ether. The ether was dried and evaporated and the residue distilled to yield 2.4 g (80%) of cyclopent-4-enylacetic acid, bp 77–80° (0.5 mm). The acid was converted into the corresponding amide by sequential treatment with thionyl chloride and gaseous ammonia. The amide had mp 129–130° (lit.[19] mp 132.5–133.5° for cyclopent-4-enylacetamide).

The Cleavage of Camphenilone. A cleavage mixture was prepared from 16 g of potassium *t*-butoxide, 0.47 ml of water, and 40 ml of dimethyl sulfoxide in the usual manner, and 2 g of camphenilone was added. The cleavage was run for 6 hr at 50°. The reaction mixture was diluted with water and extracted with ether; the extracts were dried and evaporated. The white solid residue was recrystallized from acetone to give an analytical sample of the camphenilone–dimethyl sulfoxide adduct, mp 173–174°.

Anal. Calcd for $C_{11}H_{20}O_2S$ (mol wt, 216.34): C, 61.07; H, 9.32; S, 14.82. Found: C, 60.87; H, 9.07; S, 14.42.

The aqueous phase was acidified to pH 1 with concentrated hydrochloric acid and extracted with ether. The dried extracts were evaporated giving 200 mg (9%) of a carboxylic acid. Reaction of the acid with thionyl chloride followed by ammonia gave an amide, mp 166–168° (lit.[22] mp 167–168° for 3-isopropylcyclopentane-1-carboxamide).

The Cleavage of Benzophenone. A cleavage mixture was prepared from 1.9 g of potassium *t*-butoxide, 0.07 ml of water, and 10 ml of monoglyme in the usual manner, and 300 mg of benzophenone in 3 ml of monoglyme was added. The cleavage was run for 2 hr at 30°. The reaction mixture was poured into dilute brine and extracted with ether. The extracts were dried and evaporated, leaving no residue. After being acidified to pH 1 with concentrated hydrochloric acid, the aqueous phase was again extracted with ether. The ether was dried and evaporated giving 180 mg (90%) of benzoic acid, mp 119–120°.

The Cleavage of Fluorenone. A cleavage mixture was prepared from 1.94 g of potassium *t*-butoxide, 0.12 ml of water, and 25 ml of monoglyme in the usual manner, and 500 mg of fluorenone in 5 ml of monoglyme was added. The cleavage was run for 2 hr at 30°. The same work-up procedure as described for the benzophenone cleavage was used. No neutral fraction was recovered. The acidic fraction yielded a pale yellow oil which crystallized on trituration under pentane to give 500 mg (90%) of biphenyl-2-carboxylic acid, mp 112–112.5° (lit.[16] mp 112–113°).

The Cleavage of Benzopinacolone. A cleavage mixture was prepared from 4 g of potassium *t*-butoxide, 0.385 ml of water, and 11 ml of dimethyl sulfoxide, and 1.6 g of benzopinacolone in a small amount of dimethyl sulfoxide was added. The cleavage was run for 2 min at 30°. The reaction mixture was poured into water, and the precipitate which formed was filtered off. After drying, 1.1 g (98%) of triphenylmethane was obtained, mp 92–93°. The filtrate was acidified to pH 1 with concentrated hydrochloric acid and extracted with ether. The ether was dried and evaporated giving 560 mg (100%) of benzoic acid, mp 119–120°.

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(22) S. S. Nametkin and S. S. Kagan, *J. Gen. Chem. USSR*, **16**, 885 (1946).

The Preparation and Some Reactions of 1,2-Bis(trimethyltin)benzene and Related Compounds

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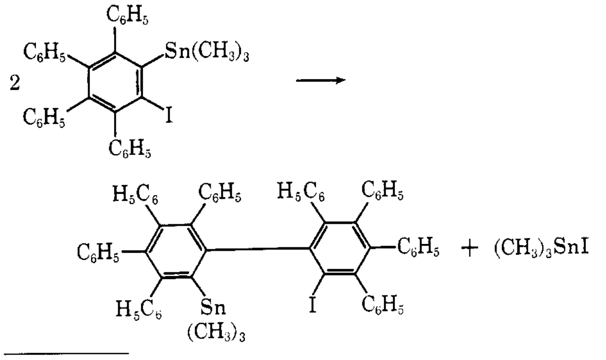
Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received September 19, 1966*

Abstract: The Diels–Alder reaction of bis(trimethyltin)acetylene with the appropriately substituted α-pyrone has been used to prepare 1,2-bis(trimethyltin)benzene, 3,4-bis(trimethyltin)toluene, and methyl 3,4-bis(trimethyltin)benzoate. Reaction of (phenylethynyl)trimethyltin with α-pyrone gave (2-biphenylyl)trimethyltin. Partial and total cleavage of these tin compounds with iodine and bromine was used to prepare 1-iodo-2-(trimethyltin)benzene, 1-bromo-2-(trimethyltin)benzene, 1,2-dibromobenzene, and a mixture of methyl 3-iodo-4-(trimethyltin)benzoate and methyl 4-iodo-3-(trimethyltin)benzoate. The thermal decomposition of 1-iodo-2-(trimethyltin)benzene was studied; one of the major products was 2-iodo-2′-(trimethyltin)biphenyl.

In a previous communication[2] we reported that the thermal (~230°) decomposition of 1-iodo-2-(trimethyltin)tetraphenylbenzene did not lead, as anticipated, to formation of tetraphenylbenzyne. Instead, a novel coupling reaction (eq 1) was observed. The possibility that the four phenyl substituents created an abnormal situation[3] and interest in this coupling reaction led us to an examination of routes to less highly substituted *o*-halo(trimethyltin)benzenes. The synthesis of these systems by a Diels–Alder route is the subject of this paper. The system utilized is thought to be of interest since it embodies a general, one-step synthesis of specifically substituted benzene derivatives.



