 1025(m), 770( $\gamma_{\text{Sn-CH}_3}$  rock; v.s.), 740( $\gamma_{\text{o-aryl}}$ ; s), 710(s), 640(w) and  $530 \text{ cm}^{-1}$  ( $\gamma_{\text{Sn-CH}_3}$ ; w).

Calcd for  $\text{C}_{12}\text{H}_{22}\text{Sn}_2$ : C, 35.70; H, 5.49.

Found (SMN): C, 35.85; H, 5.55.

The reaction was also run in refluxing xylene and n-butylether, but the yields were less satisfactory: 28.5% and 15%, respectively.

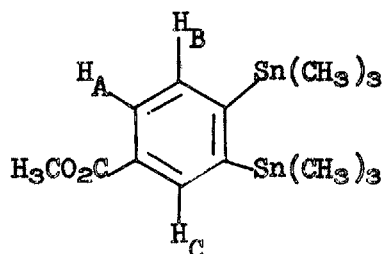
Diels-Alder Reaction of 5-Carbomethoxy- $\alpha$ -pyrone (Methyl Coumalate) and Bis(trimethyltin)acetylene : Methyl 3,4-Bis(trimethyltin)benzoate (II) - (III-AE-62).

A solution of 2.110 g. (15.0 mmole) of 5-carbomethoxy- $\alpha$ -pyrone, 5.0 g. (14.2 mmole) of bis(trimethyltin)acetylene and 0.1 g. of hydroquinone in 50 ml. of n-butyl ether (freshly distilled from sodium) were heated at reflux for 12 hr., at the end of which time the reaction mixture was dark red. Examination of the solution by t.l.c. (silica gel-pentane) revealed a new component with  $R_f$  considerably longer than those of the starting materials.

Removal of the volatiles by trap-to-trap and, then, direct distillation ( $50^\circ/0.08 \text{ mm.}$ ) left red solids and oils. The solids were insoluble in ether but soluble in acetone. Accordingly, the residue was extracted with 50 ml. of ether. One third of the solution was concentrated and introduced to a Hickman distillation apparatus. Distillation yielded a colorless liquid boiling at approximately  $120^\circ/0.09 \text{ mm.}$ ,  $n_D^{24}$  1.5654. Redistilled

material had  $n_D^{25}$  1.5613. The yield was 3.50 g. (49.4%).

The compound was identified as methyl 3,4-bis(trimethyltin)benzoate by its NMR and infrared spectra and by elemental analysis. The NMR spectrum ( $\text{CCl}_4$ ) is particularly characteristic:



$H_A$	7.71 p.p.m. (4X), $J_{AB} = 7.5$ c.p.s.;
	$J_{AC} = 2$ c.p.s.
$H_B$	7.41 p.p.m. (2X)
$H_C$	7.98 p.p.m. (2X)
O-CH <sub>3</sub>	3.77 p.p.m.
Sn(CH <sub>3</sub> )	{ 0.27 p.p.m. 0.28 p.p.m.

The infrared spectrum (film) consisted of absorptions at 3125(sh), 3050(sh), 2980(m), 2945(m), 2910(m), 2835(w), 1720( $\gamma_{C=O}$ ; v.s.), 1580(m), 1540(w), 1460(sh), 1425(s), 1380(w), 1360(m), 1290(v.s.), 1255(s), 1240(s), 1195( $\gamma_{Sn-CH_3}$  sym.; m), 1120(s), 1080( $\gamma_{Sn-aryl}$ ; s), 1070(sh), 1025(w), 975(w), 915(w), 840(w), 770( $\gamma_{Sn-CH_3}$  rock; s), 720(s), 655(w) and 525  $\text{cm}^{-1}$  ( $\gamma_{Sn-CH_3}$  str.; w). The ultraviolet spectrum (EtOH) had  $\lambda_{\text{max}}$  243m $\mu$  ( $\epsilon$  19000),  $\lambda_{\text{max}}$  279m $\mu$  ( $\epsilon$  5300),  $\lambda_{\text{max}}$  287m $\mu$ , ( $\epsilon$  3900) and  $\lambda_{\text{max}}$  296m $\mu$  ( $\epsilon$  3650).

Calcd. for  $\text{C}_{14}\text{H}_{24}\text{O}_2\text{Sn}_2$ : C, 36.42; H, 5.24.

Found (SMN): C, 36.59; H, 5.27.

Diels-Alder Reaction of 5-Methyl- $\alpha$ -pyrone and Bis(trimethyltin)-acetylene: 3,4-Bis(trimethyltin)toluene (III) - (VI-AE-28).

A solution of 0.3 g. (2.75 mmole) of 5-methyl- $\alpha$ -pyrone, 1.46 g. (4.15 mmole) of bis(trimethyltin)acetylene and 0.05 g. of hydroquinone in 10 ml. of bromobenzene (distilled from calcium hydride under reduced pressure) were heated at reflux for 35 hr. Removal of the solvent and volatiles by direct distillation (35°/0.08 mm.) left orange solids and an oil. These were dissolved in 50 ml. of carbon tetrachloride, decolorized

with activated charcoal and filtered. Removal of the solvent and distillation with a Hickman Still gave 0.630 g. of a yellow oil, b.p. 90°/0.05 mm.; another distillation gave 0.550 g. (48%) of still yellow liquid. The distillate was then dissolved in hexane and filtered through a 2 in. Silica Gel G column using 200 ml. of hexane as eluent. Distillation of the residue gave 0.450 g. (39%) of an analytically pure, colorless liquid,  $n_D^{26.8}$  1.5602.

The compound had the properties expected for 3,4-bis(trimethyltin)-toluene. The NMR ( $CCl_4$ ) had a complex multiplet at 6.75-7.38 p.p.m. ( $Ar-H$ ), a singlet at 2.28 p.p.m. ( $Ar-CH_3$ ) and a singlet at 0.30 p.p.m. ( $Sn-CH_3$ ) with relative areas of 1:1:6. The trimethyltin absorption had satellites:  $J_{Sn^{117}-H}$  52 c.p.s. and  $J_{Sn^{119}-H}$  54 c.p.s. The ultraviolet spectrum (EtOH) had  $\lambda_{sh}$  221m $\mu$  ( $\epsilon$  16800),  $\lambda_{max}$  267m $\mu$  ( $\epsilon$  500) and  $\lambda_{sh}$  273m $\mu$  ( $\epsilon$  283). The infrared spectrum (film) had absorptions at 3050(m), 3025(m), 2980(s), 2920(s), 1700(w; imp), 1580(w), 1450(m), 1260(w), 1215(w), 1200(w), 1190( $\gamma_{Sn-CH_3}$  sym.; m), 1085(m), 1040(w), 885(w), 810( $\gamma_{m-aryl}$ ; s), 765( $\gamma_{Sn-CH_3}$  rock; s), 705(s), 660(w), 570(w) and 520  $cm^{-1}$  ( $\gamma_{Sn-CH_3}$  str.; m).

Calcd for  $C_{13}H_{24}Sn_2$ : C, 37.39; H, 5.79.

Found (SMN): C, 37.12; H, 5.78.

Attempted Diels-Alder Reaction of 4,6-Dimethyl- $\alpha$ -pyrone and bis-(trimethyltin)acetylene.

A solution of 0.557 g. (4.48 mmole) 4,6-dimethyl- $\alpha$ -pyrone, 1.515 g. (4.32 mmole) of bis(trimethyltin)acetylene and 0.070 g. of hydroquinone in 30 ml. of bromobenzene (freshly distilled from  $CaH_2$ ) were heated to reflux. The reaction mixture was examined periodically by t.l.c. (alumina-and silica gel-pentane). No product had formed after 41 hr. (the starting materials have  $R_f \approx 0$  in this t.l.c. system) and reflux was continued for 148 hr., in all.

Removal of the solvent in vacuo left a brown oil with the very characteristic odor of the 4,6-dimethyl- $\alpha$ -pyrone. Examination by t.l.c. (silica gel-pentane) indicated the absence of any products. There was no absorption in the NMR spectrum ( $\text{CCl}_4$ ) below 6.0 p.p.m. and only a very weak signal in the  $\text{Sn-CH}_3$  region.

Diels-Alder Reaction of (Phenylethynyl)trimethyltin and  $\alpha$ -Pyrone:

(2-Biphenyl)trimethyltin, IV - (VI-AE-20).

A solution of 3.37 g. (12.78 mmole) of (phenylethynyl)trimethyltin, 1.50 g. (15.61 mmole) of  $\alpha$ -pyrone and 0.1 g. of hydroquinone in 25.0 ml. of bromobenzene (freshly distilled from  $\text{CaH}_2$ ) was heated at reflux for 48 hr.

Removal of the solvent in vacuo (28°/0.08 mm.) left a black oil which was dissolved in ether, and the resulting mixture filtered. Removal of the ether and distillation with a short path apparatus gave three fractions: 0.100 g. (b.p. 31°/0.1 mm.), 0.820 g. (b.p. 65-85°/0.06 mm.) and 0.942 g. (b.p. 86-92°/0.06-0.07 mm.). The first two fractions consisted primarily of starting material and rapidly decomposed on standing in the atmosphere (The reaction had apparently not gone to completion.). The final fraction is 96% pure (g.l.p.c.). On cooling, the sample began to crystallize; it was then dissolved in hexane and crystallized by addition of methanol and cooling to yield 0.753 g. of fluffy needles, m.p. 53.5-7°. An additional 0.230 g., m.p. 53-6.5°, were obtained from fraction II of the distillation. The yield is 1.17 g. (29%). An analytical sample, obtained by one further crystallization from the same solvent mixture, had m.p. 57-8°.

The compound had the properties expected for IV. The NMR spectrum ( $\text{CCl}_4$ ) consisted of a broad, single absorption at 7.1-4 p.p.m. (Ar-H) and a sharp

singlet ( $\text{Sn-CH}_3$ ) at 0.03 p.p.m. above TMS with relative areas of 1:1; the tin couplings were  $J_{\text{Sn}^{117}\text{-H}}$  52 c.p.s. and  $J_{\text{Sn}^{119}\text{-H}}$  54 c.p.s. The ultra-violet spectrum (EtOH) consisted of  $\lambda_{\text{sh}}$  237 m $\mu$  ( $\epsilon$  6700); clearly, there is reduced resonance interaction between the benzene rings. The infrared spectrum ( $\text{CCl}_4$  and  $\text{CS}_2$ ) had bands at 3110(w), 3075(sh), 3060(m), 3030(sh), 2990(sh), 2980(m), 2915(m), 2000-1600(w), 1600(w), 1575(w), 1490(w), 1460(m), 1440(m), 1425(m), 1260(w), 1245(w), 1200(w), 1190( $\gamma_{\text{Sn-CH}_3}$  sym.; m), 1110(w), 1070( $\gamma_{\text{Sn-aryl}}$ ; m), 1030(w), 1025, 1010(m), 995(w), 930(w), 910(w), 770( $\gamma_{\text{Sn-CH}_3}$  rock; s), 740( $\gamma_{\text{O-aryl}}$ ; s), 700( $\gamma_{\text{C-}}$ ; s), 645(w), 615(w), 545(w) and 520  $\text{cm}^{-1}$  ( $\gamma_{\text{Sn-CH}_3}$  str.).

Calcd for  $\text{C}_{15}\text{H}_{18}\text{Sn}$ : C, 56.83; H, 5.72.

Found (SMN): C, 56.76; H, 5.75.

Competition Between  $\alpha$ -Pyrone and 5-Carbomethoxy- $\alpha$ -Pyrone for Bis-(trimethyltin)acetylene - (VI-AE-2).

A solution of 0.740 g. (7.70 mmole) of  $\alpha$ -pyrone, 0.940 g. (6.11 mmole) of 5-carbomethoxy- $\alpha$ -pyrone, 2.318 g. (6.60 mmole) of bis(trimethyltin)-acetylene and 0.074 g. of hydroquinone in 30 ml. of bromobenzene (distilled directly from  $\text{P}_2\text{O}_5$ ) were heated at reflux for 21.5 hr. Volatile components were, then, removed by direct distillation at  $28^\circ/0.05$  mm. The entire residue was transferred to a Hickman still and distilled essentially to dryness (pot temp,  $180^\circ/0.12$  mm.). The distillate, a discolored oil, was examined by NMR ( $\text{CCl}_4$ ); absorption at 6-6.2 p.p.m. indicated the presence of unreacted  $\alpha$ -pyrone. Absorptions at 7.5-8.0 p.p.m. (characteristic of II), 3.8 p.p.m. ( $\text{ArCO}_2\text{CH}_3$ ) and at 0.35 p.p.m. (two peaks about 1 c.p.s. apart) with relative areas of 1:1:6 indicated that methyl 3,4-bis(trimethyltin)-benzoate was the only aromatic compound present. Redistillation with a short



path apparatus yielded 1.838 g. (64.5%) of a faintly yellow liquid, b.p. 123°/0.06 mm.,  $n_D^{25.5}$  1.5632 (lit.  $n_D^{24}$  1.5613). There was no forerun, thus, no o-bis(trimethyltin)benzene was present. Examination of the distillate by g.l.p.c. (F and M. isothermal at 205° and 60 ml./min. of helium using a 6 ft. column of 7.5% SE 30 on Chromosorb P) confirmed the absence of o-bis(trimethyltin)benzene, (retention time is 21 min.); the methyl 3,4-bis(trimethyltin)benzoate was not eluted after 70 min.

Competition Between  $\alpha$ -Pyrone and 5-Methyl- $\alpha$ -pyrone for Bis(trimethyltin)acetylene - (VI-AE-27).

A solution of 0.336 g. (3.06 mmole) of 5-methyl- $\alpha$ -pyrone, 0.315 g. (3.27 mmole) of  $\alpha$ -pyrone, 1.12 g. (3.16 mmole) of bis(trimethyltin)acetylene and 0.030 g. of hydroquinone in 10 ml. of bromobenzene (freshly distilled from  $\text{CaH}_2$ ) was heated at reflux for 31.5 hr. The solvent was removed in vacuo (28°/0.08 mm.) and the residue dissolved in  $\text{CCl}_4$  and examined by NMR. The NMR spectrum contained absorptions at 6.8-7.5 p.p.m. ( $\text{Ar-H}$ ), 2.23 p.p.m. ( $\text{Ar-CH}_3$ ), 1.75 p.p.m. ( $\text{C-CH}_3$  of 5-methyl- $\alpha$ -pyrone) and 0.30 p.p.m., as well as several peaks due to impurities. The ratio  $\text{ArH}:\text{ArCH}_3$  was 24:13 which indicates a ratio of o-bis(trimethyltin)benzene to 3,4-bis(trimethyltin)-toluene of 1:1.17. The NMR sample was restored to the body of the reaction mixture and, after decolorization with activated charcoal and filtration, the solution was examined by g.l.p.c. (F and M isothermal at 199° and 60 ml.He/min. using a 6 ft. x 5 mm. column of 7.5% SE 30 on Chromosorb P) and found to contain two components whose retention times corresponded exactly to those of authentic samples of o-bis(trimethyltin)benzene (I) and 3,4-bis(trimethyltin)toluene (III). Yields were, then, calculated using 1-bromonaphthalene as an internal standard and correcting for the

molar responses. The yield of I was 0.904 mmole (26%) and of III 1.043 mmole (35.4%). Calculation of the relative reactivities by the equation

$$\frac{K_{5-CH_3}}{K_{5-H}} = \frac{\text{mmole III}}{\text{mmole I}} \times \frac{\text{mmole 5-H}}{\text{mmole 5-CH}_3} \text{ gives a value of 1.23}$$

o-Bis(trimethyltin)benzene (I) Moniodinolysis : o-Iodo(trimethyltin)-benzene (V) - (IV-AE-44).

A solution of 1.00 g. (2.48 mmole) of I in 35 ml. of chloroform (Fisher reagent) was treated in a dropwise manner with a solution of 0.6304 g. (2.48 mmole) of iodine (Mallincrodt analytical reagent) in 60 ml. of chloroform. Decolorization was instantaneous.

Removal of the solvent and trimethyltin iodide in vacuo (42°/0.15 mm) left a yellow oil which was distilled with a Hickman apparatus; a colorless, aromatic liquid, b.p. 70°/0.04 mm, was obtained, 0.8485 g. (93%). Analysis of the distillate by g.l.p.c. (F and M isothermal at 208° and 70 ml./min. of He using a 6 ft. x 5 mm. column of 7.5% SE 30 on Chromosorb P) indicated a purity of about 95%; contaminants were 4% of starting material (I) and about 1% of a lower boiler, presumably o-diiodobenzene. An analytical sample was collected by g.l.p.c. and had  $n_D^{25}$  1.6031. The compound was identified as V by its spectra and elemental analyses. The NMR spectrum (CCl<sub>4</sub>) had absorptions at 7.68 p.p.m. (1H; doublet with J = 7.5 c.p.s., with further splitting),<sup>39</sup> 6.70-7.28 p.p.m. (3H; multiplet) and 0.37 p.p.m. (9H) with satellites:  $J_{Sn^{117}-H}$  53 c.p.s. and  $J_{Sn^{119}-H}$  55.5 c.p.s.

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(39) The lowest field proton is that one ortho- to the iodine by analogy to the spectrum of o-diiodobenzene in which the ortho protons occur at 7.84 p.p.m. ( $J_O$  7.9 c.p.s.): J. Martin and B. P. Dailey, J. Chem. Phys., 37, 2594 (1962).

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The ultraviolet spectrum (EtOH) had absorptions at  $\lambda_{sh}$  232  $m\mu$  ( $\epsilon$  10,550),  $\lambda_{sh}$  273  $m\mu$  ( $\epsilon$  495),  $\lambda_{max}$  278  $m\mu$  ( $\epsilon$  723) and  $\lambda_{max}$  285  $m\mu$  ( $\epsilon$  659). The infrared spectrum (film) had bands at 3045(m), 2975(m), 2910(m), 1915(w), 1830(w), 1800(w), 1670(w), 1600(w), 1565(w), 1550(m), 1450(w), 1435(m), 1420(m), 1410(s), 1265(w), 1245(m), 1200(w), 1190 ( $\gamma_{Sn-CH_3}$  sym.), 1160(w), 1120(w), 1100(w), 1085( $\gamma_{Sn-aryl}$ ; m), 1025(m), 980(w), 940(w), 770( $\gamma_{Sn-CH_3}$  rock; s), 740( $\gamma_{o-aryl}$ ; s), 720(sh), 695(w), 635(w) and  $525cm^{-1}$  ( $\gamma_{Sn-CH_3}$  str; w).

Calcd for  $C_{21}H_{13}ISn$ : C, 29.47; H, 3.57; I, 34.60.

Found (SMN): C, 29.62; H, 3.28; I, 34.23.

Methyl 3,4-bis(trimethyltin)benzoate (II), Monoiodinolysis - (III-AE-67; IV-AE-31).

A solution of 0.876 g. (1.897 mmole) of II in 40 ml. of chloroform was treated in a dropwise manner with a solution of 0.4803 g. (1.893 mmole) of iodine in 140 ml. of chloroform. Decolorization was instantaneous.

Removal of the volatiles in vacuo (30°/0.05 mm) left a yellow oil which was distilled with a Hickman apparatus. A colorless distillate, 0.7110 g. (88.5%), was obtained, b.p. 110°/0.1 mm. Redistillation gave an analytical sample,  $n_D^{25}$  1.5973,  $d_4^{23}$  2.04. The compound had the properties expected for a mixture of methyl 3-iodo-4-(trimethyltin)benzoate (VIII) and methyl 4-iodo-3-(trimethyltin)benzoate (VII). The NMR spectrum ( $CCl_4$ ) is particularly complex in the aromatic region but a strong signal at 8.32 p.p.m. (doublet with  $J = 1.4$  c.p.s.) which must be the proton ortho to both iodine and the carbomethoxy group in VIII indicated that this was the major isomer. The ratio for the areas of Ar-H (7.05-8.32 p.p.m.), the methoxyl hydrogens (3.86 p.p.m.) and the trimethyltins (two peaks at 0.42 p.p.m., 1 c.p.s. apart with relative areas of 2:3) was the expected 1:1:3. The infrared

spectrum ( $\text{CCl}_4$ ) consisted of absorptions at 3000-3100(w), 2990(m), 2920(m), 2845(w), 1735( $\gamma_{\text{C=O}}$ ; s), 1580(m), 1545(m), 1460(m), 1440(m), 1365(m), 1290(v.s), 1250(w), 1195( $\gamma_{\text{Sn-CH}_3 \text{ sym}}$ ; m), 1120(s), 1080( $\gamma_{\text{Sn-aryl}}$ ; m), 1020(m), 1005(m), 970(m), 900(w), 655(w) and  $530\text{cm}^{-1}$  ( $\gamma_{\text{Sn-CH}_3 \text{ str}}$ ; w).

Calcd for  $\text{C}_{11}\text{H}_{15}\text{O}_2\text{ISn}$ : C, 31.10; H, 3.56.

Found (SMN): C, 31.26; H, 3.34.

(2-Biphenylyl)trimethyltin (IV), Iodinolysis - (VI-AE-20).