(1)

The Diels–Alder reaction of bis(trimethyltin)acetylene with an appropriate diene, followed by monohalodestannation of the product, appeared to us to be an attractive route to the desired *o*-halo(trimethyltin)benzenes. Obviously, bis(trimethyltin)acetylene should be a poor dienophile by classical criteria. The triple bond is not electron deficient; if anything, it is electron rich, since the inductive flow of electrons from the trimethylstannyl groups is probably the predominant elec-

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(1) (a) National Institutes of Health Predoctoral Fellow, 1963–1966; (b) Alfred P. Sloan Foundation Fellow, 1962–1966.

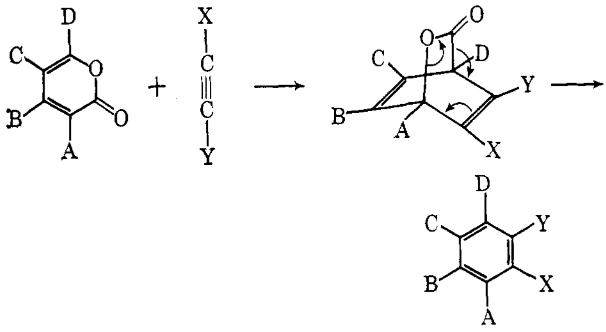
(2) D. Seyferth, C. Sarafidis, and A. B. Evnin, *J. Organometal. Chem.* (Amsterdam), **2**, 417 (1964).

(3) Tetraphenylbenzyne could, however, be generated from 1,2-dibromotetraphenylbenzene by treatment with lithium amalgam: D. Seyferth and H. H. A. Menzel, *J. Org. Chem.*, **30**, 649 (1965).

tronic action in this compound.[4] Also, the trimethyltin group is extremely bulky, and steric inhibition of the Diels–Alder reaction by large substituents is pronounced.[5] However, the long C_{sp}–Sn bond (*ca.* 2.0 A[6]) removes the three methyl groups from the triple bond. In this connection it may be noted that the Diels–Alder reaction has been effected between bis(trimethyltin)acetylene and tetraphenylcyclopentadienone[2] and several other dienes.[7]

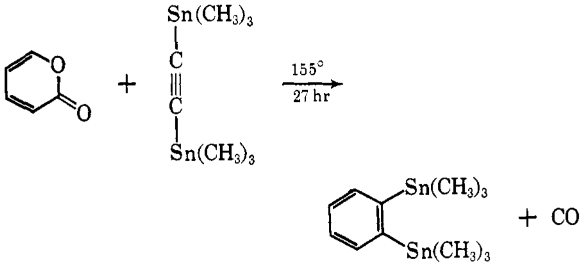
Examination of the literature revealed some generalizable systems for the direct formation of aromatic systems by the Diels–Alder reaction.[8] One, described by Hill and Carlson,[9] involves reaction of 1-acetoxybutadiene with acetylenes (or of 1,4-diacetoxybutadiene with olefins); the initially formed 1-acetoxy-2,5-cyclohexadienes (or 1,4-diacetoxycyclohex-2-enes) rapidly eliminate acetic acid under the conditions of the reaction to form aromatic systems. However, the extreme sensitivity of organotin acetylides to electrophilic cleavage and the rather low yields obtained with any but the most electron-deficient dienophiles (especially with 1-acetoxybutadiene) makes this system unsatisfactory for our purposes. The second system involves reaction of acyclic dienes with acetylenes and subsequent aromatization at high temperatures (300°), typically with iodine as catalyst.[10] This procedure requires pressure equipment and conditions too strenuous for aryltin compounds.

The α-pyrones, however, appeared to offer interesting possibilities for the direct synthesis of the desired aromatic tin compounds. Their excellent properties as Diels–Alder dienes with classical dienophiles had been noted in the earliest studies of the reaction,[11] and the fact that the 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 that the Diels–Alder adducts of α-pyrones with acetylenes decarboxylate under mild conditions to yield aromatic compounds[12,13] (eq 2). Furthermore, the parent compound, α-pyrone itself, is available in two steps from malic acid, and many of its derivatives are well known and readily prepared.[14] In view of these properties it is surprising that the literature indicates little recognition of the synthetic possibilities of these systems outside of Zimmerman and Paufler's synthesis of barrelene,[15] a few papers in the Russian literature,[16] and a paper by Märkl.[17]



(2)

Reaction of 1 equiv of α-pyrone with bis(trimethyltin)acetylene in refluxing bromobenzene resulted in formation of the desired 1,2-bis(trimethyltin)benzene (I) in approximately 50% yield (eq 3). The yield is considered quite satisfactory in view of the steric properties of the dienophile and the low yields in which the group IV analogs of I, 1,2-di-*t*-butylbenzene[18] and 1,2-bis(trimethylsilyl)benzene,[19] have been prepared by other routes. 1,2-Bis(trimethyltin)benzene was identified by means of its elemental analysis and spectral properties and by brominolysis to 1,2-dibromobenzene, which was identical in all respects with an authentic sample. The nmr spectrum (CCl_4) of I consists of a complex multiplet at δ 6.91–7.53, which is approximately an A_2B_2 pattern, and a singlet at δ 0.31 ($J_{Sn^{117}-H^1}$ = 51 cps; $J_{Sn^{119}-H^1}$ = 53 cps), with relative areas of 1:4.5. The ultraviolet spectrum of I in ethyl alcohol (see Table I) has no vibrational structure in its longest wavelength absorption, a feature that appears to be characteristic of distorted benzene rings.[20] Distortion of the benzene ring of I might be expected as a means of relieving the severe interactions of the methyl groups on adjacent tin atoms. Models[21] suggest that the interaction of the methyl groups in I is as severe as it is in 1,2-di-*t*-butylbenzene, for which a strain energy of at least 17 kcal/mole can be estimated.[22] The reason for



(3)

I

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[4] R. West and C. S. Kraihanzel, *Inorg. Chem.*, **1**, 967 (1962).

[5] J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

[6] Estimated from data in "Tables of Interatomic Distances," The Chemical Society, London, 1958.

[7] D. Seyferth and A. B. Evnin, *J. Am. Chem. Soc.*, in press.

[8] Reaction of cyclopentadienones and cyclopentadienone ketals with acetylenes yields aromatic compounds under mild conditions. These reactions, however, are not general, since only very highly substituted or specifically stabilized members of the class can be used: C. F. H. Allen and J. A. VanAllan, *J. Am. Chem. Soc.*, **72**, 5165 (1950); C. H. DePuy, M. Isaks, R. L. Eilers, and G. F. Morris, *J. Org. Chem.*, **29**, 3503 (1964); P. E. Eaton and R. A. Hudson, *J. Am. Chem. Soc.*, **87**, 2769 (1965).

[9] R. K. Hill and R. M. Carlson, *Tetrahedron Letters*, 1157 (1964).

[10] For example, see D. T. Tsybikova, V. R. Skvarchenko, and R. Ya. Levina, *Tr. Vost.-Sibirsk. Tekhnol. Inst.*, **1**, 67 (1962); *Chem. Abstr.*, **62**, 3957 (1965).

[11] O. Diels and K. Alder, *Ann. Chem.*, **490**, 257 (1931).

[12] K. Alder and H. F. Rickert, *Chem. Ber.*, **70**, 1354 (1937).

[13] G. Wittig and R. W. Hoffmann, *Angew. Chem.*, **73**, 435 (1961).

[14] J. Fried, "Heterocyclic Chemistry," Vol. I, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1950, pp 354–370, and more recent references too numerous to record here.

[15] H. Zimmerman and R. M. Paufler, *J. Am. Chem. Soc.*, **82**, 1514 (1960).

[16] (a) N. P. Shusherina, R. Ya. Levina, and I. S. Trubnikov, *Zh. Obshch. Khim.*, **29**, 294 (1959); (b) N. P. Shusherina, R. Ya. Levina, Z. S. Sidenko, and M. Yu. Lur'e, *ibid.*, **29**, 403 (1959); (c) N. P. Levina, R. Ya. Levina, and V. M. Shostakovskii, *ibid.*, **29**, 3237 (1959).

[17] G. Märkl, *Chem. Ber.*, **96**, 1441 (1963).

[18] (a) A. W. Burgstahler and M. O. Abdel-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).

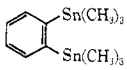
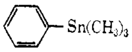
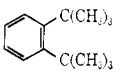
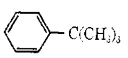
[19] H. A. Clark, A. F. Gordon, C. W. Young, and M. J. Hunter, *J. Am. Chem. Soc.*, **73**, 3798 (1951).

[20] R. T. Ingraham in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 500.

[21] Framework Molecular Models, Prentice-Hall, Inc., Englewood Cliffs, N. J.

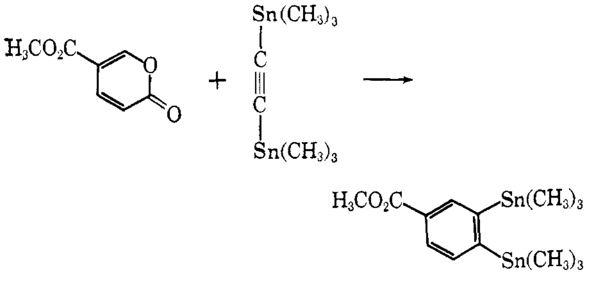
[22] See C. Hoogzand and W. Hübel, *Tetrahedron Letters*, 637 (1961).

Table I. Ultraviolet Spectra

Compound	Absorption in ultraviolet, λ, mμ (ϵ)	Solvent
	217 sh (16,700) 240 sh (2,700) 265 sh (430)[a]	EtOH
	247 sh (140); 253 max (210) 258 max (255); 264 max (210)	EtOH
	261 max (189)[a,b]	Solvent not given
	207 max (8,000) 253 max (160); 257 max (200)[c] 264 sh (160); 267 max (120)	Cyclo-C_6H_{12}

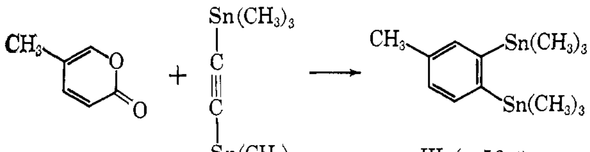
[a] No fine structure. [b] E. M. Arnett and M. E. Strem, *Chem. Ind.* (London), 2008 (1961). [c] Y. Ihaya, *Bull. Chem. Soc. Japan*, **28**, 369 (1955).

this is that the long Sn–CH_3 bonds, 2.18 A,[6] compensate for the long Ar–Sn bonds (estimate 2.08 A) and bring the methyl groups quite close together. One other aspect of the absorption spectrum of I is noteworthy: the occurrence of a band, λ_{sh} 240 mμ (ϵ 2700), which has no counterpart in the spectra of either phenyltrimethyltin or 1,2-di-*t*-butylbenzene. The absorption clearly is of too low an intensity to be a benzene primary band, and no satisfactory explanation can be offered. Table I compares the ultraviolet spectra of 1,2-bis(trimethyltin)benzene with those of phenyltrimethyltin and the carbon analogs of these compounds.