A solution of 0.650 g. (2.04 mmole) of IV in 20 ml. of chloroform was treated in a dropwise manner with a solution of 0.6 g. (2.4 mmole) of iodine until an iodine color persisted in the solution. Volatile components were removed by distillation in vacuo ( $40^\circ/1 \text{ mm.}$ ) and the residue, a yellow oil, distilled with a Hickman apparatus. An aromatic, colorless distillate, b.p.  $85^\circ/0.06 \text{ mm.}$ ,  $n_D^{25} 1.6577$ , was obtained. Examination of the distillate by g.l.p.c. (F and M program  $170-220^\circ$  at  $7.5^\circ/\text{min}$  with 60 ml/min He using a 6 ft. x 5 mm. column of 7.5% SE 30 on Chromosorb P) showed a single peak. The properties of the compound agree with those reported for 2-iodobiphenyl: b.p.  $94-5^\circ/0.007 \text{ mm.}$ ,  $n_D^{20} 1.6620$ .<sup>40</sup> The ultraviolet spectrum (n-heptane),  $\lambda_{\text{max}} 227\text{m}\mu$  ( $\epsilon$  17,700), was very close to that reported in the literature:<sup>41</sup>  $\lambda_{\text{max}} 226\text{m}\mu$  ( $\epsilon$  20,000).

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(40) D. R. Augood, J. I. G. Cadogan, D. H. Hey and G. H. Williams, J. Chem. Soc., 3413 (1953).

(41) T. M. Dunn, T. Redale, ibid., 1592 (1952).

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The mass spectrum, moreover, showed a molecular ion,  $M^+$  280, and a peak ( $M^+$  153) for biphenyl, among others. The infrared spectrum ( $\text{CCl}_4$  and  $\text{CS}_2$ ), which had not been reported, had absorptions at 3150(sh), 3110(sh), 3085(sh),

3060(sh), 3035(sh), 1950(m), 1920(w), 1870(w), 1800(m), 1750(w), 1600(m), 1580(w), 1495(m), 1460(s), 1450(s), 1425(s), 1420(sh), 1330(w), 1295(w), 1250(w), 1180(w), 1155(w), 1115(w), 1075(m), 1065(sh), 1035(m), 1015(s), 1005(s), 995(m), 945(m), 910(m), 855(w), 740( $\nu_{\text{o-aryl}}$ ; s), 720(m), 700( $\nu_{\text{C-I}}$ ; s), 645(s), 605(s), and  $555\text{cm}^{-1}$  ( $\nu_{\text{C-I}}$ ; s). The NMR spectrum ( $\text{CCl}_4$ ) had absorptions at 7.75 p.p.m. (1H; doublet,  $J = 7.7$  c.p.s. with further splitting) and 7.17 p.p.m. and 7.07 p.p.m. (8H); the low field absorption is assigned to the proton ortho to the iodine.<sup>39</sup>

*o*-Bis(trimethyltin)benzene I, Monobrominolysis: *o*-Bromo(trimethyltin)-benzene.

A solution of 0.597 g. (1.87 mmole) of I in 350 ml. of a 1:1 ether-methanol mixture (Mallinckrodt anhydrous and Fisher reagent, respectively) was cooled to  $-75^\circ$  with a Dry Ice-acetone bath and then treated dropwise with a solution of 0.301 g. (1.89 mmole) of bromine (Mallinckrodt analytical) in 50 ml. of methanol. Reaction was nearly instantaneous as evidenced by the rapid decolorization of the reaction mixture.

Removal of the solvent and trimethyltin bromide in vacuo left a slightly discolored oil. This was examined by g.l.p.c. (F and M isothermal at  $190^\circ$  with 60 ml/min. He using a 6 ft. x 5 mm column of 7.5% SE 30 on Chromosorb P) and shown to consist of a single peak (some trimethyltin bromide remained) which had a 10.5 min. retention time. No *o*-dibromobenzene or starting material (retention times 5 min. and 22 min., respectively, were evident. Distillation with a Hickman still gave 0.410 g. (86%) of aromatic colorless liquid, b.p.  $47^\circ/0.03$  mm.,  $n_D^{25}$  1.5703. An analytical sample, collected by g.l.p.c., had  $n_D^{24}$  1.5734.

The properties of the liquid were in accord with those expected for

o-bromo(trimethyltin)benzene (VI). The NMR spectrum ( $\text{CCl}_4$ ) had absorptions at 7.47 p.p.m. ( $1\text{H}$ , probably that ortho to the bromine), 6.9-7.3 p.p.m. ( $3\text{H}$ ) and 0.38 p.p.m. ( $J_{\text{Sn}^{117}\text{-H}} 53 \text{ c.p.s.}; J_{\text{Sn}^{119}\text{-H}} 55 \text{ c.p.s.}$ ) with relative areas of 1:3:8.8. The infrared spectrum (film) had absorptions at 3055(m), 2985(m), 2915(m), 2000-1750(several; w), 1575(w), 1565(m), 1470(w), 1450(m), 1435(m), 1425(s), 1270(w), 1255(s), 1195(m), 1110(m), 1090(s), 1035(m), 1010(s), 775(s), 745(s), 695(s) and  $640 \text{ cm}^{-1}$ (w). The ultraviolet spectrum (EtOH) had absorptions at  $\lambda_{\text{max}} 258 \text{ m}\mu$ ,  $\lambda_{\text{max}} 264 \text{ m}\mu$ ,  $\lambda_{\text{max}} 267 \text{ m}\mu$  and  $\lambda_{\text{sh}} 275 \text{ m}\mu$ .

Calcd for  $\text{C}_6\text{H}_5\text{BrSn}$ : C, 33.79; H, 4.10.

Found (SMN): C, 33.98; H, 4.43.

*o*-Bis(trimethyltin)benzene (I), Dibrominolysis.

A solution of 0.301 g. (0.75 mmole) of I in 30 ml. of chloroform was treated in a dropwise manner with a solution of 0.15 g. (0.94 mmole) bromine in 30 ml. of chloroform until the bromine color persisted in the reaction mixture. Removal of the solvent with a water aspirator left a slightly discolored liquid which was examined by g.l.p.c. (F and M isothermal at  $170^\circ$  and 60 ml./min. He using a 6 ft. x 5 mm. column of 7.5% SE 30 on Chromosorb P) and found to contain, in addition to traces of solvent and a considerable amount of trimethyltin bromide, a single peak whose retention time corresponded exactly to that of an authentic sample of *o*-dibromobenzene. The infrared spectrum of a collected sample was identical with that of authentic *o*-dibromobenzene and with the Sadtler Spectrum, No. 12459,<sup>42</sup> for this compound.

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(42) Sadtler Standard Spectra, Sadtler Research Laboratories, Philadelphia.

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Reaction of *o*-Bis(trimethyltin)benzene with *n*-Butyllithium: Attempted  
Preparation of *o*-Dilithio benzene - (IV-AE-60).

A solution of 1.03 g. (2.54 mmole) of *o*-bis(trimethyltin)benzene in 30 ml. of ether (freshly distilled from  $\text{CaH}_2$ ) was treated in a dropwise manner with 5.25 mmole (4.95 ml. of 1.06 N) *n*-butyllithium in 15 ml. of 2:1 ether-pentane mixture. The solution became yellow and then orange after about 10% of the lithium reagent had been added and maintained this color throughout the addition. The reaction mixture was stirred for 1.5 hr. after the completion of addition and then quenched with 0.15 ml. (8.5 mmole) of deuterium oxide (Columbia Organic Chemicals Co.); the quenching was extremely exothermic considering the diluteness of the solution. A white solid precipitated almost immediately. Examination of the crude reaction mixture by g.l.p.c. (M.I.T. Isothermal at 87° and 13.5 p.s.i. of He using a 10 ft. x 8 mm. column of 25% SE 30 on Chromosorb P) indicated the presence of three components; the two highest boilers had retention times identical with *n*-butyltrimethyltin and benzene.

The reaction mixture was distilled trap-to-trap (30°/0.45 mm) and, then, directly at 110°/0.45 mm. (receiver cooled to -75°). The distillate was, then, concentrated by distillation through a Vigreux column equipped with a fraction cutter adjusted for a 10:1 drop ratio. Analysis of the distillation residue, after removal of most of the ether, by g.l.p.c. (same conditions as above) using toluene as in internal standard and correcting for molar responses indicated a yield of 2.36 mmole (46.5%) of *n*-butyltrimethyltin (identified by retention time and IR spectrum) comparison with an authentic sample and .215 mmole (8.5%) of benzene( $\text{D}_2$ ?).

The ratio of these peaks was somewhat different than in the crude reaction mixture and it appeared that some of the benzene might have been lost during work-up. The yield of benzene was too low for satisfactory collection and it was collected together with a lower boiling peak which had the same retention time as tetramethyltin. An infrared spectrum of the mixture ( $\text{CCl}_4$ ) suggests the presence of o-dideutero benzene as it consists of absorptions at 3075(m), 3055(m), 3030(sh), 2975(s), 2915(s), 2355(m), 2270(w), 1964(w), 1955(w), 1620(w), 1595(w), 1487(sh), 1480(w), 1460(m), 1450(m), 1375(w), 1295(w), 1265(w), 1255(w), 1195(m), 1150(w), 1130(w), 1070(m), 1050(sh), 1035(w), 930(w), 910(w), 870(w), 855(w), 840(m), 695(m), 670(w), 605(s), 585(m), and  $520\text{ cm}^{-1}$ (s). The reported infrared spectrum of o-dideutero benzene<sup>43</sup> has bands at 3058, 3030, 2275, 1587, 1566, 1158, 1128, 1054, 974, 840, 779, 661, 597, and  $582\text{ cm}^{-1}$ . Tetramethyltin has absorptions at 2975, 2915, 1195 and  $520\text{ cm}^{-1}$ .

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- (43) S. Broderson and A. Langseth, Kg. Danske. Vidensk. Selskab Nat.-Fys. Skrifter, 1 (7) (1959); CA., 54, 1073i (1960).
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In another experiment, 1.8337 g. (4.54 mmole) of I was treated with 10.60 mmole of n-butyllithium and, then, stirred for 3 hr. The solution became yellow but never orange as above. The reaction mixture was quenched with benzophenone (1.79 g.; 9.84 mmole), stirred overnight and, then, hydrolyzed. Separation of the layers, washing of the aqueous layer with ether and drying (anhydrous  $\text{MgSO}_4$ ) gave a yellow solution which was distilled trap-to-trap ( $35^\circ/0.40\text{ mm}$ ) and, then, directly ( $80^\circ/0.03\text{ mm}$ ). Examination of the distillate by quantitative g.l.p.c., as above, indicated a 49.1% yield of n-butyltrimethyltin. The residue from the distillation (2.43 g.) was



examined by t.l.c. (silica gel-pentane (5):ether(1) and appeared to contain, at least, six compounds. Chromatography of 1.16 g. using a 6 in. x 7/8 in. column of Silica Gel G and a 5:1, pentane:ether eluent separated the mixture somewhat. The initial fractions contained di-n-butyldimethyltin, identified by comparison of its retention time in t.l.c. (silica gel-pentane) and infrared spectrum with an authentic sample (crude yield is about 0.87 mmole or 9.5% based on starting material I). The final fractions contained 1,1-diphenylethylene, which must arise from 2,2-diphenylethanol during chromatography, identified by its NMR spectrum (absorptions at 7.08 and 5.2 p.p.m. with relative areas of 5:1), by comparison of its infrared spectrum with Sadtler Spectrum No. 19518<sup>42</sup> for this compound and by elemental analysis.

Calcd for  $C_{14}H_{12}$ : C, 93.29; H, 6.71.

Found (SMN): C, 92.93; H, 6.69.

The central fractions contained a mixture of compounds from which a small amount of colorless crystals, m.p. 148-52°, could be isolated. Recrystallization from pentane-methanol mixtures gave colorless crystals, m.p. 160-2°, which show weak hydroxyl absorption at  $3450\text{ cm}^{-1}$  and aryl C-H absorption but no alkyl C-H bands in the infrared. The compound appears not to be the expected w,w,w'-tetraphenyl-o-xylyleneglycol, m.p. 192.5-6°<sup>44</sup> although the analysis is similar.

Calcd for  $C_{32}H_{26}O_2$ : C, 86.85; H, 6.17.

Found (SMN): C, 85.81; H, 6.12.

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44. G. Wittig and F. Bickelhaupt, Chem. Ber., 91, 890 (1958).

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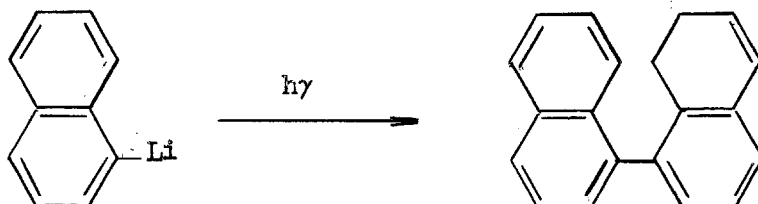
CHAPTER III  
PHOTOCHEMISTRY OF UNSATURATED  
ORGANOTIN COMPOUNDS

## DISCUSSION

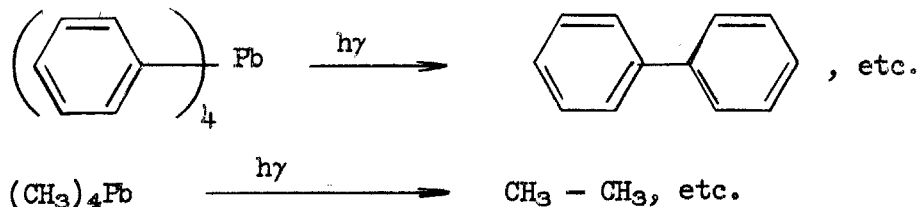
The photochemistry of main group organometallic compounds is an area that has received very little attention.<sup>1</sup> Certainly the ma-

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- (1) Light induced processes involving transition metal compounds have been examined in considerable detail due to their importance in the life process.
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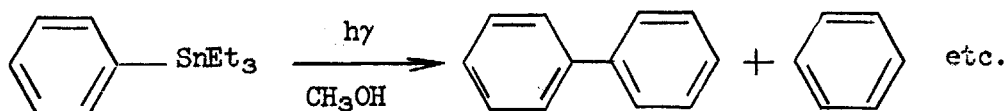
For reason for this is the facile destruction of most C-M linkages on irradiation, due both to the low energy of these bonds and to the possibility of obtaining different, stable oxidation states of the metal by consecutive transfers of electrons. Virtually the only reported photochemistry of these compounds involves scission of the C-M bond; a few examples are:



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- (2) E. E. van Tamelen, I. I. Brauman and L. E. Ellis, J. Am. Chem. Soc., 87, 4964 (1964).
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- (3) P. A. Leighton and R. A. Mortimer, ibid., 58, 448 (1936).
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- (4) G. A. Razuvaev and V. Fetykova, Zh. Obschch. Khim., 21, 1107 (1951); C.A., 46, 147 (1952).
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Nesmeyanov and coworkers<sup>5</sup> and Seyferth and Vaughan<sup>6</sup> have, however,

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- (5) A. N. Nesmeyanov, A. E. Borisov and A. N. Abramov, Izv. Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk, 570(1949); C. A., 44, 7759i (1950).

- (6) D. Seyferth and L. G. Vaughan, J. Organometal. Chem., 1, 138 (1963).
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reported that irradiation of vinylic organometallic systems results in cis-trans isomerization and not in C-M bond homolysis.

The effect of covalently bonded organometallic substituents, in particular those of Group IV, on the absorption spectra of organic chromophores have been studied. The energies of ground and excited states appear to be little different than those of the carbon analogs,

although the metals affect the rate of the excited states' singlet-triplet transfer (it increases with increasing mass of the substituent).<sup>7</sup> Photochemical transformations of appropriately substituted

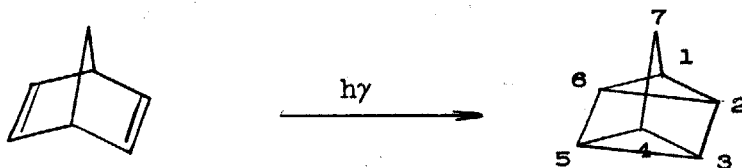
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(7) D. S. McClure, J. Chem. Phys., 17, 905 (1949).

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organometallic compounds, are, therefore, possible and it is only a question of finding the right systems and reaction conditions. With the idea that novel classes of organometallic compounds might be prepared by photoisomerizations, we undertook some examinations in this area.

The organotin substituted norbornadienes (see Chapter I) seemed to be a suitable starting point for this study. The photochemical transformation of bicyclo[2.2.1]hepta-2,5-dienes (norbornadienes) to quadricyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]heptanes (quadricyclenes), which was



first observed by Cristol and Snell<sup>8</sup>, has been examined in some detail.<sup>9</sup>

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(8) S. J. Cristol and R. Snell, J. Am. Chem. Soc., 76, 5000(1954).

(9) See, for example, G. S. Hammond, ibid., 86, 2533 (1964).

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At the time this work was begun (1963), no bicyclo[2.2.1]hepta-2,5-dienes, other than the 2,3-dicarboxy system<sup>8</sup> and the unsubstituted

compound, norbornadiene,<sup>10</sup> had been successfully photoisomerized.

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- (10) W. G. Dauben and R. L. Cargill, *Tetrahedron Letters*, 15, 197 (1961)
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There were, moreover, reports that several Diels-Alder adducts of hexachlorocyclopentadiene and acetylenes did not undergo this reaction.<sup>11</sup> Recently, there have been reports of the successful trans-

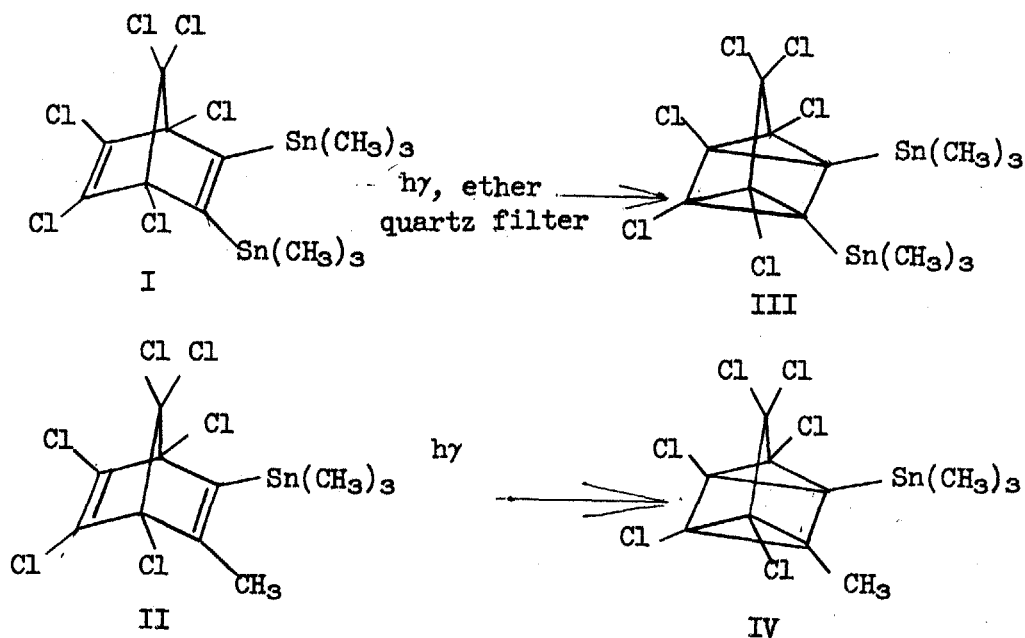
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- (11) (a) R. J. Gritter, E. Sabatino and S. Sacharow, U. S. Dept. of Commerce, PB Report 150, 407 (1960); C.A., 58, 3328b (1963).  
(b) W. E. Noland and L. R. Smith, *J. Am. Chem. Soc.*, 82, 2021 (1960).
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formation of other bicyclo[2.2.1]hepta-2,5-dienes: 7-chloro-,<sup>12a</sup>

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- (12) (a) P. R. Story and S. R. Fahrenholtz, *ibid.*, 86, 572 (1964);  
(b) H. G. Rickey and N. C. Buckley, *ibid.*, 85, 3057 (1963);  
(c) G. W. Klump and F. Bickelhaupt, *Tetrahedron Letters*, 865 (1966); (d) P. G. Gassman, D. W. Aue and D. S. Patton, *J. Am. Chem. Soc.*, 86, 4211 (1964); (e) D. M. Lemal, E. P. Gosselink, and S. D. McGregor, *ibid.*, 88, 584 (1966); (f) S. J. Cristol, J. K. Harrington, M. S. Singer, *ibid.*, 88, 1529 (1966), reported private communication from one D. I. Davies.
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7-acetoxy-,<sup>12b</sup> 7-cyano-,<sup>12c</sup> 2,3-dimethyl-7,7-dimethoxy-,<sup>12d</sup> 1,2,3,4-tetrachloro-7,7-dimethoxy-5-phenyl-,<sup>12e</sup> and, very recently, 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene.<sup>12f</sup> All of the reported quadricyclenes are thermally stable (up to ~ 150°) with the exception of the two systems with 7,7-dimethoxy substitution which apparently revert to the diene within a few hours at ambient temperatures.<sup>12d,e</sup>

Irradiation of 2,3-bis(trimethyltin)-1,4,5,6,7,7-hexachloro-bicyclo[2.2.1]hepta-2,5-diene (I) or of 2-(trimethyltin)-1,4,5,6,7,7-hexachloro-3-methylbicyclo[2.2.1]hepta-2,5-diene (II) in ether with a high pressure, mercury lamp results in their conversion to the corresponding quadricyclenes; 2,3-bis(trimethyltin)-1,4,5,6,7,7-hexachloro-quadricyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]heptane (III) and 2-(trimethyltin)-1,4,5,6,7,7-hexachloro-3-methylquadricyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]heptane (IV), respectively, in isolated, pure yields of about 45%.



The actual yields in the irradiations are considerably higher than 45% (the yield of IV was estimated by NMR to be 70%). However, isolation of the photoproducts involves column chromatography and fractional crystallization and is complicated by the tendency of III and IV to slowly decompose to tars and methyltin chlorides. The quadri-

cyclenes can be handled in the atmosphere, although for extended storage (more than a few hours), it was found necessary to store the compounds under nitrogen at 0°, or lower. The decomposition of III and IV is characteristic of many organometallic systems with halogens proximate to the metal.<sup>13</sup>

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- (13) (a) N. A. Nesmeyanov and A. E. Borisov, *Izv. Akad. Nauk, Org. Khim. Nauk*, 146 (1945); (b) R. West and F. M. Rabel, *J. Am. Chem. Soc.*, 84, 4169 (1963); (c) D. Seyferth, unpublished data.
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It must be stressed that the decomposition described above does not involve reconversion to the dienes; III and IV, unlike 1,2,3,4-tetrachloro-7,7-dimethoxy-5-phenylquadricyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]-heptane, <sup>12e</sup> do not isomerize to the corresponding diene at ambient temperatures over a period of at least several days. Attempts to observe the conversions III → II at elevated temperatures (150-230°) were inconclusive because of decomposition of the quadricyclenes by other paths.

Characterization of the quadricyclenes III and IV was made by UV, IR, and NMR spectral correlations (see Table I) on samples shown to be isomeric with the starting dienes. In particular, the photoisomers were characterized by the presence of only end absorption in quartz ultraviolet region, by the absence of  $\text{>C=C<}$  stretching absorption in the infrared spectra and, in the case of IV, by the upfield shift (versus the diene) of the C-CH<sub>3</sub> group in the NMR



TABLE I

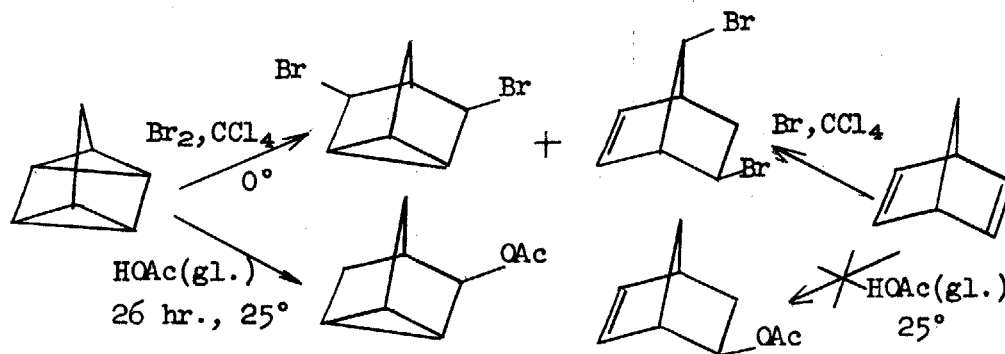
<u>Compound</u>	<u>UV Spectrum*</u>	<u>NMR Spectrum</u>
norbornadiene	$\lambda_{\max}$ 205m $\mu$ ( $\epsilon$ 2100), $\lambda_{\max}$ 214m $\mu$ ( $\epsilon$ 14,800) <sup>14</sup> $\lambda_{\max}$ 220m $\mu$ ( $\epsilon$ 870), $\lambda_{\text{sh}}$ 230m $\mu$ ( $\epsilon$ 200)	
quadricyclene	$\lambda_{\text{end}}$ 210m $\mu$ ( $\epsilon$ 1400) <sup>9</sup>	
I	$\lambda_{\max}$ 236m $\mu$ ( $\epsilon$ 5,600), $\lambda_{\text{sh}}$ 257m $\mu$ ( $\epsilon$ 1600) $\lambda_{\text{sh}}$ 285m $\mu$ ( $\epsilon$ 360)	0.35 p.p.m.
III	$\lambda_{\text{end}}$ 245m $\mu$ ( $\epsilon$ 370)	0.33 p.p.m.
II	$\lambda_{\max}$ 227m $\mu$ ( $\epsilon$ 4000), $\lambda_{\text{sh}}$ 276m $\mu$ ( $\epsilon$ 280)	C-CH <sub>3</sub> 2.03 p.p.m. Sn-CH <sub>3</sub> 0.37 p.p.m.
IV	$\lambda_{\text{end}}$ 240m $\mu$ ( $\epsilon$ 500)	C-CH <sub>3</sub> 1.32 p.p.m. Sn-CH <sub>3</sub> 0.37 p.p.m.
1,2,3,4-tetrachloro- 7,7-dimethoxy-5- phenylquadricyclo- [2.2.1.0. <sup>2,6</sup> 0 <sup>3,5</sup> ]- heptane		H 2.87 p.p.m. (12c)
2,3-dimethyl-7,7- dimethoxybicyclo- [2.2.1]hepta-2,5- diene		C-CH <sub>3</sub> 1.70 p.p.m. Vi-H 6.58 p.p.m. (12d)
2,3-dimethyl-7,7- dimethoxyquadri- cyclo[2.2.1.0. <sup>2,6</sup> 0 <sup>3,5</sup> ]- heptane	$\lambda_{\text{end}}$ 210m $\mu$ ( $\epsilon$ 380)	C-CH <sub>3</sub> 1.22 p.p.m. 5,6-H 1.18 p.p.m. (12d)
V	$\lambda_{\text{end}}$ 232m $\mu$ ( $\epsilon$ 236)	C-CH <sub>3</sub> 1.34 p.p.m. H 2.81 p.p.m.

\* in either n-heptane or ethanol; spectrum of II was identical in both solvents

(14) C. F. Wilcox, S. Winstein and W. G. MacMillan, J. Am. Chem. Soc., 82, 5450 (1960).

spectrum. Both III and IV are crystalline solids which melt with some decomposition. Outside of the work of Nesmeyanov<sup>5</sup> and Seyferth,<sup>6</sup> in which new bond systems were not actually formed, these are the first examples of photoisomerization of main group organometallic compounds.

Some of the chemistry of the C-Sn linkage in III and IV was examined, both in order to assess their utility as intermediates in the synthesis of other quadricyclenes and to determine whether rearrangement of the reactive quadricyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>] skeleton would accompany destannation by electrophiles. The reactivity of quadricyclene itself is evident from the work of Dauben and Cargill.<sup>9</sup>



Extensive halogenation of the carbon skeleton greatly reduces the susceptibility to electrophilic attack, however, as was discussed for the case of the halogenated norbornadienes (Chapter I).

Cleavage C-M<sup>IV</sup> bonds (also C-Hg linkages) by polar reagents such as halogens, halogen and other mineral acids and metal and metalloid halides is an area of considerable interest in organometal-

lic chemistry<sup>15</sup> and is, accordingly, well documented. Mechanistic

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- (15) (a) M. S. Kharasch and R. Marker, J. Am. Chem. Soc., 48, 3130 (1926); (b) J. G. A. Luitjens and G. J. M. van der Kerk, "Investigations in the Field of Organotin Chemistry," Tin Res. Council, Middlesex, England, 1955, p. 75; (c) C. Eaborn, "Organosilicon Chemistry," Butterworths, London, 1966.

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interpretation of the data is, unfortunately, less extensive and only in the cases of  $M^{IV}$ -aryl (electrophilic substitution)<sup>16</sup> and

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- (16) R. O. C. Norman and R. Taylor, "Electrophilic Substitution of Aromatics," (ed. C. Eaborn), Elsevier, Amsterdam, 1965.

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$M^{IV}$ -allyl ( $S_{E2}$ )<sup>17</sup> reactions with halogens and halogens acids is

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- (17) H. G. Kuivila and J. G. Verdine, Tetrahedron Letters, 119 (1965).

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the situation well resolved. Gielen and Nasielski have recently studied the cleavage of tetraalkyltin compounds and find a spectrum of mechanisms between  $S_{E2}$  and  $S_{E2}$  (cyclic transition state) depending on the nature of the solvent and the electrophile.<sup>18</sup> Considera-

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- (18) M. Gielen and J. Nasielski, J. Organometal Chem., 1, 173 (1963).

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tion of the relative reactivity (to halogens and halogen acids) of various groups attached to tin<sup>15b, 19</sup> strongly suggests that electrophilic attack at the C end of the C-Sn bond is involved in all cases,

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- (19) (a) D. Seyferth, J. Am. Chem. Soc., 79, 2133 (1957); (b) S. D. Rosenberg, E. Debreczeni and E. L. Weinberg, ibid., 81, 972 (1959).
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allyl >tolyl >phenyl >vinyl >methyl >ethyl >propyl

although the precise transition state is a function of the substitution and polarity of the solvent. Winstein<sup>20</sup> and Eaborn<sup>15c</sup> have

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- (20) S. Winstein and T. G. Traylor, ibid., 77, 3747 (1955).
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discussed similar mechanisms for the spectrum of C-Hg and C-Si cleavages by electrophiles, respectively.

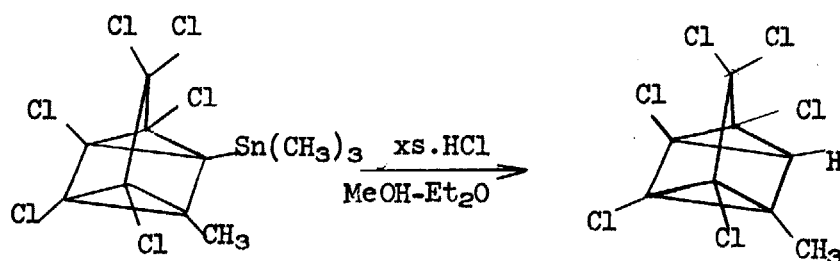
The mechanisms of C-Sn and C-Si cleavage are probably similar but the much more facile cleavage of ligands bonded to tin suggests a greater involvement of tin in the transition state. This is in line with the greater polarizability of the carbon-tin linkage, with the increased ability of tin to form intermolecular coordinate bonds,<sup>21</sup> and with lower energy of the C-Sn bond.

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- (21) F. Rijkens and G. J. M. van der Kerk, "Investigations in the Field of Organogermanium Chemistry," Germanium Research Council, Utrecht, 1964).
- 

Treatment of 2-(trimethyltin)-1,4,5,6,7,7-hexachloro-3-methylquadricyclo[2.2.1.0.<sup>2,6</sup>0<sup>3,5</sup>]heptane (IV) with one equivalent of hydrochloric

acid in a 1:1 methanol:ether mixture (conditions under which the C-Sn bond in the corresponding diene (II) is rapidly cleaved) resulted in virtually no scission of the C-Sn bond. This was clearly demonstrated by treatment of a 4.5:1 mixture of IV and II with one equivalent of hydrochloric acid; examination by t.l.c. and NMR after 8 hr. indicated that II had entirely reacted, while, by similar techniques, 70% of IV was shown to be intact after 71 hr.

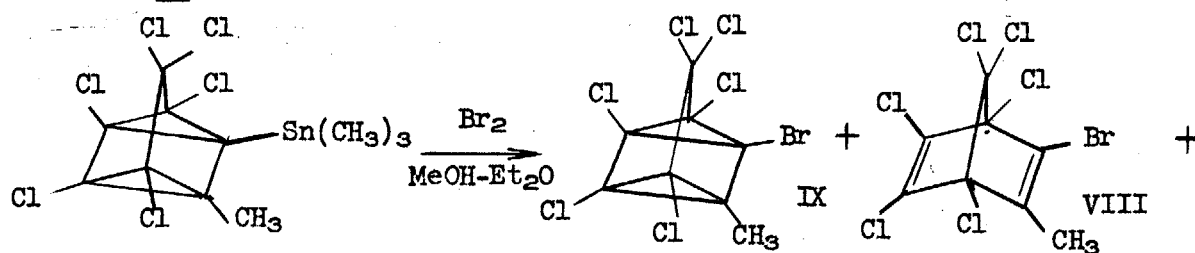
When a considerable excess ( $\sim 5X$ ) of the acid was used, cleavage of the C-Sn bond of IV was complete in about 36 hr. Examination of the crude reaction mixture (after removal of the solvent) by NMR indicated the presence of one compound: singlets at 2.81(1H) and 1.34 (3H). Distillation of the reaction mixture gave a 70% yield of a colorless liquid, b.p.  $\sim 55^\circ/0.08$  mm. which was identified by its NMR, IR, and UV spectra (see Table I) and by elemental analysis as 1,2,3,4,7,7-hexachloro-5-methylquadricyclo[2.2.1.0.<sup>2,6</sup>0<sup>3,5</sup>]heptane (V).



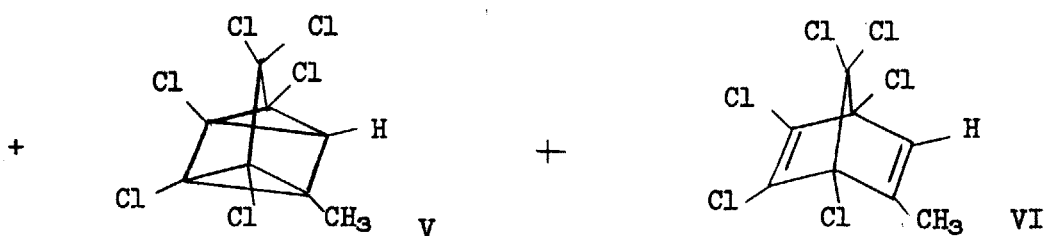
Any question of skeletal rearrangement is ruled out by thermal conversion (at  $200^\circ$ ) of V to 1,2,3,4,7,7-hexachloro-5-methylbicyclo[2.2.1]hepta-2,5-diene (VI), identified by comparison with an authentic sample. Isomerization of V to VI does not occur at ambient temperatures.

Treatment of III under identical conditions gave analogous results: 1,2,3,4,7,7-hexachloroquadricyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]heptane (VII) was formed in good yield. This reaction was run on a rather small scale and an analytically pure sample was not obtained. Spectral data (NMR shows a singlet at 2.94 p.p.m. and ultraviolet and infrared absorptions are very similar to V) and molecular weight determination by mass spectral analysis ( $M^+$ ,  $C_7H_2Cl_5^{35}Cl_1^{37}$ , 298) on a sample of >90% purity are evidence for structure VI.

When III was treated with one equivalent of bromine, under the same conditions used in the protolysis, analysis of the crude reaction mixture (after removal of solvent) by NMR spectroscopy suggested the presence of four products (four different methyl absorptions). Three of the components could be isolated from the mixture by a combination of column chromatography and g.l.p.c. and were identified as 2-bromo-1,4,5,6,7,7-hexachloro-3-methylbicyclo[2.2.1]hepta-2,5-diene (VIII), V and VI. The fourth compound could not be isolated but was tentatively assigned the structure 2-bromo-1,4,5,6,7,7-hexachloro-3-methylquadricyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]heptane (IX) by its NMR absorption at 1.43 p.p.m., the exact position,  $\pm 0.005$  p.p.m., of the  $C-CH_3$  in the photoproduct obtained by irradiation of VIII.



cont.



The yield of the four products based on the starting tin compound is 75%, and they are in the approximate ratio IX:VIII:VI:V of 1:1:1:2.

A rerun of this reaction using rigorously purified reagents and atmosphere yielded IX, VIII and VI in approximately equal amounts, but only traces of V; a compound with a peak at 1.30 p.p.m. in the NMR spectrum was also present, but could not be identified. When the brominolysis was carried out in chloroform (55 hr.), no protodestannation occurred and the products were IX and VIII in a 1:5 ratio; some starting material was still present.

In the broad spectrum of addition reactions of halogen halides, and halogens, mechanistic discussion is frequently complicated by the simultaneous occurrence of polar and free radical reaction paths. With hydrogen chloride, however, radical paths are relatively unfavorable, due primarily to the considerable energy of the H-Cl bond and are not generally observed in additions to olefins, even in the presence of radical initiators.<sup>22</sup> Accordingly, it is reasonable, in

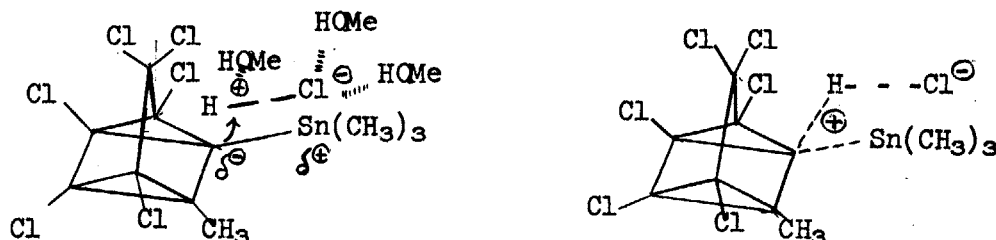
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(22) For a discussion see E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rhinehart and Winston, New York, 1959, p. 730-6, and references contained therein.

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light of the discussion above on the mechanism of the C-Sn cleavage,

to interpret the protodestannylation of IV as involving an initial electrophillic attack of a solvated proton at C-2 followed by an assisted cleavage of the C-Sn bond. This path of reaction may or



may not place a (partial) positive charge on the ring depending on the timing of the C-Sn cleavage, but if it does, this can apparently occur without rearrangement of the quadricyclic skeleton. It must be pointed out that formation of a positive charge at the 2-position of a quadricyclene is not favorable as is the case with the 7-position,<sup>23</sup> where the charge is highly stabilized by interaction with

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- (23) The preparation and properties of the 7-quadricyclic carbonium ion are reported: P. R. Story and S. Fahrenholtz, J. Am. Chem. Soc., 86, 527 (1964).
- 

the cyclopropyl rings (it is doubly cyclopropylcarbinyll).

The low reactivity of the quadricyclic-tin bonds of III and IV versus the corresponding olefin-tin bonds in I and II is interesting. Since the percentage of s character in the carbon orbitals involved in the C-Sn bonds of II and IV is quite similar<sup>24</sup> which

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- (24) K. Tori, R. Muneyaki and H. Tanida, Can. J. Chem., 41, 3142 (1963).
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means that the 2-carbon has a similar electron density in both systems, the difference in reactivity is probably not due to a difference in the rate of attack by the electrophile. The absence of transannular reactions in the course of C-Sn cleavage of II suggests that a carbonium ion intermediate is not involved in this case (see Chapter I discussion), which might have accounted for the difference. The best explanation available, is that the transition state for the C-Sn cleavage of II is stabilized by an interaction of the electrophile with the  $\pi$  electrons of the C<sub>2</sub>-C<sub>3</sub> double bond, without actual bond formation and the placement of charge on the ring. This probably implies that the C-Sn bond is nearly broken in the transition state. Nesmeyanov has offered a similar explanation for the observed retention of configuration of  $\beta$ -chlorovinylmercury compounds during C-Hg heterolysis.<sup>25</sup>

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(25) A. N. Nesmeyanov, and A. E. Borisov, Tetrahedron Letters, 1, 158 (1957).

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The stability of the C-C bonds in the destannated quadricyclenes V, VI and IX to attack by electrophiles (V also does not react with bromine in carbon tetrachloride at 30°) is in marked contrast to the behavior of unhalogenated systems. The similar unreactivity of the highly halogenated norbornadienes (see Chapter 1) indicates that in both systems this is the result of the chlorines' withdrawal

of considerable electron density from the ring system. The extremely low field absorption, 2.81 p.p.m., of the cyclopropyl hydrogen in V is in agreement with this explanation (models suggest that the deshielding of this proton is not due to its proximity to one of the chlorines).

The occurrence of protodestannation as well as bromodestannation in the reaction of IV with bromine raises the possibility that radical as well as ionic pathways are involved, especially when contrasted with the very "clean" results of cleavage by hydrogen chloride. This is not unreasonable in view of the reported difficulty of suppressing radical chain reactions in the bromination of olefins, even in polar solvents when the reactions are rapid<sup>22</sup> (in this case the medium is relatively nonpolar and the reaction slow) and even in the absence of impurities.<sup>28</sup> Since nothing is known about chain

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(26) M. L. Poutsma, J. Am. Chem. Soc., 87, 2172 (1965).