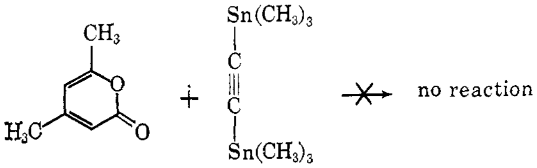
(4)

II (50–65%)

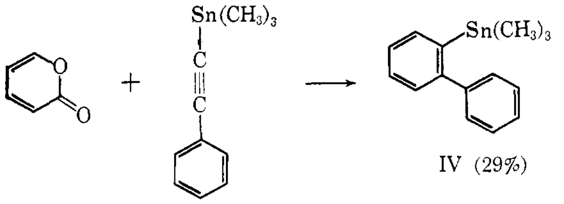


(5)

III (~50%)



(6)



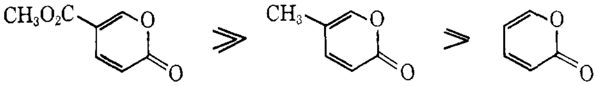
(7)

IV (29%)

The scope and limitations of the reactions of α-pyrones with organotin acetylenes were examined in a limited fashion. Equations 4–7 summarize the results.

The availability of variously substituted α-pyrones made possible the evaluation of electronic effects and steric effects on the Diels–Alder reactions of bis(trimethyltin)acetylene. If it behaves as a classical dienophile, then it should be more reactive toward a methyl-substituted α-pyrone than toward an α-pyrone bearing a carbomethoxy substituent.

There is a problem inherent in the use of substituted α-pyrones to examine electronic effects in Diels–Alder reactions. Fried has noted that phenyl and carbomethoxy substituents stabilize the α-pyrone nucleus,[14] 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 stabilizing effect on the α-pyrone nucleus. Nevertheless, competion reactions were carried out between α-pyrone and 5-carbomethoxy-α-pyrone (methyl coumalate) and between α-pyrone and 5-methyl-α-pyrone. The reactions were carried out in refluxing bromobenzene, and the product mixtures were analyzed both by nmr spectroscopy and quantitative glpc. The results showed the reactivity of these α-pyrones toward bis(trimethyltin)acetylene to decrease in the order



The greatly increased reactivity of the electron-deficient 5-carbomethoxy-α-pyrone can only be due to an electronic effect (α-pyrone and bis(trimethyltin)-acetylene give I in 50% yield under these conditions). The slight enhancement obtained with the electron-donating, 5-methyl substituent does not contradict this, since the electronic effect of a methyl group apparently is small in these cases[23] and may easily be compensated for by its stabilization of the α-pyrone nucleus. The qualitative observation that (phenylethynyl)trimethyltin reacts less readily with α-pyrone than does bis(trimethyltin)acetylene, despite a decrease in the steric hindrance, is in accordance with the results of the competition experiments if the trimethyltin group is assumed to be significantly electron donating (*via* the $+I$ effect). The apparent greater reactivity of an electron-deficient diene in the Diels–Alder reaction with electron-rich dienophiles has been observed previously by other workers in certain cases,[24] and such behavior has been characterized by the term "inverse electron demand."[24b] It would appear that the α-pyrone + bis(trimethyltin)acetylene system provides another example of a Diels–Alder reaction with "inverse electron demand."

The failure of 4,6-dimethyl-α-pyrone to react must be due to steric effects, since models[21] indicate severe interactions between the 6-methyl group and the trimethyltin group long before the two molecules are within bonding distance. This system serves to define

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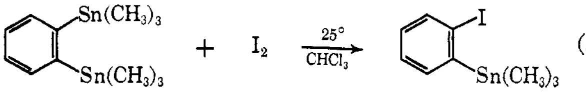
[23] J. Sauer and D. Lang, *Angew. Chem.*, **76**, 603 (1964).

[24] (a) C. W. Smith, D. G. Norton, and S. A. Ballard, *J. Am. Chem. Soc.*, **73**, 5267 (1951); (b) J. Sauer and H. Wiest, *Angew. Chem.*, **74**, 353 (1962); (c) M. G. Ettlinger and C. S. Lewis, *Texas J. Sci.*, **14**, 58 (1962); (d) J. Sauer, A. Mielert, D. Lang, and D. Peter, *Chem. Ber.*, **98**, 1435 (1965).

a limitation on the reaction of α-pyrones with bis(trimethyltin)acetylene, although 6 substituents do not create problems with less hindered dienophiles.[16] The fact that α-pyrones react as readily as they do with these very hindered dienophiles is a powerful recommendation for their utililization as a general tool for the synthesis of specifically substituted benzene derivatives.

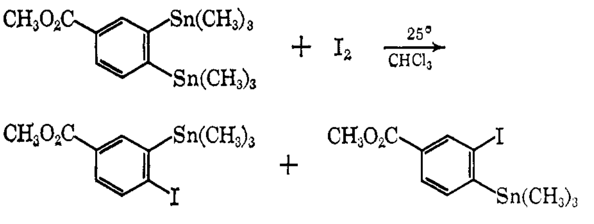
Methyl 3,4-bis(trimethyltin)benzoate (II), 3,4-bis(trimethyltin)toluene (III), and (2-biphenylyl)trimethyltin (IV) are new compounds and were characterized by combustion analyses and by means of their spectra. IV also was converted to the known 2-iodobiphenyl by treatment with iodine. Several features of the spectra of these systems are noteworthy. III 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 $(CH_3)_3Sn$ protons appear at 0.03 ppm above tetramethylsilane owing to shielding by the ring current of the skewed *o*-phenyl group; this is typical of other compounds examined in this study which have a phenyl group β to a trimethyltin moiety.