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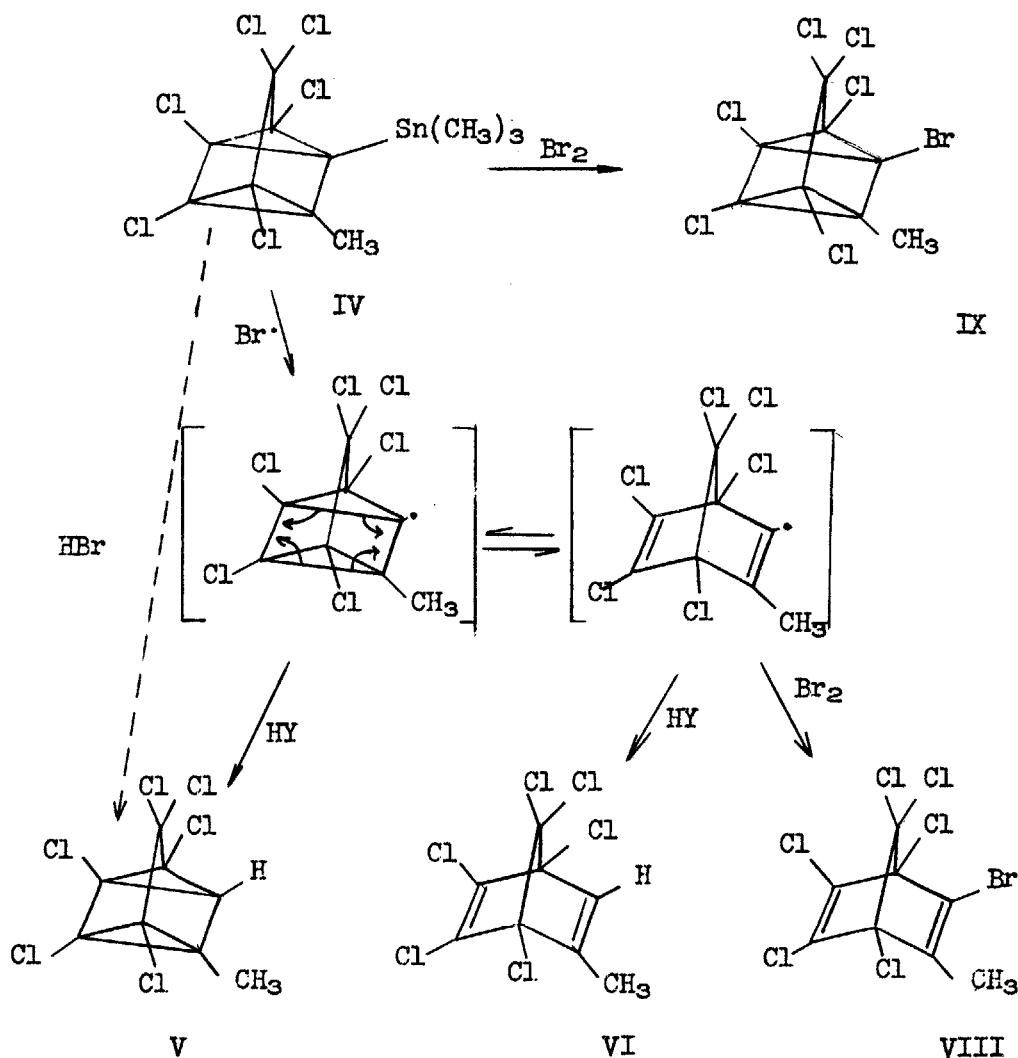
reactions involving C-Sn linkages<sup>27</sup> or about quadricyclic radicals, one

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(27) Radical chain reactions involving aryl silanes have been postulated: L. E. Nelson, N. C. Angelotti and P. R. Weyenberg, *ibid.*, 85, 2662 (1963). C. Eaborn, I. M. T. Davidson, and C. J. Wood, J. Organometal. Chem., 4, 489 (1965).

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can only hypothesize that formation of V, VI and VIII occurs by way of a 2-quadricyclic radical as depicted below. The increase in the

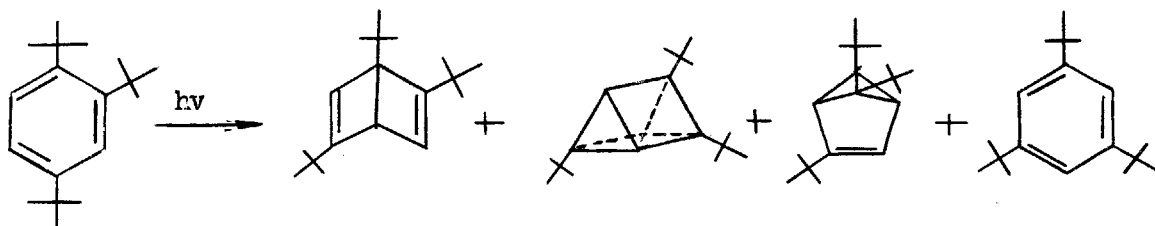


ratio of VIII to IX in the nonpolar solvent system ( $\text{CHCl}_3$ ), the decrease in the yield of V when hydrogen sources such as water and peroxides were removed from the solvent mixture and the observed stability to isomerization of 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-dienyl radicals (see Chapter IV) are in accordance with this hypothesis.

The irradiation of 2-bromo-1,4,5,6,7,7-hexachloro-3-methylbicyclo[2.2.1]-hepta-2,5-diene(VIII) was carried out in an attempt to prepare an authentic sample of the corresponding quadricyclene (IX) and to assess the generality of the photoisomerization of highly halogenated norbornadienes. The reaction conditions were identical to those used in the irradiations of I and II. The course of the reaction was followed by NMR spectroscopy. After 17 hr. the spectrum consisted of singlets at 1.92 p.p.m. (starting material) and 1.4 p.p.m. in the ratio of 1.8:1; since the ratio did not change significantly in the next 18 hr., the irradiation was discontinued. The absorption at 1.42 p.p.m. is reasonably assigned to the methyl group of IX by comparison with the NMR spectra of related quadricyclenes (see Table I).

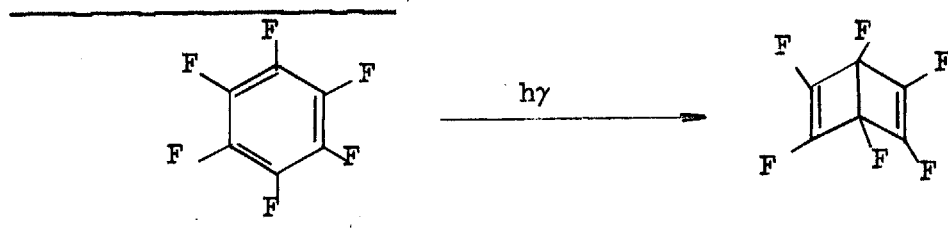
Attempts to separate the photoproduct from VIII by either column chromatography or fractional crystallization were not successful. Very strong evidence for the formation of the quadricyclene IX (in addition to the absorption at 1.42 p.p.m. in the NMR) is given by correlation of bands in the infrared spectrum of the irradiation mixture with those in V, by the ultraviolet spectrum of a recrystallized sample of the mixture (of known ratio from NMR), which has the same maxima as an authentic sample of VIII but with the expected reduction in intensity, and by thermal conversion of the mixture to pure VIII. No satisfactory explanation can be given for the relatively unfavorable photolysis of VIII compared with those of I and II.

Attempts to effect photoisomerization of o-bis(trimethyltin)-benzene were not successful. Recent investigations into the photochemistry of aromatic compounds suggest that the isomeric Dewar benzene, prismane and benzvalene compounds are formed, at least transiently, in all cases and are sufficiently stable to isolate in systems where the benzene ring is destabilized by strong steric interactions, and perhaps, in other cases as well.<sup>28-31</sup> It was of

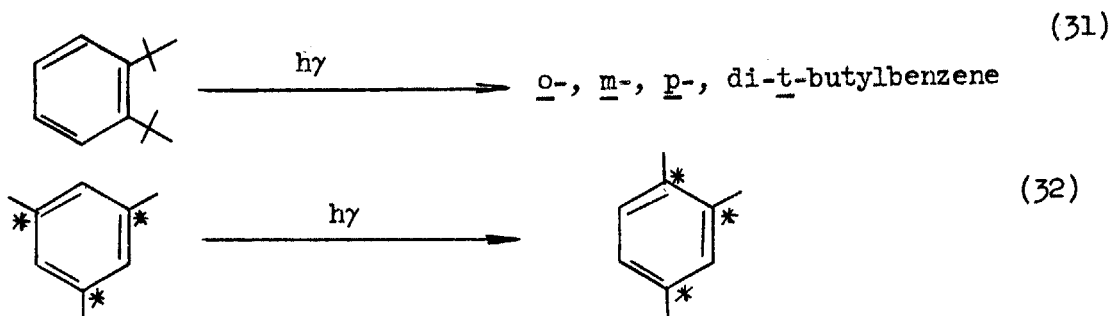


(28) E. E. van Tamelen and S. P. Pappas, J. Am. Chem. Soc., 84, 3789 (1964).

(29) K. E. Wilzbach and L. Kaplan, ibid., 87, 4005 (1965).



(30) I. Haller, ibid., 88, 2070 (1966).



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- (31) A. W. Brugstahler, P. L. Chen and M. O. Abdul-Rahman, ibid., 86, 5281 (1964).
- (32) K. E. Wilzbach and L. Kaplan, ibid., 87, 675 (1965); see also the more recent papers by these authors, ibid., 88, 2067, 2881 (1966).
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interest, therefore, to see if a stable, nonaromatic isomer of o-bis-(trimethyltin)benzene (XI) could be obtained by irradiation, or if isomerization to the other aromatic isomers would occur. Although encouraged by the successful photoisomerization of organometallic-substituted norbornadienes (I) and (II), we were not optimistic in this case because formation of  $\phi$  radicals by C-Sn homolysis should be energetically more favorable than in I and II and should be further encouraged by the relief of strain in XI. There was also the report by Razuvaev<sup>4</sup> of the decomposition of diphenyldiethyltin upon irradiation to give phenyl radicals.

o-Bis(trimethyltin)benzene was irradiated under a variety of conditions: in ether with quartz and vycor filters using both 100 watt and 450 watt, high pressure, mercury lamps and in olefin-free hexane with quartz and vycor filters, with both lamps. Extensive formation of tars occurred in all cases and the only isolable products were starting material (XI) and varying amounts of phenyltrimethyltin; examination of crude reaction mixtures by NMR spectroscopy and of distillates of the reaction residues failed to indicate the presence of any non-aromatic isomer or any m- or p-bis(trimethyltin)benzene.

The formation of divalent tin compounds appears to occur during these irradiations. Evidence for their formation are the orange and red colors formed during the photolysis and the decolorization of the reaction mixtures with precipitation of an amorphous, high melting (>350°) white solid upon exposure to the atmosphere.<sup>33</sup>

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- (33) R. K. Ingham, S. D. Rosenberg and H. Gilman, Chem. Revs., 60, 459 (1960).
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The data described above strongly suggest that homolytic cleavage of C-Sn bonds is the major photochemical reaction of XI, under the conditions investigated. These results are analogous to those obtained with aryl iodides (the energies of C-I and C-Sn bonds are similar, approximately 50 kal.),<sup>34</sup> where photodissociation of the C-I

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- (34) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths, London, 1958.
- 

bond was found to be a very favorable process.<sup>35</sup>

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- (35) (a) N. Kharasch and W. Wolff, J. Org. Chem., 26, 283 (1961);  
(b) J. Kampmeier and E. Hoffmeister, J. Am. Chem. Soc., 84, 3787 (1962).
- 

In summary, it appears that photoisomerization of organometallic compounds is possible, even favorable, in systems such as the vinyl metals but is superceded by photodissociation in other systems.

The different susceptibilities of the C-Sn bonds in I or II and in XI to homolytic cleavage cannot be explained at this time. Since it is likely that the energies of vinyl-tin and aryl-tin bonds are similar, the increased reactivity of the carbon-tin bond in XI may be due to the relief of strain (see discussion in Chapter II). Neuman's very recent study of the photochemistry of vinyl iodides indicates, however, that rather minor changes in the irradiation conditions and molecular geometry markedly change the ratio of photoisomerization, photoelimination, and photodissociation, all of which seem to involve different excited-state intermediates.<sup>36</sup> It is very likely that the

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(36) R. C. Neuman, J. Org. Chem., 31, 1853 (1966).

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excited states involved in the photoisomerization of norbornadienes (apparently triplets<sup>9</sup>) and of benzenes are extremely different.



## EXPERIMENTAL

The discussion of experimental and analytical techniques in the first chapter holds true for this section as well. In particular, it is reiterated that all reactions were carried out in moisture-free flasks in an atmosphere of prepurified nitrogen.

Irradiation of 2,3-Bis(trimethyltin)-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (I): Formation of 2,3-Bis(trimethyltin)-1,4,5,6,7,7-hexachloroquadricyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]heptane (III)-(II-AE-12; V-AE-15).

A solution of 3.093 g. (4.95 mmole) of I in 300 ml. of ether (Mallinckrodt anhydrous ether, freshly distilled from calcium hydride) in a quartz flask equipped with magnetic stirring apparatus and a reflux condenser was irradiated for 24 hr. with a 100 watt, high pressure mercury, external source, Hanovia lamp, maintained a distance of 2 in. from the reaction vessel. An electric fan was used to prevent local overheating. The course of the irradiation was followed by t.l.c. (silica gel-pentane). After only 3 hr. a new compound with an  $R_f$  slightly lower than that of the starting material was the major component of the reaction mixture. A photostationary equilibrium appeared, on the basis of t.l.c., to have been reached after 17 hr.

Removal of the solvent in vacuo (30°/0.3 mm.) left a brown oil which was adsorbed on 2 g. of silica gel and then chromatographed on a 5 in. x 7/8 in. Silica Gel G column using pentane as the eluent;

fractions of approximately 20 ml. were taken. A clean separation was not obtained but the diene(I) was concentrated into the first few fractions. A total of 2.145 g. (70%) of oils and solids were eluted. Fractional crystallization of the initial fractions and recrystallization of the other fractions from pentane-methanol mixtures gave 1.389 g. (45%) of colorless crystals (no starting material appears in t.l.c.), m.p. 120-5° (dec.). Recrystallization from the same solvent gave, m.p. 136-9° (dec.). An analytical sample had m.p. 139-41° (dec.).

The photoproduct had the properties expected for the quadricyclene III. The elemental analysis and molecular weight were the same as for starting material. The ultraviolet spectrum consisted only of end absorption (see Table I), and there was no absorption in the  $>C=C<$  stretching region of the IR spectrum. The infrared spectrum ( $CCl_4$  and KBr) had bands at 2985(m), 2920(m), 1400(w), 1310(w), 1295(w), 1280(m), 1195( $\gamma_{Sn-CH_3}$  sym.; w), 1180(s), 1175(s), 1145(m), 1045(w), 1030(m), 925(w), 900(m), 835(s), 775( $\gamma_{Sn-CH_3}$  rock; s), 720(m), 595(w), and  $530\text{ cm}^{-1}$  ( $\gamma_{Sn-CH_3}$  str.; m).

Anal. Calcd. for  $C_{13}H_{18}Cl_6Sn_2$  (624.4): C, 25.01; H, 2.91; Cl, 34.07. Found (G) (612.2)<sup>37</sup>: C, 25.08; H, 2.96; Cl, 34.40.

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(37) By osmometry in benzene by Mrs. N. Alvord of M. I. T.

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Although the photoisomerization  $I \rightarrow III$  is reproducible under

the conditions described, irradiations for much longer times (42 hr.) or with a more intense light source (9.5 hr. with a 450 watt, Hanovia, high pressure mercury, immersion lamp) failed to yield isolable amounts of the photoproduct (III).

Irradiation of 2-(trimethyltin)-1,4,5,6,7,7-hexachloro-3-methyl-bicyclo[2.2.1]hepta-2,5-diene (II): Formation of 2-(trimethyltin)-1,4,5,6,7,7-hexachloro-3-methylquadricyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]heptane (IV) - (V-AE-29, 38).

The reaction was carried out as described above with 3.34 g. (7.05 mmole) of II in 250 ml. of ether (freshly distilled from  $\text{CaH}_2$ ). The solution was irradiated for 22.5 hr. Removal of the solvent in vacuo left a yellow oil which was examined by NMR ( $\text{CCl}_4$ ) and found to contain singlets at 2.0 p.p.m. ( $\text{C}-\underline{\text{CH}_3}$  of starting material) and at 1.33 p.p.m. in the ratio of 1:5.5, as well as absorption around 0.35 p.p.m. Thin layer chromatography (silica gel-pentane) indicated a single major product with an  $R_f$  slightly lower than that of the starting material. Column chromatography (silica gel - pentane) yielded a total of 2.815 g. (85%) of crystalline solids and oils. The starting material was concentrated into the first fraction (0.2839 g.). Crystallization of the remaining fractions from the pentane-methanol mixture gave three crops, 2.105 g., of colorless crystals, m.p. 60-8° (t.l.c. indicates that no starting material is present). An analytical sample obtained by two recrystallization from the same solvent had m.p. 64-67.5°.

The photoproduct had the properties expected for structure IV. The NMR and UV spectra are discussed above (see Table I). The infrared spectrum ( $\text{CCl}_4$ ) had 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( $\gamma_{\text{Sn-CH}_3}$  sym.; 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  $\text{cm}^{-1}$  ( $\gamma_{\text{Sn-CH}_3}$  str.; m).

Anal. Calcd. for  $\text{C}_{11}\text{H}_{12}\text{Cl}_6\text{Sn}$ : C, 27.78; H, 2.54; Cl, 44.73.  
Found (SMN): C, 28.08; H, 2.77; Cl, 44.82.

Irradiation of 2-Bromo-1,4,5,6,7,7-hexachloro-3-methylbicyclo-[2.2.1]hepta-2,5-diene(VIII) - (VI-AE-3).

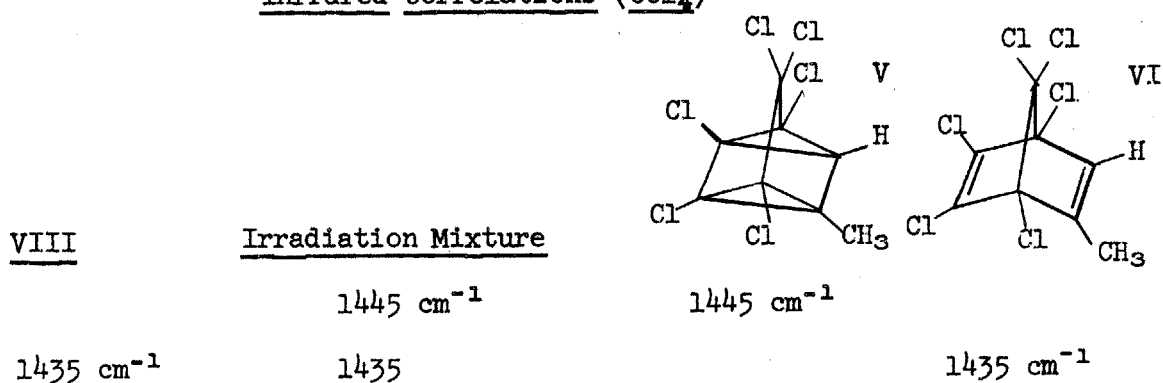
Under conditions identical to those described above, 1.2120 g. (2.55 mmole) of VIII in 100 ml. of ether (fresh can of Mallinckrodt anhydrous) were irradiated for 35 hr. A sample of 13 ml. was withdrawn after 17 hr., the ether removed with a water aspirator and the residue examined by NMR spectroscopy. The spectrum ( $\text{CCl}_4$ ) had singlets of 1.96 p.p.m. ( $\text{C-CH}_3$  of starting material) and at 1.42 p.p.m. in the ratio 1.8:1. The irradiation was continued for an additional 18 hr. Examination of a sample (after removal of solvent) by NMR spectroscopy showed absorption at 1.96 p.p.m. and 1.42 p.p.m. in the ratio 1.41:1. Since the system appeared to be near to photoequilibrium, the irradiation was discontinued.

An attempt was made to separate the mixture by column chroma-

tography on Silica Gel G and on Woelm Alumina (neutral, activity 1). However, all fractions contained starting material, as evidenced, by absorption around  $1600\text{ cm}^{-1}$  in their infrared spectra. Attempts to fractionally crystallize portions of the chromatography residues from pentane-methanol mixtures were also unsuccessful.

Strong circumstantial evidence that the photoproduct has the structure 2-bromo-1,4,5,6,7,7-hexachloro-3-methylquadricyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]-heptane (IX) was given by the absorption at 1.42 p.p.m. in the NMR spectrum of the irradiation mixture, by correlation of bands in the infrared spectrum with those of the related quadricyclene V (see below), by comparison of the ultraviolet spectrum of the mixture with that of pure starting material (see below) and by thermal conversion of the mixture (On a g.l.p.c. column of 7.5% SE 30 on Chromosorb P which was heated to  $200^{\circ}$  and had a He flow of 60 ml./min.; the  $R_F$  was 25 min.) to the pure diene (VIII), identified by comparison of NMR and IR spectra with those of an authentic sample.

Infrared Correlations ( $\text{CCl}_4$ )



<u>VIII</u>	<u>Irradiation Mixture</u>	<u>V</u>	<u>VI</u>
1380 cm <sup>-1</sup>	1380 cm <sup>-1</sup>	1390 cm <sup>-1</sup>	1380 cm <sup>-1</sup>
	1365		
	1330	1330	
	1310	1305	1265
1220	1225	1210	1250
	1190	1195	1205
1155	1155	1150	1150

Ultraviolet Spectra

<u>VIII</u>	<u>Irradiation Mixture *</u>
$\lambda_{\max}$ 224m $\mu$ ( $\epsilon$ 4090)	$\lambda_{\max}$ 224m $\mu$ ( $\epsilon$ 3100)
$\lambda_{\max}$ 277m $\mu$ ( $\epsilon$ 344)	$\lambda_{\text{sh}}$ 277m $\mu$ ( $\epsilon$ 206)

\* The NMR spectrum of the sample used for measurement of the ultraviolet spectrum had absorptions at 1.96 p.p.m. and 1.42 p.p.m. with relative areas of 1.3:1. The sample is, thus, 60% starting material and 40% photo-product.

2-(Trimethyltin)-1,4,5,6,7,7-hexachloro-3-methylquadricyclo-  
[2.2.1.0.<sup>2,6</sup>0<sup>3,5</sup>]hepta (IV), Brominolysis - (V-AE-32, 39; VI-AE-7).

A solution of 0.6234 g. (1.31 mmole) IV in 50 ml. of ether-methanol (1:1 mixture of Mallinckrodt anhydrous ether and Fisher reagent methanol) was cooled to -20° and a solution of 0.225 g. (1.41 mmole) of bromine (Mallinckrodt analytical reagent) in 40 ml. of methanol

added slowly, dropwise. The persistence of the bromine color in the reaction mixture indicated that reaction was very slow at  $-20^{\circ}$ , and the temperature was gradually raised to  $30^{\circ}$ . The remainder of the bromine solution was added and the reaction mixture stirred overnight ( $\sim 15$  hr.).

Removal of the volatiles in vacuo ( $28-40^{\circ}/0.3$  mm.) left an oily brown residue which was chromatographed on a silica gel column using pentane as the eluent. The final fractions of the chromatography were found to consist of a single compound (g.l.p.c. indicated a purity of greater than 85%). Distillation of these fractions yielded a colorless liquid, b.p.  $\sim 55^{\circ}/0.12$  mm. The compound was identified as 1,2,3,4,7,7-hexachloro-5-methylquadricyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]heptane by spectral and elemental analysis. The NMR and UV spectra (see Table I) correlate with the spectra of other halogenated quadricyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]heptanes. The compound, moreover, has absorption at  $1.655\mu$  ( $6042\text{ cm}^{-1}$ ) in the near infrared ( $\text{CCl}_4$ ), which is characteristic of the 6-quadricyclic hydrogen.<sup>37</sup> The infrared spec-

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(37) The isomeric diene 1,2,3,4,7,7-hexachloro-5-methylbicyclo[2.2.1]hepta-2,5-diene (VI) absorbs at  $1.645\mu$  and the quadricyclene is expected to absorb at slightly higher frequency: P. Gassmann and M. Hooker, J. Am. Chem. Soc., 87, 1079 (1965).

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trum (film) has bands at 3080(w), 2980(w), 2930(m), 2865(w), 1605(imp.), 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  $\text{cm}^{-1}$ (w).

Anal. Calcd. for  $\text{C}_8\text{H}_4\text{Cl}_6$ : C, 30.71; H, 1.29. Found(S): C, 30.48; H, 1.42.

The remainder of the chromatography residues, 0.299 g., was examined by g.l.p.c. (F and M isothermal at 222° and 60°ml./min. of He using a 6 ft. x 5 mm. column of 7.5% SE 30 on Chromosorb P) and NMR spectroscopy. The NMR spectrum ( $\text{CCl}_4$ ) had absorptions at 6.19 p.p.m., (4X,  $J = 2.2$  c.p.s.), 2.81 p.p.m. (1X), 2.0 p.p.m. (2X,  $J = 2.2$  c.p.s.), 1.94 p.p.m., 1.42 p.p.m., and 1.35 p.p.m.; the four highest field (methyl) absorptions are in the approximate ratio of 1:1:1:1. The multiplets at 6.19 p.p.m. and 2.0 p.p.m. were readily assignable to the vinyl and methyl protons, respectively, of 1,2,3,4,7,7-hexachloro-5-methylbicyclo[2.2.1]hepta-2,5-diene (VI); the lowest boiling component in g.l.p.c. had an infrared spectrum identical with that of an authentic sample of VI. The absorption at 1.94 p.p.m. could be assigned to the methyl group of 2-bromo-1,4,5,6,7,7-hexachloro-3-methylbicyclo[2.2.1]hepta-2,5-diene (VIII); the highest boiling and major component of the gas chromatograph had the correct melting point, 98-100°, infrared spectrum and elemental analysis for VIII.

Anal. Calcd. for  $\text{C}_8\text{H}_3\text{BrCl}_6$ : C, 24.53; H, 0.77. Found (S): C, 24.24; H, 0.75.

The absorptions at 2.81 p.p.m. and 1.35 p.p.m. were assignable to the cyclopropyl and methyl hydrogens, respectively, of 1,2,3,4,7,7-hexachloro-5-methylquadricyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]heptane. The only



unassigned absorption was that one at 1.42 p.p.m.; this, however, was the precise position of the absorption of the photoproduct of VIII and was tentatively assigned the structure 2-bromo-1,4,5,6,7,7-hexachloro-3-methylquadricyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]heptane (IX)

The yields of V, VI, IX, and VIII were approximately 35%, 15%, 15%, and 15%.

The brominolysis of IV was rerun under rigorously anhydrous conditions (Mallinckrodt anhydrous ether from a fresh can and methanol distilled directly from barium oxide). The purity of the starting stannane was checked by NMR spectroscopy, and the extent of the diene impurity (II) was estimated as < 4%. The reaction vessel was covered with aluminum foil. After the completion of the addition of the bromine solution, the reaction mixture was stirred for 85 hr. Removal of the solvent in vacuo and examination of the residue by NMR spectroscopy revealed the presence of VIII, IX and VI in the ratio of 2:1:1; only a trace of V was present (very weak signal at 2.81 p.p.m.) and there was an absorption at 1.22 p.p.m. that could not be assigned. As a check on the assignment of the absorption of 1.42 p.p.m. to IX the NMR spectrum of a sample of the mixture obtained by irradiation of VIII was superimposed and the absorptions assigned in each system to 2-bromo-1,4,5,6,7,7-hexachloro-3-methylquadricyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]heptane coincided exactly (within .2 c.p.s.).

In another experiment, 0.925 g. (1.95 mmole) of IV (no  $>C=C<$  visible by IR) in 50 ml. of chloroform (Mallinckrodt reagent, dried

over anhydrous magnesium sulfate) in a dry, nitrogen-filled flask was treated with 2.07 mmole of bromine in 25 ml. of chloroform. The addition was started at 0° but reaction was extremely slow at this temperature and the reaction mixture was warmed to room temperature and the addition completed there. The reaction mixture was, then, stirred for 2 days at the ambient temperature. Removal of the volatiles in vacuo (trap-to-trap at 28°/0.5 mm. and then directly at 40°/0.25 mm.) left an oil which was examined by NMR spectroscopy. The spectrum (CCl<sub>4</sub>) had peaks at 1.94 p.p.m. (VIII), 1.43 p.p.m. (IX), 1.32 p.p.m. (C-CH<sub>3</sub> of IV) and 0.36 p.p.m. (Sn-CH<sub>3</sub> of IV); the ratio VIII:IX:IV was 3.5:1:1. Filtration of the reaction residue through a short silica gel column using pentane as the eluent yielded 0.448 g. of oil (corresponds to an 11% recovery of starting material and 46% yield of brominolysis products using the ratios obtained by NMR spectroscopy). Examination of the residue by g.l.p.c. (using conditions identical to those described above) indicated that it consisted of a 10:1 mixture of VIII and VI, identified by their retention times and infrared spectra. The occurrence of VI is due to destannation and rearrangement of the unreacted starting material (IV) on the g.l.p.c. column. This was demonstrated by shooting samples of IV on the column and establishing the identity of the only high boiling component as VI by infrared spectroscopy.

2-(Trimethyltin)-1,4,5,6,7,7-hexachloro-3-methylquadricyclo-  
[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]heptane (IV), Protolysis - (V-AE-52, 65; VI-AE-5).

A solution of 0.331 g. (0.696 mmole) of IV (shown by NMR to contain  $4 \pm 1\%$  of the corresponding diene as impurity) in 30 ml. of ether (fresh can of Mallinckrodt anhydrous) in a flask wrapped with aluminum foil was treated, over 1 hr., with 6 ml. of 0.6 N (3.6 mmole) of methanolic-HCl (DuPont conc. HCl diluted with reagent methanol). The reaction mixture was, then, stirred for 41 hr., at the end of which time, examination of the mixture by t.l.c. (silica gel-pentane) showed that all of the tin compound had reacted.

Removal of low boiling materials in vacuo (trap-to-trap and then directly at  $28^\circ/0.5$  mm.) left a yellow oil. This was neutralized with sodium carbonate (solid), dissolved in carbon tetrachloride and filtered. An NMR spectrum ( $\text{CCl}_4$ ) of this crude reaction mixture showed singlets at 2.81 p.p.m. and 1.34 p.p.m. with relative areas of 1:3 (A doublet was discernible at 1.91 p.p.m. ( $J = 2.2$ ) with an area of 0.04 relative to that of the absorption at 1.34 p.p.m.; this is due to protolysis of the diene impurity in the starting material). Distillation of the residue with a micro-Hickman Still gave 0.153 g. (70%) of colorless liquid, b.p.  $\sim 55^\circ/0.08$  mm., the infrared spectrum of which was identical to that of an authentic sample of 1,2,3,4,7,7-hexachloro-5-methylquadricyclo[2.2.1.0<sup>2,6</sup>.0<sup>3,5</sup>]heptane (V), with the exception of a weak band at  $1600\text{ cm}^{-1}$  due to the diene impurity.

In another experiment, a sample of IV containing 18% of the isomeric diene was treated, under conditions identical to those described above, with one equivalent of hydrogen chloride. Examination of the reaction mixture by t.l.c. (silica gel-pentane) after 8 hr. indicated that all of the diene (II) had reacted but that most of the quadricyclic tin compound (IV) remained. After 71 hr., an aliquot was withdrawn, the solvent removed and the residue examined by NMR spectroscopy; the ratio of starting material(IV) to destannated product(VI) was 7:3.

Under identical conditions a 5.2:2 mixture (by NMR ) of IV and the isomeric diene was treated with a three fold excess of methanolic hydrogen chloride and stirred for 60 hr. After neutralization and removal of the solvent, the crude reaction mixture was examined by NMR spectroscopy and found to contain the singlets at 2.81 p.p.m. and 1.34 p.p.m. characteristic of the quadricyclene VIII and the quartet at 6.19 p.p.m. ( $J = 2.2$ ) and doublet at 1.91 p.p.m. characteristic of the isomeric diene. The ratio  $\frac{\Delta H}{ViH}$  is 2.6:1 and  $\frac{\Delta CH_3}{Vi-CH_3}$  is 2.3:1 (or taking an average 2.45:1), very close to that of the ratio of starting isomers.

A sample of V (containing 4% of the isomeric diene [VI]) was injected onto a g.l.p.c. column which was at a temperature of 200° (F and M isothermal with injection temperature of 210° and detector temperature of 215° and a helium flow of 60 ml./min. with a 6 ft. x 5 mm.

column of 7.5% SE 30 on Chromosorb P). The chromatograph contained a single peak with a  $R_f$  of 18 min.; a collected sample had an infrared spectrum identical with that of an authentic sample of the isomeric diene, 1,2,3,4,7,7-hexachloro-3-methylbicyclo[2.2.1]hepta-2,5-diene (VI).

2,3-Bis(trimethyltin)-1,4,5,6,7,7-hexachloroquadricyclo[2.2.1.0.2,6,3,5]  
heptane (III), Protolysis - (VI-AE-12).

A solution of 0.298 g. (0.477 mmole) of III (no  $\text{C}=\text{C}$  visible in the infrared spectrum) in 50 ml. of a 1:1 methanol-ether mixture was treated, over 1 hr., with 6 mmole of hydrogen chloride in 10 ml. of methanol. The solution was, then, stirred for 66 hr. Removal of the solvent in vacuo left an oily residue which was examined by NMR. The spectrum ( $\text{CCl}_4$ ) had absorptions at 3.23 p.p.m., 2.93 p.p.m. and 0.31 p.p.m. with relative areas of 1:1:3:8; there was no absorption in the region 5-7 p.p.m. Two distillations with a micro-Hickman Still gave 0.085 g. (60%) of colorless liquid, b.p.  $\sim 65^\circ/0.1$  mm. The NMR spectrum ( $\text{CDCl}_3$ ) had a singlet at 2.97 p.p.m. and absorption at 0.38 p.p.m. (either unreacted III or the product of a single C-Sn cleavage), with relative areas of 3:2.

The absorption at 2.97 p.p.m. was thought to be due to the quadricyclic hydrogens of 1,2,3,4,7,7-hexachloroquadricyclo[2.2.1.0.2,6,3,5]-heptane and the purity of the sample is estimated at 90% (assuming that the 0.38 p.p.m. absorption represents at least 9 protons). The

infrared spectrum (film) was in agreement with the structure VII, consisting of absorptions at 3080(m), 2980(imp., w), 2945(imp., w), 2900(imp., w), 2900(imp., w), 1325(m), 1305(m), 1250(m), 1220(s), 1205(m), 1165(m), 1115(s), 1080(w), 1050(br., 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  $\text{cm}^{-1}$ (m). The absorptions between 1325  $\text{cm}^{-1}$  and 1165  $\text{cm}^{-1}$  appear to be characteristic of the highly chlorinated quadricyclenes. A mass spectrum, although showing absorptions above  $M^+300$ , had the molecular ion,  $M^+298$ , ( $\text{C}_7\text{H}_2\text{Cl}_5^{35}\text{Cl}_1^{37}$ ) for VII and the expected absorption of maximum intensity at  $M^+263$  ( $\text{C}_7\text{H}_2\text{Cl}_4^{35}\text{Cl}_1^{37}$ ), due to loss of the 7-chlorine substituent and formation of the relatively stable 7-quadricyclic carbonium ion.<sup>38,39</sup>

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(38) Mass spectrum obtained by Dr. R. Siekman with a Hitachi RMU-6D; his assistance is greatly appreciated.

(39) Quadricyclene, itself, shows a weak molecular ion and a very strong ion at  $^+\text{C}_7\text{H}_7$ : Z. Dolejšek, Z. Hanus, and V. Prinzbach, *Angew. Chem.*, 74, 902 (1962).

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Irradiation of o-Bis(trimethyltin)benzene (XI).

Irradiations of dilute solutions of XI (conc.  $< 3 \times 10^{-4}$ ) were carried out under the following conditions:

<u>Solvent</u>		<u>Filter</u>	<u>Lamp</u>	<u>Duration</u> (hr.)	<u>(Expt. #)</u>
1. ether (dist. $\text{CaH}_2$ )		quartz	260 w.	26	IV-AE-45
2. ether	"	vycor	450 w.	22	IV-AE-58
3. hexane	" 40	vycor	450 w.	18	V-AE-4
4. hexane	"	quartz	100 w.	18	V-AE-73
5. hexane	"	vycor	450 w.	3	VI-AE-8
6. hexane	"	vycor	100 w.	25	VI-AE-22

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(40) The hexane was freed from olefins by repeated extraction with  $\text{H}_2\text{SO}_4(\text{c})$ , then, washed with water and dried, prior to distillation.

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In each case, the solvent was removed in vacuo ( $30^\circ/0.3$  mm.) after the completion of irradiation and the residue dissolved in carbon tetrachloride and examined by NMR spectroscopy. In no case was there any absorption between 1.0-6.5 p.p.m. The residue was distilled with a Hickman apparatus and then examined by g.l.p.c., if sufficient material remained, or examined directly by g.l.p.c. if it did not. In all cases there was only one component with a b.p.  $>250^\circ$  (est.), and its infrared spectrum was identical to that of starting material. Significant amounts of phenyltrimethyltin were formed in all cases (up to 30% in run 5); it was identified by comparison of its retention time in g.l.p.c. and its infrared spectrum with those of an authentic sample

All of the reaction mixtures turned yellow immediately after the onset of irradiation and became orange thereafter. On exposure of these colored solutions to the atmosphere, they rapidly decolorized, precipitating a fine, amorphous solid, m.p.  $>350^{\circ}$ . The solid had characteristic Sn-CH<sub>3</sub> absorptions in the infrared (KBr) at  $2980\text{ cm}^{-1}$ ,  $2920\text{ cm}^{-1}$ ,  $1200\text{ cm}^{-1}$  and  $770\text{ cm}^{-1}$ .



## CHAPTER IV

THERMAL DECOMPOSITION OF 2-METALLO-

1,4,5,6,7,7-HEXACHLOROBICYCLO[2.2.1]HEPTA-

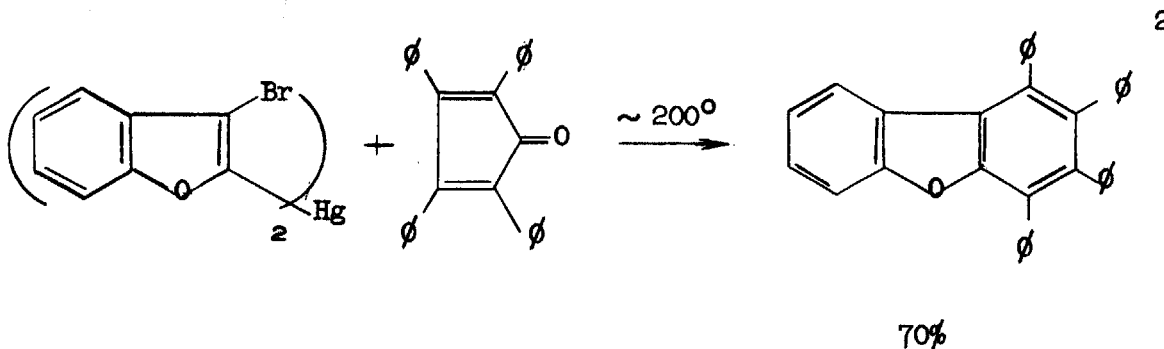
2,5-DIENES AND (o-HALOARYL)TRIMETHYLTIN COMPOUNDS

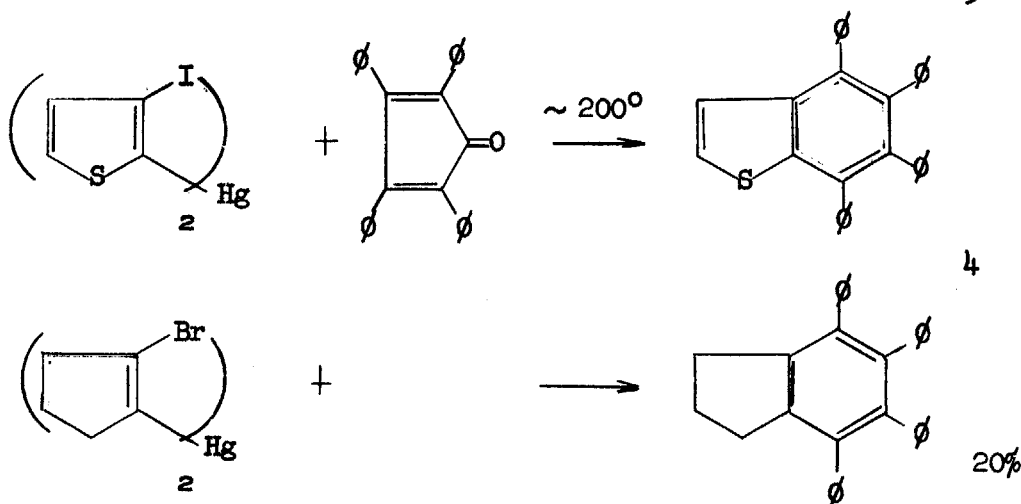
## DISCUSSION

With the availability of a variety of  $\beta$ -haloorganotin compounds from the reactions of various diene-bis(trimethyltin)acetylene Diels-Alder adducts, it became possible to broaden the scope of our study of the thermal reactions of these systems.<sup>1</sup> We were particularly

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- (1) D. Seyferth, C. Sarafidis and A.B. Evnin, J. Organometal. Chem., 2, 417 (1964).
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interested in seeing whether 2-metallo-3-halo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-dienes would react analogously to the *o*-iodo-(trimethyl)tin aromatic system and give coupled products. An alternate possibility was that an intramolecular elimination of the metallic halide would occur, generating hexachlorobicyclo[2.2.1]hept-2-ene-5-yne. Although the unfavorable energetics of this system have already been discussed (see Chapter 1), thermal elimination of mercuric halide has afforded a satisfactory route to several short-lived cycloalkynes which could not be generated from the  $\beta$ -halolithium reagents at moderate temperatures.





- (2) G. Wittig and G. Kolb, *Angew. Chem.*, 74, 479 (1962).
- (3) G. Wittig and V. Wahl, *ibid.*, 73, 492 (1962).
- (4) G. Wittig, J. Weinlich and E.R. Wilson, *Chem. Ber.*, 98, 458 (1965).

Largely because of the excellent background provided by Wittig's studies we chose to make a preliminary examination of the thermal decomposition of bis(2-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-dienyl)mercury (I). Heating I in the presence of tetraphenylcyclopentadienone(cyclone) at 230° (3 hrs.) does not lead to the formation of a Diels-Alder adduct of a bicycloalkyne but rather to a complex mixture of perhalogenated organic compounds and mercuric halides. The identical mixture of products is obtained when I is thermally decomposed in the absence of cyclone. The mercuric halides were always isolated in > 50% yield and were characterized by the formation of adducts with triphenylphosphine, by precipitation of silver halide from methanolic silver nitrate and by t.l.c.; it was demonstrated by elemental analysis that

mixtures of mercuric bromide and chloride were present. The organic products of the reaction fall into two groups which are separable by fractional sublimation. The volatile component (sublimes by  $90^{\circ}/0.03 \text{ mm.}$ ) is a mixture of 2,3-dibromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1.]hepta-2,5-diene(II) and 2-bromoheptachlorobicyclo[2.2.1.]hepta-2,5-diene(III), identified by a comparison of retention times in g.l.p.c. and of infrared spectra with those of authentic samples. The yields of II and III are, typically, 20% and 10%, respectively. The other group of products appears to be a mixture of at least three similar, high-melting, yellow compounds. Attempts to isolate the components of the mixture by a combination of fractional crystallization, fractional sublimation and column chromatography were partially successful. However, structural assignments could not be made with any certainty for any of them. One of the compounds, A, (m.p.  $\sim 240^{\circ}$  with dec.) appears to be a perhalogenated aromatic system on the basis of its infrared and ultraviolet [ $\lambda_{\text{max}}^{\text{EtOH}}$  213  $\text{m}\mu$ ( $\epsilon$ 4500),  $\lambda_{\text{max}}$  274  $\text{m}\mu$ ( $\epsilon$ 20000), and  $\lambda_{\text{max}}$  343  $\text{m}\mu$ ( $\epsilon$ 4000)] spectra and its formation of a deep green complex with  $\text{AlCl}_3^5$ . An apparent

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(5) N.D.Cheronis, *Semimicro Experimental Chemistry*, Hadrian Press, New York, 1960, p. 145.