Some of the chemistry of the adducts I–IV has been examined both in order to prepare the 1-halo-2-(trimethyltin)benzenes, which, as mentioned, were of interest to us, and to determine their synthetic possibilities. Treatment of 1,2-bis(trimethyltin)benzene with 1 equiv of iodine at room temperature resulted in rapid formation of 1-iodo-2-(trimethyltin)benzene (V) in virtually quantitative yield (eq 8). Monoiodinolysis of methyl 3,4-bis(trimethyltin)benzoate occurred analogously, but gave a mixture of the two possible positional isomers, VI and VII, in a ratio of 2:3 (eq 9). The reaction of 1 equiv of bromine with I was not selective at room temperature, forming both mono- and dibromo products, but at −75°, 1-bromo-2-(trimethyltin)benzene (VIII) was the only product (86%). 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 the 1-halo-2-(trimethyltin)benzenes toward electrophiles. The sensitivity of halodestannation to both factors has been demonstrated by Nasielski and co-workers.[25]



(8)

V



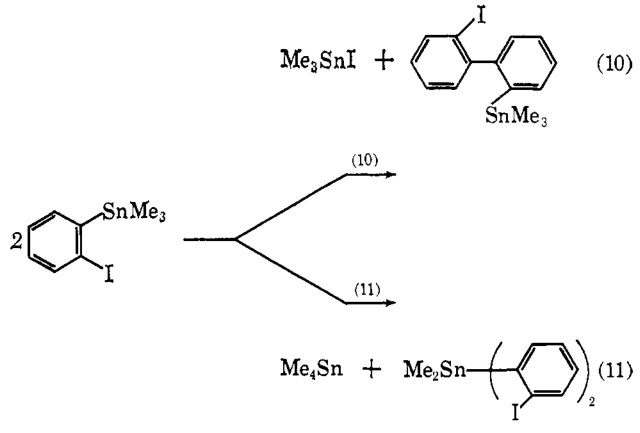
(9)

VI VII

Compounds V–VIII have not been described previously. It is interesting that V and VIII show fine structure in their longest wavelength absorption in the ultraviolet, suggesting that the benzene ring no longer is distorted from planarity by steric repulsions as it apparently is in 1,2-bis(trimethyltin)benzene. All four compounds are stable, pleasantly aromatic oils. A report[26] on the preparation of 1-chloro-2-(tri-*n*-butyltin)benzene (by a rather questionable route) in which it was described as an unstable, evil-smelling liquid is, thus, somewhat curious.

Treatment of 1,2-bis(trimethyltin)benzene with 2 equiv of bromine in chloroform gave 1,2-dibromobenzene in high yield, indicating that C–Sn cleavage in the 1-halo-2-(trimethyltin)benzenes presents no problems. The cleavage of these tin compounds with other electrophilic reagents, with preparative applicability in mind, is under investigation. The cleavage of 1,2-bis(trimethyltin)benzene by organolithium reagents as a route to 1,2-dilithiobenzene also is under study. Recent developments in the synthesis of organotin acetylenes[27] have made available many new alkynyltin compounds of type $R_3SnC{\equiv}CY$ (Y = Ar, alkyl, CN, CH_2OR, etc.), and the use of these in Diels–Alder reactions is being examined.

The successful preparation of 1-iodo-2-(trimethyltin)benzene has permitted a study of its thermal decomposition. Of interest was the question whether its decomposition would follow the path illustrated for its perphenylated analog in eq 1, or whether it would proceed differently (*e.g.*, *via* a benzyne intermediate). When V was heated at 230° for 3.5 hr, the products obtained were trimethyltin iodide, tetramethyltin, 2-iodo-2′-(trimethyltin)biphenyl (*ca.* 20%), and a compound tentatively identified as dimethylbis(2-iodophenyl)tin. In addition, starting material was recovered in 46% yield. Thus in this case also the coupling reaction (eq 10) is observed, but simultaneous occurence of a disproportionation reaction (eq 11) complicates matters. 1-Iodo-2-(trimethyltin)benzene appears to be more stable than its more highly substituted analog, 1-iodo-2-(trimethyltin)tetraphenylbenzene,[2] and this provides some evidence for the importance of steric acceleration in the coupling reaction (eq 1). The coupling reaction of V appears not to be a radical process, since neither iodobenzene nor trimethylphenyltin were observed among the products,



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

(26) C.-L. Tseng, S.-H. Tung, and K.-M. Chang, *K'o Hsueh T'ung Pao*, 165 (1964); *Chem. Abstr.*, **61**, 7035 (1964).

(27) Summarized in D. Seyferth and R. B. King, "Annual Surveys of Organometallic Chemistry," Vol. I, Elsevier Publishing Co., Amsterdam, 1965, p 133, and Vol. II, 1966, p 172.

but the mechanism of this coupling reaction remains unknown.

Experimental Section

General Comments. Infrared spectra were recorded using either a Perkin-Elmer Infracord 337 or 237 spectrophotometer, ultraviolet spectra with a Cary 14 instrument. Nmr spectra were obtained with a Varian Associates A60 nmr spectrometer. Chemical shifts are given in parts per million downfield from tetramethylsilane (TMS), which was used as an internal standard. In some systems, the occurrence of absorptions due to the compound at about 0.0 ppm necessitated the use of alternate internal standards. In these cases chloroform or cyclohexane typically was employed. The sweep calibration (chloroform cyclohexane, and TMS in carbon tetrachloride) always was checked concurrently.

Elemental analyses were performed by Dr. S. M. Nagy, MIT Microchemical Laboratory, the Galbraith Laboratories, Knoxville, Tenn., and the Schwarzkopf Micronanalytical Laboratory, Woodside, N. Y. Melting points are corrected. Thin-layer chromatograms were obtained using either 50 × 150 mm glass plates or 25 × 75 mm microscope slides coated with a uniform layer of Silica Gel G (Brinckman Instruments). Development generally was accomplished with iodine, but in some cases 50% sulfuric acid was used.