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molecular formula of  $\text{C}_{14}\text{Cl}_{10}$  (a high resolution mass spectrum suggests a molecular ion,  $\text{M}^+$  521.6834) and a rough similarity of its UV spectrum to that of perfluorophenanthrene<sup>6</sup> suggests that it might be perchloro-

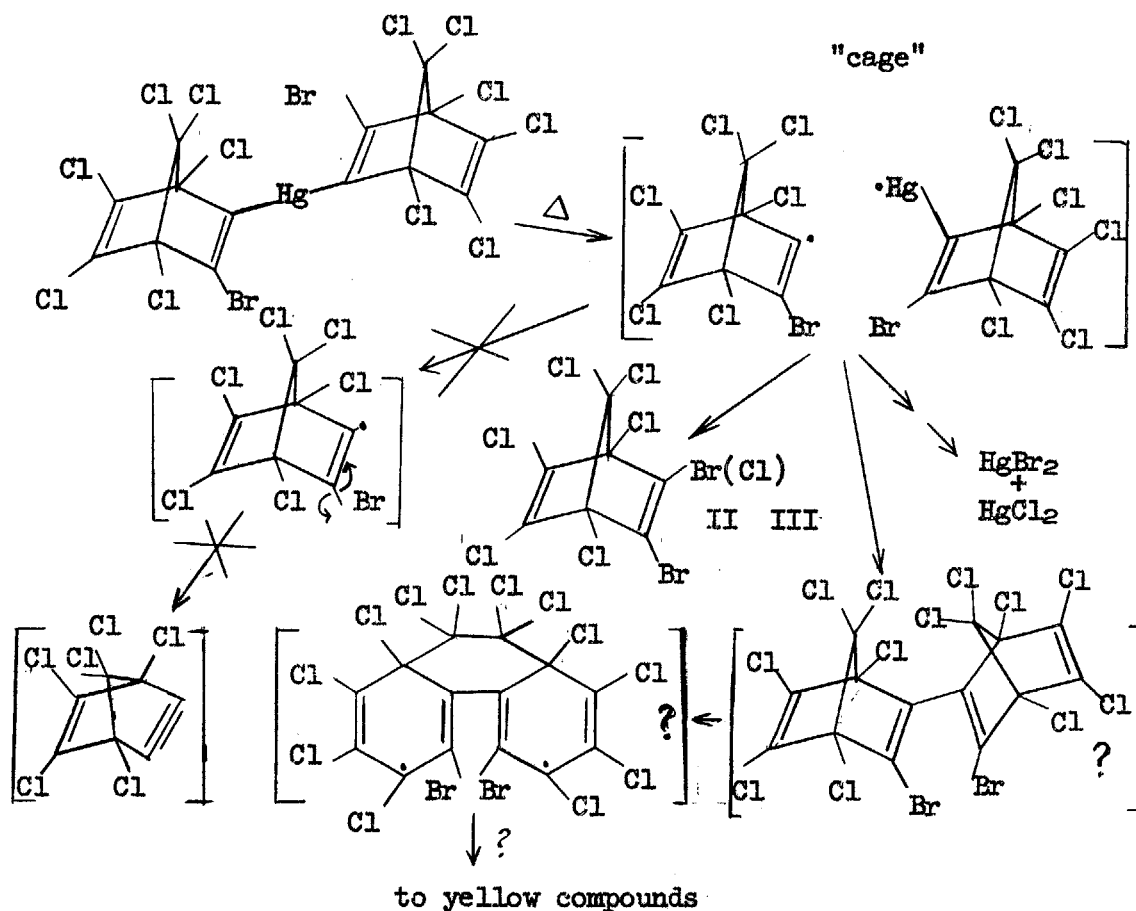
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(6) D. Harrison, M. Stacey and J.C. Tatlow, *Tetrahedron*, 1893 (1963).

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phenanthrene, but this could not be confirmed. Another component, B, had m.p. 296-9° and IR and UV spectra similar to those of A but an elemental analysis corresponding to  $C_{14}Cl_{11}Br$ .

The formation of the perhalonorbornadienes (II) and (III) and of a mixture of mercuric chloride and bromide is best explained by initial homolysis of a C-Hg bond of (I) and subsequent radical reactions of the fragments. The failure of tetraphenylcyclopentadienone to enter the reaction sequence as either a hydrogen source or to trap a bicycloalkyne indicates that the perchloronorbornadienyl radical reacts rapidly, probably with an adjacent norbornadienyl moiety, and does not lose a bromine atom to form a diradical (cycloalkyne) to a significant extent.



Dimerization of two norbornadienyl radicals and subsequent reactions involving destruction of the bridgehead<sup>7</sup> might be the source of the yellow compounds described above.

- (7) Cleavage of the bridgehead bonds in 1,2,3,4,7,7-hexachlorobicyclo-[2.2.1]hepta-2,5-dienes generally occurs at 230-300° but might be somewhat more facile here due to steric effects: H.M. Molotsky, U.S. Pat. 2,946,817 (1960); C.A., 55, 5856 (1961).

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The mechanism described above, which depicts an initial C-Hg homolysis in I followed by a reaction within "a cage", has a very strong analogy in Razuvaev's studies of the thermal decomposition of diisopropylmercury<sup>8</sup> and dicyclohexylmercury.<sup>9</sup> Both of these systems decompose on

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- (8) G.A. Razuvaev, O.N. Druzhkov, W.F. Zhiltsov and G.G. Pelukov, Zh. Obschch. Khim., 35, 174 (1965); C.A., 62, 13168(1965)
- (9) G.A. Razuvaev, G.G. Petukov, S.F. Zhiltsov and L.F. Kudryatsev, Dokl. Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk, 144, 810 (1962); C.A., 57, 15136a(1962)

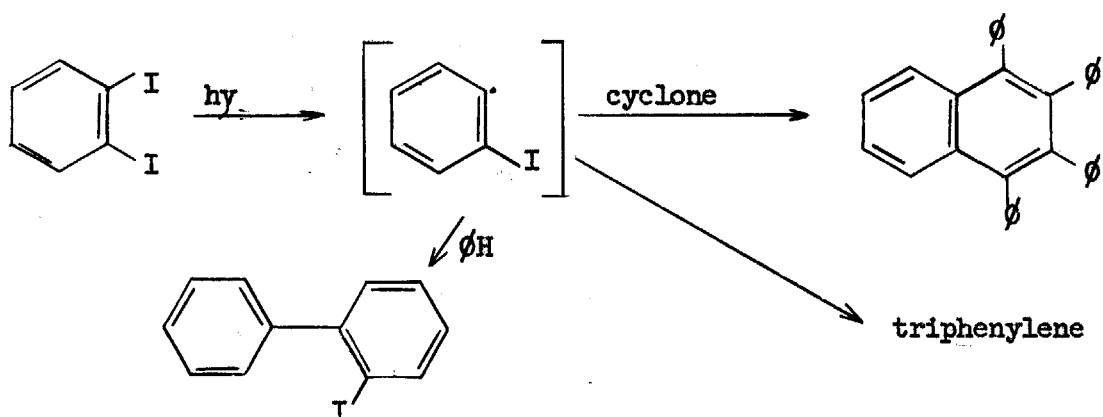
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heating (100-210°) to give a mixture of the products expected from radical reactions: RH, R-R, etc., where R is either isopropyl or cyclohexyl. In neither case, however, was there significant interaction with the solvent which was benzene or deuteriobenzene; almost no products with either phenyl groups or deuterium were formed.

Radical reactions of vinylic organometallic compounds have been postulated previously<sup>10,11</sup> but proof for the formation of vinyl radicals

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- (10) A.N. Nesmeyanov and A.E. Borisov, Tetrahedron, 1, 158 (1957).
- (11) M.M. Koton, T.M. Kiseleva and N.P. Zapelova, Zh. Obschch. Khim., 30, 186 (1960); C.A., 54, 22436e (1960).
-

was not presented in those cases. The formation of cycloalkynes from  $\beta$ -halomercury compounds observed by Wittig's group<sup>2,3,4</sup> may, at first sight, appear to contradict a radical mechanism but their results are very reasonably interpreted as involving initial C-Hg scission followed by elimination of halogen and formation of the diradical (cycloalkyne). There is evidence for a two step formation of cycloalkynes in the work of Kampmeier.<sup>12</sup>




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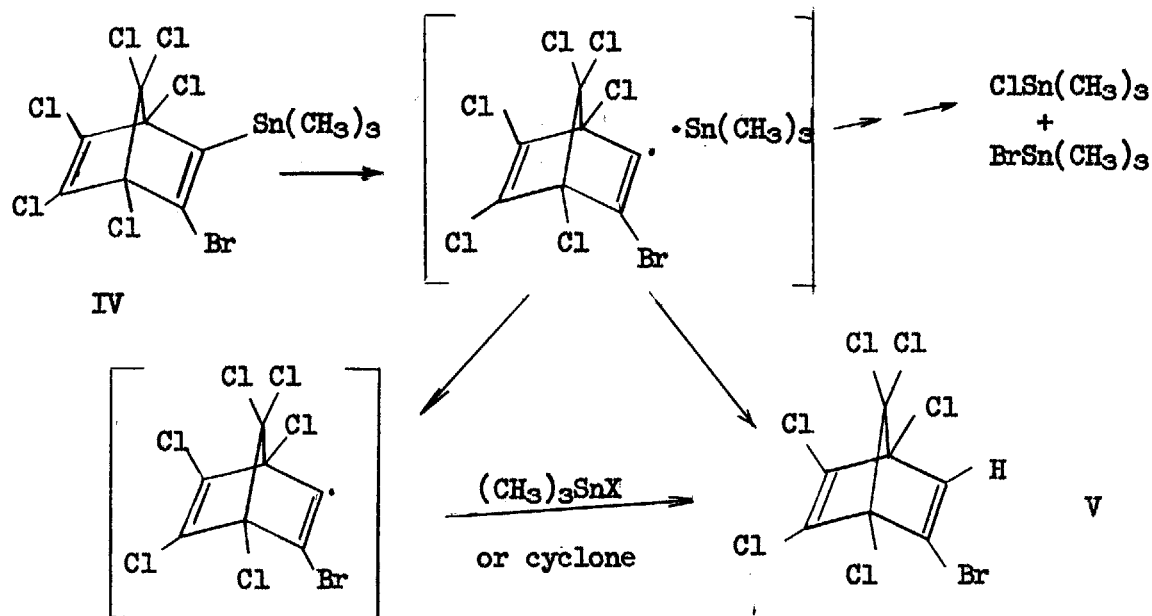
(12) J. Kampmeier and E. Hoffmeister, J. Am. Chem. Soc., 84, 3787 (1962).

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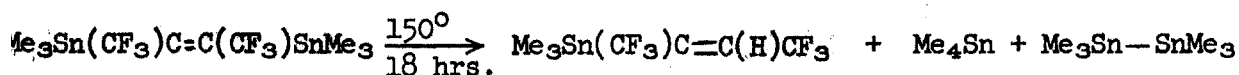
In the case of I, elimination of a bromine atom to form the bicycloalkyne is apparently so energetically unfavorable that it does not occur to any extent. (See discussion in Chapter 1.)

If our hypothesis of a radical mechanism is correct, thermal decomposition of organotin compounds analogous to I should give similar results, with the possible exception that abstraction of a halogen, which is favored in I by the geometry of the molecule, might be supplanted by hydrogen abstraction.

When 2-(trimethyltin)-3-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene(IV) was decomposed in the presence of cyclone, no Diels-Alder adduct was formed, and the major product (51%) was 2-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (V), identified by comparison of NMR and



infrared spectra with those of an authentic sample. The occurrence of V is difficult to explain by any sequence other than C-Sn homolysis to form a 2-norbornadienyl radical, and its subsequent abstraction of a hydrogen from either a trimethyltin moiety or from cyclone. The literature affords an analogy both for the proposed homolysis of a vinyl-tin bond and for the ability of  $\text{Me}_3\text{SnX}$  to act as a hydrogen source.<sup>13</sup>

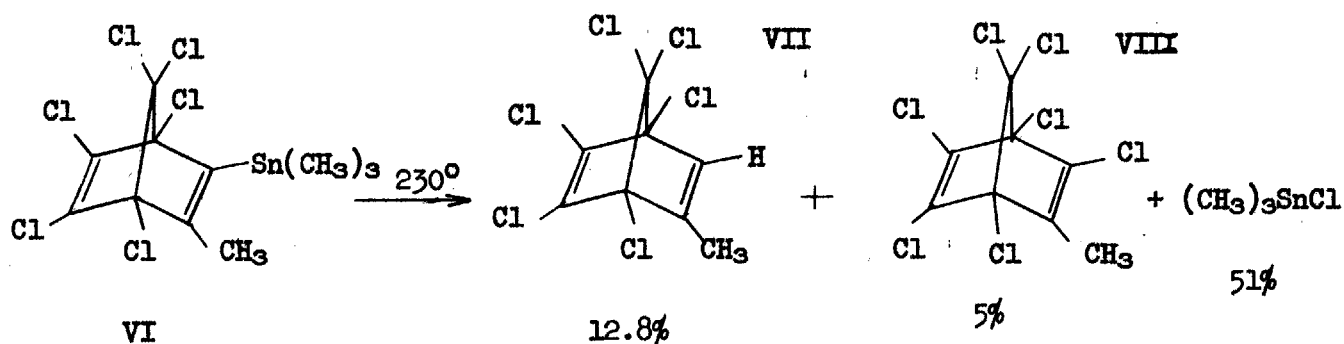


(13) W.R. Cullen, D.S. Dawson and G.E. Styan, J. Organometal. Chem., **3**, 406 (1965).

Thermal decomposition of the analogous 2-(trimethyltin)-1,4,5,6,7,7-hexachloro-3-methylbicyclo[2.2.1]hepta-2,5-diene (VI) in the absence of



cyclone resulted in the formation of the products of both hydrogen and chlorine abstraction by an intermediate 2-norbornadienyl radical. The occurrence of halogen abstraction in this case and not in the decomposition of IV possibly implicates cyclone as a hydrogen atom donor in



that case. In line with this hypothesis, thermal decomposition of VI in the presence of cyclone gave the same two bicyclic products but the ratio VII/VIII had increased to 3.5:1. Decomposition of VI was also observed in the course of g.l.p.c. analysis. Injection of samples of either VI or its quadricyclic photoisomer onto g.l.p.c. columns (coated with G.E.'s Silicone SE-30) at about 200° resulted in the elution of complex mixtures, the highest boiling component of which was VII, identified by comparison of its retention time and infrared spectrum with those of an authentic sample.

The observed stability of 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-hepta-2,5-dienes not substituted with tin or mercury further emphasizes the role of the weak C-M bond in the thermal decompositions of I, IV and

VI.<sup>14</sup> This is dramatically demonstrated when the tin atom of IV is

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- (14) The bond dissociation energy (D) of the C-Hg bond in dialkylmercury compounds is 40-50 kcal.: T.L. Cottrell, "The Strengths of Chemical Bonds", Academic Press, New York, 1954. The D's for alkyltin and aryltin bonds are in the range of 68-78 kcal.: A.L. Yergey and F.W. Lampe, J. Am. Chem. Soc., 87, 4204 (1965).
- 

replaced by silicon. The resultant 2-(trimethylsilyl)-3-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene can be collected by g.l.p.c. without any decomposition at a column temperature of 225°; the retention time of the silane under these conditions is approximately 1 hr.

Although the data described above do not rigorously demonstrate the intermediacy of 2-norbornadienyl radicals in the thermal decomposition of I, IV and VI by the classical criteria of free radical chemistry,<sup>15</sup>

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- (15) Common criteria such as cumene participation and kinetics, would be difficult to apply because of the high temperature and heterogeneity of these reactions and because of the apparent occurrence of "cage" reactions.
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the nature and distribution of the products can only be explained by such intermediates. Any doubts as to the existence of vinylic radicals have, moreover, been dispelled by the unequivocal generation of these species from classical precursors (peresters) by Kampmeier<sup>16</sup> and by Singer.<sup>17</sup>

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- (16) J. Kampmeier and R.M. Fantazier, J. Am. Chem. Soc., 88, 1959 (1966).

- (17) L.A. Singer and N.P. Kong, Tetrahedron Letters, 2089 (1966).
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Vinyl metal compounds, such as those described above, are of no synthetic utility as sources of free radicals but other unsaturated organometallics might be useful in cases where classical free radical precursors are more difficult to come by.<sup>18</sup>

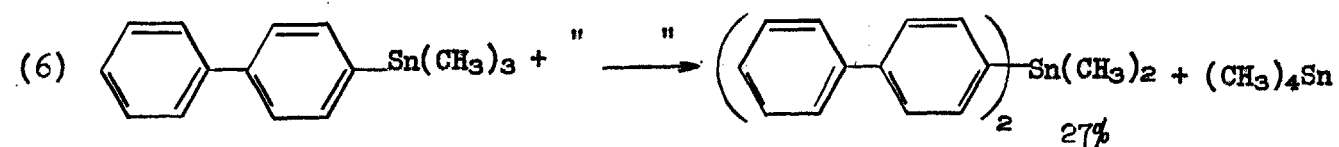
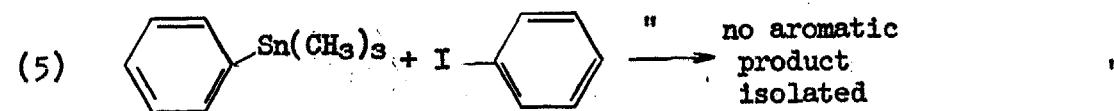
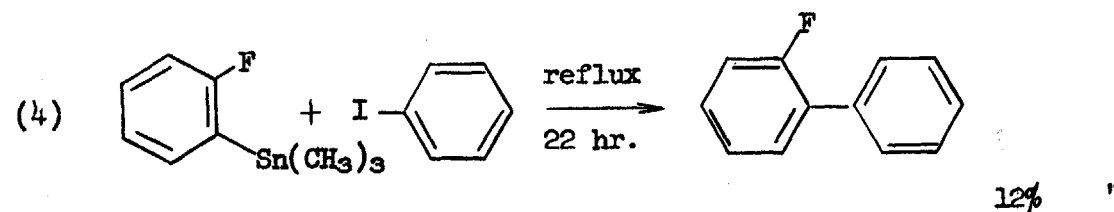
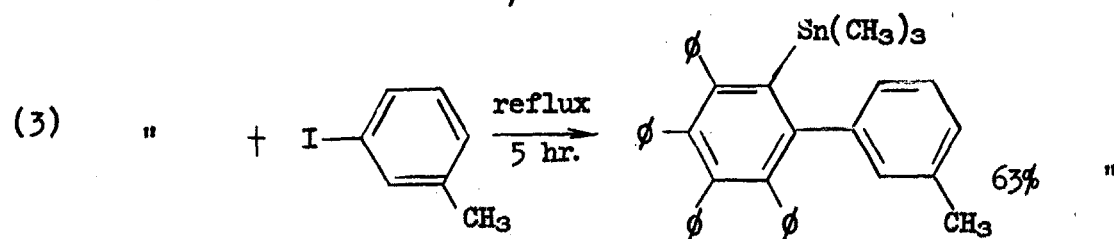
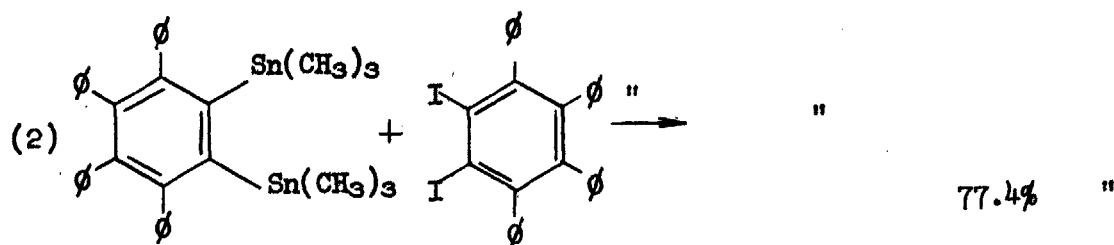
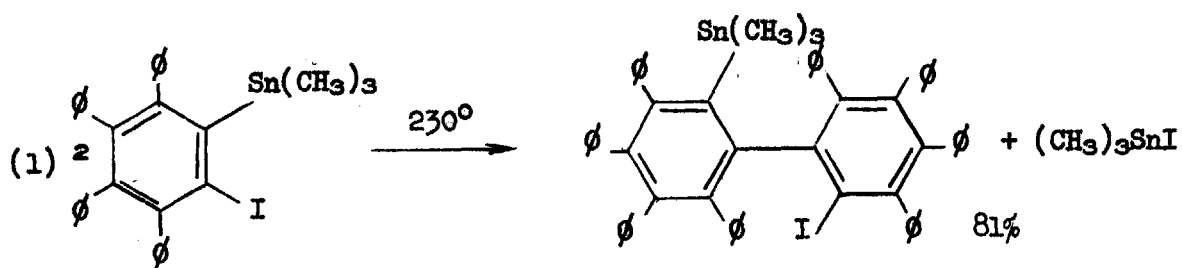
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- (18) One such area might be that of acetylenic radicals which have recently been generated from the somewhat treacherous acetylenic halides: A.M. Tarr, O.P. Strausz and H.E. Gunning, Trans. Faraday Soc., 62(5), 1221 (1964).
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Interpretation of the results obtained by thermal decomposition of aryltrimethyltin compounds, in particular those with a halogen ortho to the trimethyltin, is more difficult than it is for the organometallic substituted norbornadienes. Our initial expectation was that o-iodo-(trimethyltin)benzene systems would eliminate trimethyltin iodide and form benzyne in a manner analogous to that observed with benzene<sup>19</sup> and

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- (19) G. Wittig and F. Ebel, Ann. Chem., 650, 20 (1961).
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other aromatic systems<sup>2,3</sup> with mercury and iodine in the ortho positions. The similar thermal behavior of the C-Sn and the C-Hg bonds in I, IV and VI and the absence of factors that would prevent elimination of a halogen to form a diradical in this case made the expectation seem very reasonable.

We did not, however, observe this sort of reaction. Instead, our initial studies indicated that thermal decomposition of o-iodo(trimethyltin)-benzenes, or of mixtures of aryltrimethyltin compounds and aryl iodides, yielded coupled products (biaryls) or the products of disproportionation of the organotin compound.



Although comparisons among these data are somewhat hazardous in view of the dissimilar reaction conditions, it is evident that high yields of coupled products were obtained only when the aryltin compound was sterically strained (1-3). When it was not, either a low yield (4), no yield (5) or the products of disproportion (6) were obtained.

The coupling reaction observed above bears a formal similarity to the Ullmann reaction in which aryl halides (generally iodides) are coupled under heterogeneous conditions with a copper-bronze "catalyst" at a temperature of about 200°. It is unlikely in this case, as it apparently is with the Ullmann reaction,<sup>20</sup> that free aromatic radicals are

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(20) P. Fanta, Chem. Revs., 64, 613 (1964).

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involved, since the products of hydrogen and iodine abstraction do not generally occur and since the coupling is positionally specific. Specific radical displacements are not observed with aromatic radicals<sup>21</sup>, although such

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(21) C. Walling, Free Radicals in Solution, Wiley, New York, 1957.

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reactions are well characterized for halogen radicals and aryl halides<sup>22</sup> and have recently been reported for silyl radicals and aryl silanes.<sup>23</sup>

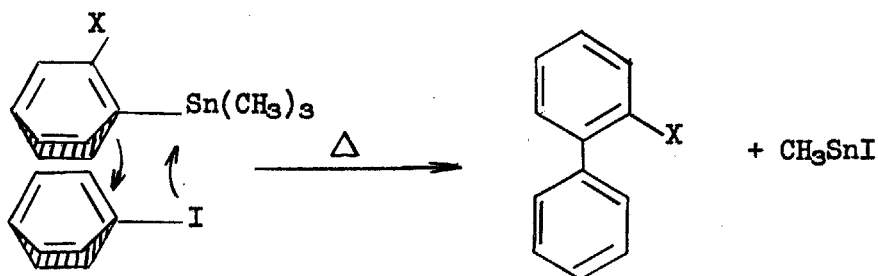
(22) B. Miller and C. Walling, J. Am. Chem. Soc., 79, 4187 (1957).

(23)(a) L.E. Nelson, N.C. Angelotti and D.R. Weyenberg, ibid., 85, 2262 (1963).

(b) C. Eaborn, I.M.T. Davidson and C.J. Wood, J. Organometal. Chem., 4, 489 (1965).

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Since free radical intermediates are unlikely, and free polar intermediates are unreasonable under the reaction conditions, the best postulate of a reaction mechanism involves a complex of the aryl tin compound and aryl iodide with the formation of the aryl-aryl and the tin-iodine bonds in a roughly concerted manner. The polariz-



ability of both tin and iodine would facilitate such a reaction. The observed accelerating effect of the phenyl groups is, presumably, due to a "loosening" of the C-Sn linkage because of the severe steric interactions between phenyl and trimethyltin groups. Although complex formation between such highly hindered species is not intuitively attractive, Ullmann reactions of systems such as o-iodo-t-butylbenzene proceed with facility.<sup>24</sup> One appealing aspect of this hypothesis

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(24) M. S. Lesslie and U. J. H. Mayer, J. Chem. Soc., 611 (1961).

is that it is very close to the mechanism generally proposed for the disproportionation reactions of unsymmetrical organometallic compounds.<sup>25</sup>

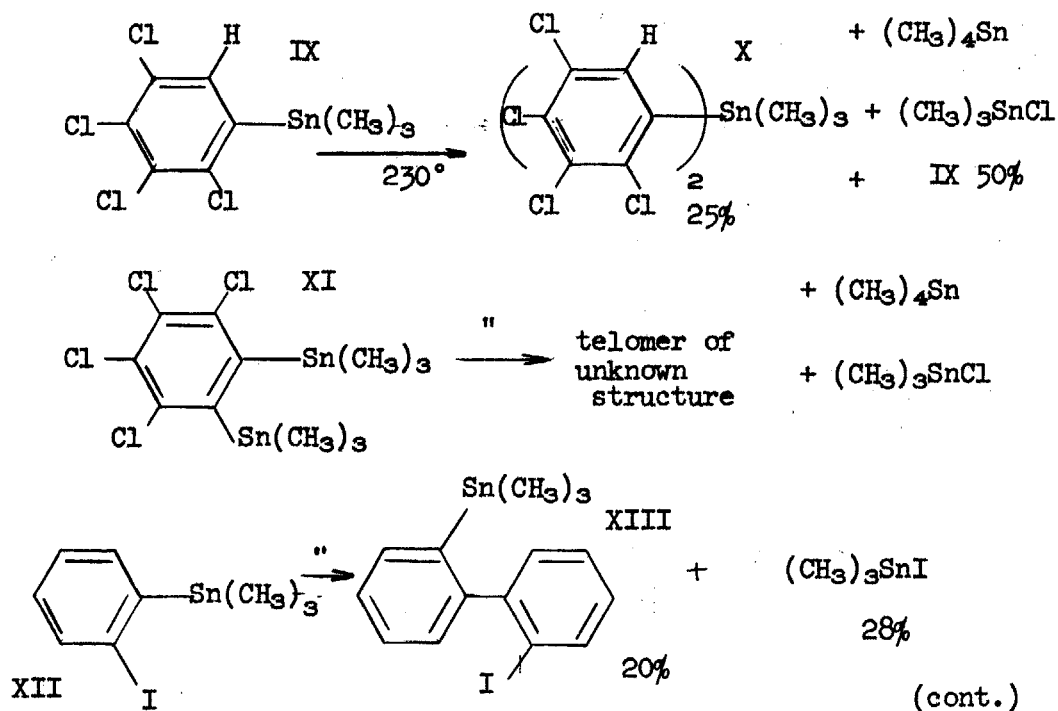
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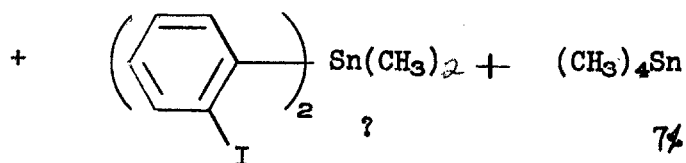
(25) See, for example, R. E. Dessy, Y. K. Lee and J. Y. Kim, J. Am. Chem. Soc., 83, 1163 (1961).

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Decomposition via two similar but competitive paths is a hypothesis that fits rather well with the data available. Extremely bulky substituents, while favoring reaction, should preclude disproportionation and, accordingly, a high yield of coupled product is obtained in (1-3). Electronic effects are more difficult to predict but disproportionation should be encouraged by the removal of the aryl iodide from the reaction mixture.

The few further examples of thermal decompositions of aryltri-methyltin compounds that could be studied in the time available do not permit a more rigid definition of the mechanism of the coupling reaction. They are, however, in accord with the hypothesis presented above.





The formation of only disproportionation products in the thermal decomposition of 1-(trimethyltin)-2,3,4,5-tetrachlorobenzene (IX) would appear to emphasize the role of the weak, highly polarized aryl-iodine bond in the coupling reaction. In accordance with this concept, heating IX with an excess of p-iodotoluene (210° for 22 hr.) appears, on the basis of preliminary data, to give the coupling product, 2,3,4,5-tetrachloro-4'-methylbiphenyl.

The thermal decomposition of 1,2-bis(trimethyltin)tetrachlorobenzene (XI), failed to yield an identifiable aromatic product. A crystalline product was obtained, m.p. 362-7° (dec.). but an osmometrically determined molecular weight and an elemental analysis indicate a highly complex, telomeric structure for the material. As a check on the occurrence of free radical reactions, the crude reaction mixtures were examined by NMR spectroscopy for aromatic hydrogens; none were present.

o-Iodo(trimethyltin)benzene (XII) is more stable thermally than is its tetraphenyl analog which would appear to be good evidence for steric acceleration of the decomposition of 1,2-bis(trimethyltin)-tetraphenylbenzene. Decomposition of XII by radical paths is ruled out by the absence of phenyltrimethyltin and iodobenzene, the expect-



ed products of radical decomposition, in the reaction mixture. Characterization of the products of reaction was extremely difficult due to their very high boiling points ( $> 400^\circ$ ) and similar behavior in absorption chromatography. Only the structure of the coupling product is unambiguously established.

(2-Iodo-2'-biphenyl)trimethyltin (XIII) was identified by its NMR spectrum, and by elemental and mass spectral analysis. The NMR is particularly characteristic, consisting of a doublet ( $J = 8$  c.p.s.) with secondary splitting at 7.85 p.p.m. (1H), a plex band 6.77 p.p.m.-7.6 p.p.m. (7H) and a singlet at 0.04 p.p.m. (9H) upfield from tetramethylsilane. The low field aromatic absorption is analogous to that of the 3-hydrogen in 2-iodobiphenyl which appears at 7.8 p.p.m. ( $J = 8$  c.p.s.). The trimethyltin absorption appears at the same place as it does in (2-biphenyl)trimethyltin. The mass spectrum shows a weak molecular ion peak,  $M^{+441}$ , ( $C_{15}H_{13}Sn^{120}I$ ) and a very strong stannonium ion resulting from loss of a methyl group ( $M^{+428}$ :  $C_{14}H_{15}Sn^{120}I$ ), which is in complete agreement with the fragmentation expected for this molecule on the basis of Glocking's studies of arylalkyltin compounds.<sup>26</sup>

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(26) P. B. Chambers, F. Glocking, J. R. C. Light and M. Weston, Chem. Comm., 281 (1966).

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The presence of bis(o-iodophenyl)dimethyltin (XIV), the product of disproportionation of XII, in the reaction mixture has not

been unequivocally established, as an analytical sample could not be obtained. (It is inseparable from XII by column or thin layer chromatography and could not be isolated in pure form by g.l.p.c.)

Its presence is implied by the following data. Chromatography fractions free from starting material (by t.l.c.) show two peaks by g.l.p.c. and two kinds of  $\text{Sn-CH}_3$  absorption in the NMR spectra. The high field absorption at + 0.04 p.p.m. is due to XIII, and the lower field peak, 0.8 p.p.m., occurs at the same place as the protons in bis(2,3,4,5-tetrachlorophenyl)dimethyltin (X). Treatment of these same fractions with excess HCl results in the formation of 2-iodobiphenyl and iodobenzene, the expected cleavage products of XIII and XIV, respectively, in approximately equal amounts.

The thermal behavior of o-iodo(trimethyltin)benzene XII and its mercury analog, bis(o-iodophenyl)mercury, XV<sup>19</sup> appear to be quite different. Under identical conditions, XII is relatively stable and gives a low yield of coupling and disproportionation products and XV decomposes to triphenylene (31%). The intermediacy of benzyne in the formation of triphenylene was not established in that case for XV, although it was (by trapping experiments) in the gas phase thermal decomposition and the photolytic decomposition. Dessy has reported that bis(perchlorophenyl)mercury is "stable" up to 383°<sup>27</sup> which sug-

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(27) F. E. Paulik, S. I. E. Green and R. E. Dessy, J. Organometal. Chem., 3, 229 (1965).

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gests that the observed thermal decomposition of XV at 230° is initiated by dissociation of the C-I bond; this is probably the case in the photodecomposition of XV (by analogy to Kampmeiers results<sup>12</sup>). If this were so, XII and XV would be expected to behave more similarly than they do. It is possible that XV forms triphenylene by consecutive coupling reaction<sup>28</sup> and that coupling of XII fortuitously stops

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(28) Triphenylene is not the product of trimerization of benzyne, or of reaction of benzyne with biphenylene: R. D. Bartle, H. Heaney, D. W. Jones and P. Lees, *Tetrahedron*, 3289 (1965).

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at an earlier stage (XIII) due to steric and energetic considerations. All of this is in marked contrast to the similar and apparently homolytic decompositions of 2-(trimethyltin)-3-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene and bis(2-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-dienyl)mercury.

The greater thermal stability of the aryl-tin bond, on the one hand, and the greater photolytic stability of the perhalonorbornadienyl-tin bond, on the other, also raise questions which cannot be answered at present. Clearly, factors other than the dissociation energies of the C-Sn bonds in these systems (the difference is certainly less than 10 kcal.) are involved in determining this dichotomy in their behavior. However, the difficulties inherent in attempts to relate the photochemical behavior of molecules to their behavior when energy is introduced by different means (thermally, or by electron

impact, among others) are enormous, even in much simpler systems.<sup>29</sup>

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(29) See, for example, N. J. Turro, D. C. Neckers, P. A. Leermakers, D. Seldner and P. D'Angelo, J. Am. Chem. Soc., 87, 4097(1965).

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The organometallic systems discussed above, which display the whole spectrum of behavior under these various conditions, would obviously be a fruitful area for studying such relationships. At the same time, they indicate the complexity of the problems involved in such a study.

## EXPERIMENTAL

The discussion of experimental and analytical techniques in the first chapter holds true for this section as well. In particular, it is reiterated that all reactions were carried out in moisture-free flasks, in an atmosphere of prepurified nitrogen.

Bis(2-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-dienyl)mercury (I), Thermolysis - (IV-AE-4,9; V-AE-21).

A dry, 50 ml. round bottomed flask was equipped with a sublimation apparatus and charged with 3.0485 g. (3.19 mmole) of I. The apparatus was evacuated (90°/0.05 mm.) for 3 hr. and, then, filled with nitrogen. The reaction vessel was rapidly heated to 225° with a silicone oil bath and maintained at that temperature for 3 hr. Some white crystals sublimed onto the cold finger during the thermolysis.

Sublimation (90°/0.05 mm.) of the reaction mixture yielded 1.0592 g. of off-white crystals. The residue was sublimed (150°/0.02 mm.) and yielded an additional 0.533 g. The sublimates were combined and extracted with carbon tetrachloride. The component insoluble in carbon tetrachloride, 0.5968 g., melted with decomposition at 220-50°. In a previous experiment conducted in an identical manner, this component was shown to be a mercuric halide by comparison of  $R_f$ s in t.l.c. (silica gel-benzene) with authentic samples, by formation of a complex with triphenylphosphine<sup>30</sup> and by formation

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(30) R. C. Evans, J. Chem. Soc., 1209 (1940).

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yellow-white precipitate with methanolic silver nitrate. A portion of the material was resublimed and submitted for elemental analysis.

Anal. Calcd. for  $\text{HgBr}_2$ ,  $\text{HgCl}_2$ : Hg, 63.5; Hal., 36.5. Found (S): Hg, 64.0; Hal., 37.4.

If a one to one ratio of mercuric bromide to mercuric chloride is assumed, the yield of mercuric halide is 60%.

The portion of the sublimate that was soluble in carbon tetrachloride (0.996 g., by difference) was examined by g.l.p.c. (F and M isothermal at  $210^\circ$  using a 6 ft. x 5 mm. column of 7.5% SE 30 on Chromosorb P) and found to consist of two major components and traces of a third. The two major components were identified as 2,3-dibromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (II) and 2-bromoheptachlorobicyclo[2.2.1]hepta-2,5-diene (III), by comparison of retention times and infrared spectra (collected samples) with the authentic materials. The yields of II and III were 0.753 mmole (23.9%) and 0.379 mmole (11.9%), respectively, on the basis of quantitative g.l.p.c. using 1-chloronaphthalene as an internal standard and correcting for the molar responses.

The residue from the sublimation was dissolved in 75 ml. of benzene, adsorbed on a few grams of silica gel and filtered through a column of Silica Gel G using pentane (1 l.) as the eluent. The residue from the chromatography, 0.493 g. of orange-tan crystals, was fractionally crystallized from benzene. The first two crops, 0.071 g.

of yellow crystals, were recrystallized twice from benzene to give yellow needles, B, m.p. 296-9° (dec.). The compound absorbed in the ultraviolet (CH<sub>2</sub>Cl<sub>2</sub>) at  $\lambda_{\max}$  ( $\epsilon$  21,000) and  $\lambda_{\max}$  356m $\mu$  ( $\epsilon$  4,600),<sup>31</sup>

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(31) A molecular weight of 600 was assumed for the calculations.

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The infrared spectrum (KBr) had bands at 1625(m), 1520(s), 1260(m), 1160(s), 1080(m), 935(m), 800(w), 785(m), 720(s), 655(s), 620(m), 570(m), 555(m), and 510 cm<sup>-1</sup>(w). A structure could not be assigned to the compound.

Anal. Found (S): C, 26.40; Cl, 61.90; Br, 11.87. Calcd. for C<sub>14</sub>Cl<sub>11</sub>Br: C, 26.66; Cl, 61.44; Br, 12.52.

Addition of hexane to the mother liquors yielded golden crystals which were repeatedly recrystallized from benzene-hexane mixtures. Material melting sharply could not be obtained. A sample of the yellow needles, A, m.p. 235-45° (dec.), had an infrared spectrum similar to that of B.

The possibility that some products might have been lost in the chromatographic filtration of the sublimation residue was excluded by the fact that in another experiment, conducted in an identical manner but worked up entirely by fractional sublimation, an analogous mixture of yellow compounds was isolated.

In another experiment under the same conditions, a sample of the yellow compound, A, m.p. 239-44°, was isolated and analyzed by high resolution mass spectrometry.<sup>32</sup> The strongest peak in the

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(32) The spectrum was obtained with the assistance of Mr. John Hayes, of M. I. T., whose help is greatly appreciated.

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spectrum occurred at  $M^+521.6834$  and corresponds to  $C_{14}Cl_8^{35}Cl_2^{37}$ ; there were no ions of any importance above this. Other favorable ions were identified as  $C_{14}Cl_8$ ,  $C_{14}Cl_4$ ,  $Cl_7Cl_4$ , and  $C_7Cl_3$ .

An attempt to oxidize a sample of A with fuming sulfuric acid (3 hr. at  $90^\circ$ ) yielded a yellow solid, m.p.  $\sim 250^\circ$  (dec.), which showed carbonyl absorption in the infrared spectrum ( $\nu_{C=O}$   $1730\text{ cm}^{-1}$ ), but which could not be purified. Under identical conditions, perfluorophenanthrene was converted to perfluorophenanthrone.<sup>6</sup>

When an intimate mixture of 0.5752 g. (0.602 mmole) of I and 0.4594 g. (1.195 mmole) of cyclone (Aldrich reagent), was heated at  $225^\circ$  for 2.5 hr., under conditions described above, the decomposition of I appeared to follow a similar course. During the reaction, white platelets condensed on the unheated sides of the flask and, after thorough washing with carbon tetrachloride, 0.086 g., m.p.  $228-35^\circ$  (dec.) was obtained; the material gave a white precipitate of silver halide when treated with methanolic silver nitrate. Sublimation of the reaction mixture ( $60^\circ/0.2\text{ mm.}$ ) yielded 0.1257 g. of oily crystals; the sublimate consisted of two components on the basis of t.l.c. [silica gel-pentane (4):benzene (1)], one with a very low  $R_f$  ( $HgX_2$ ) and one (later identified as a mixture of II and III) with an  $R_f \approx 1.0$ . The residue from the sublimation was chromatographed



on alumina (Woelm, neutral, activity 1) using pentane (3):benzene(1), pentane(2):ether (1) and ether as eluents. The first few fractions contained 0.0802 g. of yellow microcrystals and only traces of black oils and solids were eluted thereafter. The yellow solids formed a deep green complex when warmed with freshly sublimed aluminum chloride.<sup>5</sup> The infrared spectrum (KBr) showed no absorption in the C-H stretching region. The ultraviolet spectrum (EtOH)<sup>31</sup> had  $\lambda_{\max}$  213m $\mu$  ( $\epsilon$ 45,000),  $\lambda_{\max}$  274 m $\mu$  ( $\epsilon$  20,000) and  $\lambda_{\max}$  343m $\mu$  ( $\epsilon$  4500).

Thermolysis of 2-(Trimethyltin)-3-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (IV) in the Presence of Cyclone (V-AE-28).