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

Preparation of α-Pyrone.[28] Into a 50-ml, round-bottomed flask was placed 14.47 g (0.103 mole) of coumalic acid (mp 209–214°; lit.[29] mp 206–209° dec), prepared according to the method of Wiley and Smith.[29] The flask was connected by a Pyrex adapter (24/40 joints) wrapped with resistance wire to a Vycor tube (20 mm o.d. × 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 wrapped carefully 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 ± 25° (measured by an iron–constantan thermocouple), and the temperature of the pot and inlet system was gradually brought up to 170°. The trap was cooled to −75° with a Dry Ice–acetone bath and the system kept open to the vacuum source throughout. (The pressure rose to 0.3 mm during 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 gave 8.20 g (83%) of colorless, sweet-smelling oil, bp 95° (16 mm), $n^{25}\text{D}$ 1.5251, d^{29} 1.262 [lit.[30] bp 103–105° (21 mm), $n^{22}\text{D}$ 1.5277].

The liquid was characterized as α-pyrone by means of its spectral properties and elemental analysis. These are recorded below as they were not reported by previous workers. The nmr spectrum (in acetone) was the complicated pattern expected for an ABXY system with absorptions at 6.2-5 ppm (2 H: H_3, H_5) and 7.35–7.85 ppm (2 H: H_4, H_6). The infrared spectrum had bands at 3150 (w), 3100 (w), 3025 (m), 1795 (sh), 1745 (s, C=O), 1725 (s, C=O), 1650 (m, C=C), 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 (m) cm^{-1}. The doublet for the carbonyl and the C=C stretch at 1650 cm^{-1} are highly characteristic of the α-pyrone nucleous.[31]

Anal. Calcd for $C_5H_4O_2$: C, 62.50; H, 4.19. Found: C, 62.31; H, 4.48.

1,2-Bis(trimethyltin)benzene. A solution of 4.03 g (42.0 mmoles) of α-pyrone, 14.05 g (40.0 mmoles) of bis(trimethyltin)acetylene, and 0.3 g of hydroquinone in 250 ml of bromobenzene (freshly distilled from P_2O_5) was heated at reflux for 31 hr. The solution turned yellow and then red, apparently owing to some decomposition of α-pyrone. Removal of the solvent by distillation at 30° (0.1 mm) left an oily, red residue. This was extracted with 100 ml of diethyl ether and filtered; the ether was evaporated from the extracts. Distillation of the oil which remained with a short-path apparatus gave 7.84 g of faintly yellow oil, bp 92–94° (0.145 mm), $n^{25}\text{D}$ 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 to give 1.12 g of colorless oil, $n^{25}\text{D}$ 1.5573. Redistillation of the crude product gave 8.27 g, $n^{25}\text{D}$ 1.5629 (51.4%). An analytically pure sample had $n^{25}\text{D}$ 1.5640.

If the crude reaction mixture was first filtered through a short alumina or silica gel column, using pentane or hexane as eluent, and then was distilled, analytically pure material was obtained directly.

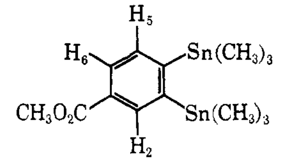
The product had the properties expected for 1,2-bis(trimethyltin)benzene. The nmr and ultraviolet spectra have been discussed in the Discussion section. The infrared spectrum (liquid film) showed absorption at 3125 (w), 3100 (w), 3045 (m), 2970 (m), 2915 (m), 1445 (w), 1425 (w), 1260 (m), 1205 (sh), 1190 (m), 1095 (m), 1025 (m), 770 (vs), 740 (s), 710 (s), 640 (w), and 530 (w) cm^{-1}.

Anal. Calcd for $C_{12}H_{22}Sn_2$: C, 35.70; H, 5.49. Found: C, 35.85; H, 5.55.

The reaction also was carried out in refluxing xylene and di-*n*-butyl ether, but the yields (28.5 and 15%, respectively) were less satifactory.

Methyl 3,4-Bis(trimethyltin)benzoate. A solution of 2.11 g (13.7 mmoles) of 5-carbomethoxy-α-pyrone,[32] 5.0 g (14.2 mmoles) of bis(trimethyltin)acetylene, and 0.1 g of hydroquinone in 50 ml of di-*n*-butyl ether (freshly distilled from sodium) was heated at reflux for 12 hr, at the end of which time the reaction mixture was dark red. Removal of volatiles by trap-to-trap and then direct distillation [50° (0.08 mm)] left red solids and oils. The solids were insoluble in ether but soluble in acetone. The residue was extracted with 50 ml of ether. The ether extracts were concentrated and distilled using a Hickman distillation apparatus to give a colorless liquid boiling at 120° (0.09 mm), $n^{24}\text{D}$ 1.5654. Redistilled material had $n^{25}\text{D}$ 1.5613. The yield was 3.50 g (55%).

The compound was identified as methyl 3,4-bis(trimethyltin)benzoate (II) by means of its nmr and infrared spectra and by elemental analysis. The nmr spectrum (CCl_4) is particularly characteristic.



H_6 quartet at 7.71 ppm; $J_{5,6}=7.5$ cps,
$J_{2,6}=2$ cps
H_5 doublet at 7.41 ppm
H_2 doublet at 7.98 ppm
O-CH_3 singlet at 3.77 ppm
$Sn(CH_3)_3$ singlets at 0.25 and 0.27 ppm

The infrared spectrum (liquid film) consisted of absorptions at 3125 (sh), 3050 (sh), 2980 (m), 2945 (m), 2910 (m), 2835 (w), 1720 (vs, C=O), 1580 (m), 1540 (w), 1460 (sh), 1425 (s), 1380 (w), 1360 (m), 1290 (vs), 1255 (s), 1240 (s), 1195 (m), 1120 (s), 1080 (s, Sn-aryl), 1070 (sh), 1025 (w), 975 (w), 915 (w), 840 (w), 770 (s), 720 (s), 655 (w), and 525 (w) cm^{-1}.

The ultraviolet spectrum (EtOH) had $\lambda_{\max}$ 243 mμ (ε 19,000), 279 (5300), 287 (3900), and 296 (3650).

Anal. Calcd for $C_{14}H_{24}O_2Sn_2$: C, 36.42; H, 5.24. Found: C, 36.59; H, 5.27.

3,4-Bis(trimethyltin)toluene. A solution of 0.3 g (2.75 mmoles) of 5-methyl-α-pyrone,[33] 1.46 g (4.15 mmoles) of bis(trimethyltin)acetylene, and 0.05 g of hydroquinone in 10 ml of dry bromobenzene was 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 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, bp 90° (0.05 mm). The latter was dissolved in hexane and filtered through a 2-in., Silica Gel G column using 200 ml of hexane as eluent. Distillation of the chromatography residue gave 0.450 g (39%) of pure, colorless liquid, $n^{27}\text{D}$ 1.5602. The compound had the proper-

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[28] The preparation is based on one alluded to in ref 15.

[29] R. H. Wiley and N. R. Smith, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 201.

[30] H. von Pechmann, *Ann. Chem.*, **264**, 272 (1891).

[31] K. N. Nakanishi, "Practical Infrared Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1961, p 42.

[32] J. H. Boyer and W. Schoen, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 532.

[33] J. Fried and R. C. Elderfield, *J. Org. Chem.*, **6**, 566 (1941). The next to last step in the reaction sequence, the conversion of 4-methyl-2-hexen-5-one-1,6-dioic acid to 5-methyl-6-carboxy-α-pyrone, involves a bomb tube reaction, which, contrary to the literature, generates considerable pressure.

ties expected for 3,4-bis(trimethyltin)toluene. The nmr spectrum (CCl_4) had a complex multiplet at 6.75–7.38 (Ar–H), a singlet at 2.28 (Ar–CH_3), and a singlet at 0.30 ppm (Sn–CH_3) with relative areas of 1:1:6. The trimethyltin absorption had satellites: $J_{Sn^{117}-H^1}$ = 52 cps and $J_{Sn^{119}-H^1}$ = 54 cps. The ultraviolet spectrum (EtOH) had λ_{sh} 221 mμ (ϵ 16,800), λ_{max} 267 (500), and λ_{sh} 273 (283). The infrared spectrum (liquid film) had absorptions at 3050 (m), 3025 (m), 2980 (s), 2920 (s), 1580 (w), 1450 (m), 1260 (w), 1215 (w), 1200 (w), 1190 (m), 1085 (m), 1040 (w), 885 (w), 810 (s, *m*-aryl), 765 (s), 705 (s), 660 (w), 570 (w), and 520 (m) cm^{-1}.

Anal. Calcd for $C_{13}H_{24}Sn_2$: C, 37.39; H, 5.79. Found: C, 37.12; H, 5.78.

Attempted Diels–Alder Reaction of 4,6-Dimethyl-α-pyrone and Bis(trimethyltin)acetylene. A solution of 0.557 g (4.48 mmoles) of 4,6-dimethyl-α-pyrone,[34] 1.515 g (4.32 mmoles) of bis(trimethyltin)-acetylene, and 0.70 g of hydroquinone in 30 ml of bromobenzene was heated to reflux. The reaction mixture was examined periodically by thin layer chromatography (alumina– and silica gel–pentane). No product had formed after 41 hr (the starting materials have $R_f \sim 0$ in this tlc system), and reflux was continued for 148 hr in all. Removal of the solvent left a brown oil with the very characteristic odor of the 4,6-dimethyl-α-pyrone. Examination by tlc (silica gel–pentane) indicated the absence of any products. There was no absorption in the nmr spectrum (CCl_4) below 6.0 ppm and only a very weak signal in the Sn–CH_3 region.

(2-Biphenylyl)trimethyltin. A solution of 3.37 g (12.78 mmoles) of (phenylethynyl)trimethyltin, 1.50 g (15.61 mmoles) of α-pyrone, and 0.1 g of hydroquinone in 25 ml of bromobenzene was heated at reflux for 48 hr. Removal of the solvent under vacuum [28° (0.08 mm)] left a black oil, which was dissolved in ether. The mixture was filtered. Removal of the ether and distillation with a short-path apparatus gave three fractions: 0.10 g (bp 31° (0.1 mm)], 0.820 g [bp 65–85° (0.06 mm)], and 0.942 g [bp 86–92° (0.06–0.07 mm)]. The first two fractions consisted primarily of starting material. The final fraction was 96% pure (by glpc). On cooling, this fraction began to crystallize; it then was dissolved in hexane and crystallized by addition of methanol and cooling to give 0.753 g of fluffy needles, mp 53.5–57°. An additional 0.23 g, mp 53–56.5°, was obtained from the second fraction; total yield: 1.17 g, 29%. An analytical sample was obtained by one further recrystallization from hexane–methanol, mp 57–58°.

The nmr spectrum (CCl_4) of the product consisted of a broad, single absorption at 7.1–7.4 ppm (Ar–H) and a sharp singlet (Sn–CH_3) at 0.03 ppm above TMS, with relative areas of 1:1; the tin-proton couplings were $J_{Sn^{117}-H^1}$ = 52 cps and $J_{Sn^{119}-H^1}$ = 54 cps. The ultraviolet spectrum (EtOH) consisted of λ_{sh} 237 mμ (ϵ 6700); clearly, there is reduced resonance interaction between the benzene rings. The infrared spectrum (CCl_4 and CS_2) had bands at 3110 (w), 3075 (sh), 3060 (m), 3030 (sh), 2990 (sh), 2980 (m), 2915 (m), 1600 (w), 1575 (w), 1490 (w), 1460 (m), 1440 (m), 1425 (m), 1260 (w), 1245 (w), 1200 (w), 1190 (m), 1110 (w), 1070 (m), 1030 (w), 1025 (w), 1010 (m), 995 (w), 930 (w), 910 (w), 770 (s), 740 (s), 700 (s), 645 (w), 615 (w), 545 (w), and 520 (s) cm^{-1}.