A 25 ml., pear-shaped flask was charged with 0.951 g. (1.76 mmole) of IV and 1.355 g. (3.53 mmole) of cyclone which were intimately mixed. The flask was attached via glass connections to a trap cooled to -75° with a Dry Ice-acetone bath and to a vacuum pump. The entire apparatus was then evacuated to 0.04 mm. and filled with nitrogen three times. With the apparatus under a positive pressure of nitrogen, the pot was gradually (4 hr.) heated to 205°. After 2 hr. (bath temperature of 150°), a colorless distillate formed and a vacuum (30 mm.) was applied to facilitate its removal. After the completion of reaction a trap-to-trap (80°/0.04 mm.) and direct distillation (110°/0.03 mm.) were preformed. Analysis of the distillate by g.l.p.c. (F and M. programmed run 76°-220° at 10°/min. using

a 6 ft. x 5 mm. column of 7.5% SE 30 on Chromosorb P) indicated the presence of three components. These were identified as trimethyltin chloride, trimethyltin bromide and 2-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (V) by comparison of retention times and infrared spectra with those of authentic samples. Yields were calculated using mesitylene as an internal standard and correcting for molar responses, and were found to be: trimethyltin chloride, 0.118 mmole (6.7%), trimethyltin bromide, 0.041 mmole (2.3%), and 2-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene, 0.131 mmole. Column chromatography of the residue from the distillation on silica gel using pentane as the eluent gave 0.4549 g. of light yellow oil which had a single absorption in the NMR spectrum ( $\text{CCl}_4$ ) at 6.75 p.p.m. Distillation with a Hickman Still yielded 2.90 g. (0.761 mmole) of a light yellow liquid, b.p.  $60^\circ/0.05$  mm., whose infrared spectrum was identical to that of authentic 2-bromo-1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene (V). The yield of V was 0.898 mmole (51%).

Thermal Decomposition of 2-(Trimethyltin)-1,4,5,6,7,7-hexachloro-3-methylbicyclo[2.2.1]hepta-2,5-diene (VI) - (VI-AE-10).

Under conditions identical to those described above for the reaction of IV, 1.4453 g. (3.03 mmole) of VI was heated at  $230^\circ \pm 5^\circ$  for 4 hr. After cooling to room temperature, the reaction mixture was distilled directly at  $30^\circ/0.07$  mm., volatile components being trap-

ped at  $-75^{\circ}$ . Analysis of the distillate by quantitative g.l.p.c. (F and M isothermal at  $110^{\circ}$  and 60 ml. of He/min. using a 9 ft. x 5 mm. column of 7.5% SE 30 on Chromosorb P) with toluene as an internal standard and correcting for the molar responses indicated the formation of 1.54 mmole (51%) of trimethyltin chloride, identified by comparison of its retention time and infrared spectrum with those of an authentic sample.

The distillation residue was dissolved in ether and examined by thin layer chromatography (silica gel-pentane); a component with the same  $R_F$  as the starting material but different appearance was present, and there was also a yellow spot of lower  $R_F$ . A column filtration was utilized ( $8\frac{1}{2}$  in. x  $7/8$  in. column of silica gel with 500 ml. of hexane and 250 ml. of hexane (2):benzene (1) as the eluents) to purify the mixture sufficiently for g.l.p.c. analysis. The residues from chromatography, 0.51 g. of yellow oil, were examined by NMR spectroscopy ( $\text{CCl}_4$ ) and found to contain 1,2,3,4,7,7-hexachloro-3-methylbicyclo[2.2.1]hepta-2,5-diene (VII) (characteristic quartet at 6.2 p.p.m. and doublet at 2.0 p.p.m.), as well as a compound which absorbed at approximately 1.98 p.p.m. and smaller amounts of materials absorbing at 2.59 p.p.m. and 4.1 p.p.m. The two major components were identified by comparison of retention times in g.l.p.c. (F and M isothermal at  $200^{\circ}$  and 60 ml./min. He on a 6 ft. x 5 mm. column of 7.5% SE 30 on Chromosorb P) and infrared spectra (of collected sample) with those of authentic samples as VII and heptachloro-3-methylbicyclo-

[2.2.1]hepta-2,5-diene (VIII). Their yields were calculated as 0.384 mmole (12.6%) and 0.179 mmole (5.8%), respectively, by quantitative g.l.p.c. using 1-chloronaphthalene as a reference and correcting for molar responses. Smaller amounts of two higher boiling components (28 min. and 39 min. -vs- 14 min. for VII and 19 min. for VIII) were also present. The infrared spectrum (collected sample) of the compound with a  $R_f$  of 28 min. suggests that it has a carbon skeleton similar to that of VII and VIII, and is possibly a dimer; there was, however, insufficient material for a structural determination.

1-(Trimethyltin)-2,3,4,5-tetrachlorobenzene (IX), Thermolysis - (V-AE-23).

In an apparatus identical to that used in the thermolysis of IV, 0.9682 g. (2.60 mmole) of IX was heated at  $230^\circ \pm 5^\circ$  for 3 hr. During the thermolysis a few microliters of a colorless distillate collected in the trap; g.l.p.c. analysis of this indicated the presence of two components. The volatile products were identified as tetramethyltin and trimethyltin chloride by comparison of retention times and infrared spectra with those of authentic samples.

Sublimation of the residue ( $60^\circ/0.03$  mm.) yielded 0.4728 g. (1.28 mmole) of starting material (IX), m.p.  $62.5-7^\circ$ . The sublimation residue was dissolved in hexane and crystallization was induced by additions of methanol and cooling. Three crops were obtained,

0.189 g. in all, m.p. 130-40°. Two recrystallizations from ether-methanol solutions gave colorless crystals, m.p. 140-141.5°.

The compound was identified as bis(2,3,4,5-tetrachlorophenyl)-dimethyltin by its NMR spectrum and elemental analysis. The NMR spectrum ( $\text{CCl}_4$ ) consisted of singlets at 7.30 p.p.m. (Ar-H) and 0.75 p.p.m. with relative areas of 1:3.1 (expect 1:3). The infrared spectrum ( $\text{CCl}_4$ ) had absorptions at 2965(w), 2940(w), 1600(w), 1510(w), 1380(s), 1320(s), 1295(w), 1240(w), 1190( $\gamma_{\text{Sn-CH}_3}$  str.; m), 1175(w), 1150(m), 1070( $\gamma_{\text{Sn-aryl}}$ ; m), 880(w), 845(m), 710(w), 635(m), and 530  $\text{cm}^{-1}$  ( $\gamma_{\text{Sn-CH}_3}$  str.; w). The UV spectrum (EtOH) consisted of  $\lambda_{\text{max}}$  211m $\mu$  ( $\epsilon$  115,000),  $\lambda_{\text{max}}$  238m $\mu$  ( $\epsilon$  30,000),  $\lambda_{\text{sh}}$  275m $\mu$  ( $\epsilon$  700),  $\lambda_{\text{max}}$  284m $\mu$  ( $\epsilon$  830), and  $\lambda_{\text{max}}$  293m $\mu$  ( $\epsilon$  230); the maxima are essentially identical to those of the starting material (see Chapter I) and the extinction coefficients are about twice as great, as expected for bis(2,3,4,5-tetrachlorophenyl)dimethyltin.

Anal. Calcd. for  $\text{C}_{14}\text{H}_8\text{Cl}_8\text{Sn}$ : C, 29.06; H, 1.39; Cl, 49.01. Found (SMN, G): C, 28.81; H, 1.42; Cl, 48.66.

1,2-Bis(trimethyltin)tetrachlorobenzene (XI), Thermal Decomposition-(V-AE-40).

Using an apparatus identical to that described above, 1.089 g. (2.01 mmole) of XI was heated at  $230^\circ \pm 5^\circ$  for 4 hr. During the reaction a colorless distillate, 0.268 g., collected in the trap. Examination of the distillate by quantitative g.l.p.c. (F and M

isothermal at 90° and 60 ml./min. of He using a 9 ft. x 5 mm. column of 7.5% SE 30) employing toluene as an internal standard and correcting for the molar responses indicated that tetramethyltin and trimethyltin chloride (identified by comparison of retention times and infrared spectra with those of authentic samples) had been formed to the extent of 0.563 mmole and 0.716 mmole, respectively.

Extraction of the residue with ether gave a yellow solution and left 0.215 g. of a colorless powder, m.p. 363-8° (dec.). The ethereal solution was concentrated and examined by NMR spectroscopy ( $\text{CCl}_4$ ); there was no absorption evident in the region 6-8 p.p.m. Examination of this material by t.l.c. (silica gel-pentane) indicated that, at least, 5 compounds, including starting material, were present. The ether-insoluble powder was recrystallized twice from hot benzene and gave 0.165 g. of colorless microcrystals, m.p. 361-7° (dec.). The infrared spectrum (KBr) consisted of absorptions at 2990(w), 2920(w), 1625(m), 1495(w), 1330(s), 1205(m), 1270(s), 1205(w), 1195( $\gamma_{\text{Sn-CH}_3}$  sym.; w), 1175(m), 1145(s), 1110(w), 1060( $\gamma_{\text{Sn-aryl}}$ ; s), 835(s), 820(s), 780( $\gamma_{\text{Sn-CH}_3}$  rock; s), 725(w), 635(m), 585(m), 570(w), 540( $\gamma_{\text{Sn-CH}_3}$ ; s), and  $530\text{ cm}^{-1}$  ( $\gamma_{\text{Sn-CH}_3}$ ; w).

The elemental analysis and molecular weight do not agree with those of either possible dimer of starting material and the osmometric molecular weight indicates a much more complex structure.

Anal. Calcd. for coupled product:  $\text{C}_{20}\text{H}_{24}\text{Cl}_8\text{Sn}_3$  (M. W. 904):  
C, 26.56; H, 2.13; Cl, 31.37. Anal. Calcd. for product of disprop.:

$C_{21}H_{27}Cl_7Sn_3$  (M. W. 883): C, 28.54; H, 3.08; Cl, 28.09. Found  
(M. W. 1850)<sup>33</sup>: C, 28.55; H, 2.99; Cl, 37.27.

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(33) By osmometry in benzene; the Galbraith Laboratories.

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o-Iodo(trimethyltin)benzene (XII), Thermal Decomposition -  
(V-AE-17, VI-AE-17).

Using an apparatus identical to that employed in the thermal decomposition of IV, 4.241 g. (11.3 mmole) of XII was heated at  $235^\circ \pm 5^\circ$  for 3.5 hr. A colorless distillate collected in the Dry Ice-acetone cooled trap during the reaction. The system was cooled to room temperature and a trap-to-trap ( $30^\circ/0.1$  mm.) and direct distillation ( $50^\circ/0.1$  mm.) carried out. The distillate, 0.547 g., was examined by NMR spectroscopy ( $CCl_4$ ) and found to contain only two absorptions, 0.85 p.p.m. and 0.08 p.p.m. with relative areas of 4:1; the positions of the absorptions corresponded exactly to those of trimethyltin iodide and tetramethyltin (A solution was prepared from authentic samples). No phenyltrimethyltin ( $\underline{CH}_3$  at 0.3 p.p.m.) or iodobenzene appeared to be present; this was confirmed by analysis of the distillate by g.l.p.c. No attempt was made to determine the yields of the volatiles by g.l.p.c. since previous attempts at quantitative g.l.p.c. with trimethyltin iodide had been unsuccessful. Using the ratios obtained by NMR spectroscopy the yields of

trimethyltin iodide and tetramethyltin are 1.56 mmole (27.6%) and 0.389 mmole (6.8%), respectively.

The distillation residue was examined by t.l.c. (silica gel-pentane) and found to contain a major component with  $R_f$  identical to that of starting material. Four products, all with lower  $R_f$ s, were also evident, the major product being that one with the highest  $R_f$  after starting material. Fractionation of the residue by short path distillation was performed; nothing distilled as the temperature was slowly raised from 30-90°/7 mm. The pot was, then, cooled and the distillation continued at 0.1 mm.; a distillate of 1.369 g. (b.p. 80°/0.15 mm.-91°/0.08 mm.,  $n_D^{25}$  1.6072;  $n_D^{25}$  of starting material is 1.6031) was obtained. Examination of the distillate by t.l.c. indicated that it was nearly pure starting material, accompanied by a few percent of the compound with next highest  $R_f$ .

The residue from this distillation was then chromatographed on a 7 in. x 7/8 in. column of Silica Gel G using hexane (Fisher reagent) as the eluent. Initial fractions contained 0.474 g. of starting material, pure on the basis of t.l.c. The remaining fractions, which contained mixtures of the products of lower  $R_f$  and some starting material, were rechromatographed under similar conditions with a longer column. The initial fractions from the second chromatography contained 0.112 g. of starting material [total recovery of starting material is 1.955 g. (47.2%)]. Intermediate fractions, 0.75 g., contained less than 10% of starting material on the basis of t.l.c.



Examination of various fractions by NMR spectroscopy ( $\text{CCl}_4$ ) showed absorption at 7.6-7.95 p.p.m. 6.8-7.4 p.p.m., 0.80 p.p.m. and +0.04 p.p.m., with relative areas of approximately 1:5:2:4. Examination of these fractions by g.l.p.c. (F and M isothermal at  $230^\circ$  and 60 ml/min. of He using a 6 ft. x 5 mm. column of 7.5% SE 30 on Chromosorb P) revealed the presence of two products ( $R_f$ s of 10 min. and 33 min.) and small amounts of starting material ( $R_f$  7.5 min.). The highest boiling and major product (estimated yield is 15-20% based on NMR spectra and g.l.p.c. data) was collected by g.l.p.c. repassed and, then, distilled with a micro Hickman Still, b.p.  $\sim 100^\circ/0.02$  mm. The compound has the properties expected for (2-iodo-2'-biphenyl)trimethyltin. The infrared spectrum (film) had absorptions at 3165(sh), 3050(m), 2975(m), 2915(m), 2850(w), 1950(w), 1915(w), 1800(w), 1680(w), 1585(w), 1555(w), 1495(w), 1450(s), 1430(m), 1260(w), 1250(w), 1200(w), 1190( $\gamma_{\text{Sn-CH}_3}$  sym.; w), 1160(w), 1110(w), 1080(w), 1075( $\gamma_{\text{Sn-aryl}}$ ; w), 1050(w), <sup>34</sup> 1020(m), <sup>34</sup> 1000(s), <sup>34</sup> 955(w), 870(w), 765( $\gamma_{\text{Sn-CH}_3}$  rock; s),

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(34) Identical bands appear in the spectrum of 2-iodobiphenyl (Chapter II) and are apparently characteristic of 2-substituted biphenyls: C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press, New York, 1963.

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755( $\gamma_{\text{O-aryl}}$ ; s), 725(w), 710(w), 675(w), 660(w), 640(w), 620(w), and 530  $\text{cm}^{-1}$  ( $\gamma_{\text{Sn-CH}_3}$  str.; w). The ultraviolet spectrum (EtOH) had  $\lambda_{\text{sh}}$  240  $\text{m}\mu$  ( $\epsilon$  18000),  $\lambda_{\text{sh}}$  248  $\text{m}\mu$  ( $\epsilon$  9500), and  $\lambda_{\text{max}}$  257  $\text{m}\mu$  ( $\epsilon$  9100). The

mass spectrum of the compound was discussed above.

Anal. Calcd. for  $C_{15}H_{18}SnI$ : C, 40.67; H, 3.87. Found (SMN):  
C, 41.30; H, 3.89.

A chromatography fraction of 0.051 g., which contained less than 2% of starting material (no absorption at 0.4 p.p.m. in the NMR spectrum) and was ~ 95% of the components with the highest  $R_f$  in t.l.c. after starting material was treated with 2 equivalents of methanolic hydrogen chloride. Removal of the solvent in vacuo left a yellow oil which was examined by g.l.p.c. The chromatograph contained three components in addition to trimethyltin chloride. The highest boiling ( $R_f$  of 20 min. on a 6 ft. x 5 mm. column of 7.5% SE 30 on Chromosorb P programmed from 170°-222° at 7.5°/min. with a 60 ml./min. flow of He) was identified as 2-iodobiphenyl by comparison of retention time and infrared spectrum (of a collected sample) with authentic material. The next highest boiling component trailed very badly and could not be collected. The third component was iodobenzene, identified by its retention time and infrared spectrum, which were identical with those of an authentic sample. The peak area of 2-iodobiphenyl is about the same as that for iodobenzene. The ratio of the areas of absorptions at 0.8 p.p.m. and + 0.04 p.p.m. in the NMR spectrum of the starting material was 3:4.

## ADDENDA

### Diels-Alder Reaction of Tetraphenylcyclopentadienone (Cyclone) and (Phenylethynyl)trimethyltin. (I-AE-26,30)

A solution of 4.25 g. (16.1 mmole) of (phenylethynyl)trimethyltin and 5.87 g. (15.7 mmole) of cyclone in 100 ml. of xylene (freshly distilled from sodium) was heated at reflux for 126 hrs. Removal of the solvent in vacuo left a red-grey solid. This was dissolved in methylene chloride, concentrated and crystallized by addition of methanol. Four crops of crystals, total 8.00 g. (82.2%), m.p. 327-33°, were obtained. Two further crystallizations from methylene chloride-methanol mixtures yielded colorless micro-crystals, m.p. 332-5°.

The compound has the elemental analysis and molecular weight expected for (trimethyltin)pentaphenylbenzene.

Calcd.  $C_{39}H_{34}Sn$  (62:.3): C, 75.38; H, 5.52.

Found: (SMN) (600)<sup>1</sup>: C, 75.17; H, 5.63.

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(1) By osmometry in benzene by Mrs. N. Alvord of M.I.T.

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### Diels-Alder Reaction of Cyclone and Propynyltrimethyltin (I-33).

A solution of 3.60 g. (17.7 mmole) of propynyltrimethyltin, and 5.62 g. (14.6 mmole) of cyclone in 100 ml. of xylene (freshly distilled from sodium) was heated at reflux for 147 hrs. Removal of the volatiles in vacuo left a grey-red residue. Attempts to separate the product from

unreacted cyclone by fractional crystallization from methylene chloride-methanol or ether-methanol solutions were not successful. Chromatography of the residue on a column of alumina (Woelm, neutral, activity 1) using a hexane-benzene mixture as the eluent gave 5.1 g. (64% crude yield) of colorless crystals, m.p. 177-93°. An analytical sample was obtained by several additional crystallizations from ether-methanol mixtures, m.p. 200-3°. The compound was identified as 1-(trimethyltin)-2-methyltetraphenylbenzene by its NMR spectrum and elemental analysis. The NMR ( $\text{COCl}_3$ ) consisted of absorptions at 7.00 p.p.m., 6.67 p.p.m., 2.24 p.p.m. and +0.11 p.p.m. with relative areas of 21 (for the aromatic hydrogens): 3:9. The unusually high field absorption of the trimethyltin moiety is doubtless the result of shielding by the ring current of the adjacent phenyl group.

Calcd. for  $\text{C}_{34}\text{H}_{22}\text{Sn}$ : C, 73.01; H, 5.77.

Found (SMN): C, 73.00; H, 5.74.

1-(Trimethyltin)-2-methyltetraphenylbenzene, Protolysis: 1-Methyl-2,3,4,5-tetraphenylbenzene (I-AE-40)

A solution of 1.37 g. (2.46 mmole) of 1-trimethyltin-2-methyltetraphenylbenzene in 50 ml. of ether was treated with an excess of hydrogen bromide (Matheson, gas) in methanol. Removal of the volatiles in vacuo left 0.93 g. (93 %) of colorless crystals, m.p. 177-81°. Recrystallization from ether-pentane mixtures gave colorless crystals, m.p. 185-86° (lit.<sup>2</sup> m.p. 185-86°). The NMR spectrum ( $\text{CCl}_4$ ) had absorptions at 7.33

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(2) V. S. Abramov and A. P. Pakhamova, Zh. Obschch. Khim., 24, 1198 (1954); C. A., 50, 4869e (1956).

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p.p.m. (1x), 7.04 p.p.m. (2x), 6.75 p.p.m. (2x) and 2.14 p.p.m. (1x) with relative areas of 1:10:10:3.

Calcd. for  $C_{31}H_{24}$ : C, 93.90; H, 6.10.

Found (SMN): C, 93.67; H, 6.29.

(Trimethyltin)pentaphenylbenzene, Brominolysis: Bromopentaphenylbenzene  
(I-AE-21)

A solution of 1.22 g. (1.96 mmole) of (trimethyltin)pentaphenylbenzene in 50 ml. of methylene chloride was treated in a dropwise manner with a solution of 0.319 g. (2.00 mmole) of bromine in 20 ml. of methylene chloride. Evaporation of the solvent with dropwise addition of methanol gave 0.98 g. (91.6%) of colorless crystals, m.p. 279-297°. Several recrystallizations from methylene chloride-methanol gave 0.75 g., m.p. 295-9°. The elemental analysis is in agreement with the structure bromopentaphenylbenzene.

Calcd. for  $C_{36}H_{25}Br$ : C, 80.44; H, 4.78.

Found (SMN): C, 79.88; H, 4.69.

### ACKNOWLEDGEMENTS

The author is deeply grateful to Professor Dietmar Seyferth for his assistance and guidance in many aspects of this research. In particular, the availability of advice and direction when it was needed and of a free rein when it was appropriate is very much appreciated. The author is also indebted to Dr. Christos Sarafidis for his instruction and encouragement in the early stages of this research, to Robert Damrauer and David Blank for helpful discussions and to Dr. Robert Siekman for assistance with mass spectral analyses.

The support of the Massachusetts Institute of Technology (teaching assistantship, 1962-3), the National Science Foundation (Summer Fellowship, 1963), and the National Institute of Health (Predoctoral Fellowship, 1963-6) is gratefully acknowledged.

Finally , the author recognizes the enormous debt he owes his wife and sons for their wholehearted and self-sacrificing support of this program.

### BIOGRAPHICAL NOTE

The author was born in New York City on March 10, 1941. His primary education was obtained in the New York City School System and secondary education was at Trinity School, also in that city. From 1958-62, the author attended Princeton University, receiving the A.B. degree in June, 1962. In September of that year, studies towards a doctoral degree in chemistry were commenced at the Massachusetts Institute of Technology, and the requirements for the degree of Doctor of Philosophy in Organic Chemistry were completed in September 1966.

The author is married to the former Judith Piel Ward and is the father of two sons, Luke Basil and Timothy Winston.