Anal. Calcd for $C_{15}H_{18}Sn$: C, 56.83; H, 5.72. Found: C, 56.76; H, 5.75.

Competition between α-Pyrone and 5-Carbomethoxy-α-pyrone for Bis(trimethyltin)acetylene. A solution of 0.740 g (7.70 mmoles) of α-pyrone, 0.940 g (6.11 mmoles) of 5-carbomethoxy-α-pyrone, 2.318 g (6.60 mmoles) of bis(trimethyltin)acetylene, and 0.074 g of hydroquinone in 30 ml of bromobenzene was heated at reflux for 21.5 hr. Volatile components were removed at 28° (0.05 mm), and the residue was distilled essentially to dryness using a Hickman still [pot temperature to 180° (0.12 mm)]. The distillate, a discolored oil, was examined by nmr (CCl_4): characteristic absorption at 6–6.2 ppm indicated the presence of unconverted α-pyrone; absorptions at 7.5–8.0 ppm (characteristic of II), 3.8 ppm ($ArCO_2CH_3$), and 0.25 ppm (two peaks about 1 cps 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 gave 1.838 g (64.5%) of a faintly yellow liquid, bp 123° (0.06 mm), $n^{25}D$ 1.5632. There was *no* forerun, and thus no 1,2-bis(trimethyltin)benzene was present. Examination of the distillate by glpc (F & M, isothermal at 205° and He flow 60 cc/min, using a 6-ft column of 7.5% General Electric Co. SE-30 on Chromosorb P) confirmed the absence of the latter (retention time is 21 min).

Competition between α-Pyrone and 5-Methyl-α-pyrone for Bis(trimethyltin)acetylene. A solution of 0.336 g (3.06 mmoles) of 5-methyl-α-pyrone, 0.315 g (3.27 mmoles) of α-pyrone, 1.12 g (3.16 mmoles) of bis(trimethyltin)acetylene, and 0.03 g of hydroquinone in 10 ml of bromobenzene was heated at reflux for 31.5 hr. The solvent was removed under vacuum as before, and the residue was dissolved in carbon tetrachloride and examined using nmr. The spectrum contained absorptions at 6.8–7.5 ppm (Ar–H), 2.23 ppm (Ar–CH_3), 1.75 ppm (C–CH_3 of 5-methyl-α-pyrone), and 0.30 ppm, as well as several peaks due to impurities. The ratio of Ar–H to Ar–CH_3 was 24:11.5, which indicates a ratio of 1,2-bis(trimethyltin)benzene to 3,4-bis(trimethyltin)toluene of 1:1.2. 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 glpc (F & M, isothermal at 199°) and found to contain two components whose retention times corresponded exactly to those of the expected products. Yields then were calculated using 1-bromonaphthalene as an internal standard and correcting for the molar responses. The yield of I was 0.822 mmole (26%) and that of III was 1.092 mmoles (35.7%).

Monoiodinolysis of 1,2-Bis(trimethyltin)benzene. A solution of 1.00 g (2.48 mmoles) of the tin compound in 35 ml of chloroform was treated (dropwise) with 0.6304 g (2.48 mmoles) of iodine in 60 ml of chloroform. Discharge of the iodine color was instantaneous. Removal of solvent and trimethyltin iodide under vacuum [42° (0.15 mm)] left a yellow oil which was distilled to give a colorless, aromatic liquid, bp 70° (0.04 mm). The yield was 0.8485 g (93%). Analysis of the distillate by glpc (F & M, isothermal at 208° and He flow 70 cc/min, 7.5% SE-30 on Chromosorb P) indicated a purity of about 95%; contaminants were 4% of starting tin compound and about 1% of a lower boiler, probably 1,2-diiodobenzene. An analytical sample collected by glpc had $n^{25}D$ 1.6031. The nmr spectrum (CCl_4) had absorptions at 7.68 ppm (1 H, doublet with J = 7.5 cps, with further splitting[35]), 6.70–7.28 ppm (3 H, multiplet), and 0.37 ppm (9 H) with satellites: $J_{Sn^{117}-H^1}$ = 53 cps and $J_{Sn^{119}-H^1}$ = 55.5 cps. The ultraviolet spectrum (EtOH) had absorptions at λ_{sh} 232 mμ (ϵ 10,550), λ_{sh} 273 (495), λ_{max} 278 (723), and λ_{max} 285 (659). The infrared spectrum (liquid film) had bands at 3045 (m), 2975 (m), 2910 (m), 1600 (w), 1565 (w), 1550 (m), 1450 (w), 1435 (m), 1420 (m), 1410 (s), 1265 (w), 1245 (m), 1200 (w), 1190 (m), 1160 (w), 1120 (w), 1100 (w), 1085 (m), 1025 (m), 980 (w), 940 (w), 770 (s), 740 (s), 720 (sh), 635 (w), and 525 (w) cm^{-1}.

Anal. Calcd for $C_9H_{13}ISn$: C, 29.47; H, 3.57; I, 34.60. Found: C, 29.62; H, 3.28; I, 34.23.

Monoiodinolysis of Methyl 3,4-Bis(trimethyltin)benzoate. A solution of 0.876 g (1.897 mmoles) of the tin compound in 40 ml of chloroform was treated (dropwise) with 0.4803 g (1.893 mmoles) of iodine in 140 ml of chloroform. Removal of the volatiles under vacuum left a yellow oil which subsequently was distilled to give 0.711 g (88.5%) of colorless liquid, bp 110° (0.1 mm). Redistillation gave an analytical sample, $n^{25}D$ 1.5973. The product had the properties of a mixture of methyl 3-iodo-4-(trimethyltin)benzoate (VII) and methyl 4-iodo-3-(trimethyltin)benzoate (VI). The nmr spectrum (CCl_4) was particularly complex in the aromatic region, but a strong signal at 8.32 ppm (doublet with J = 1.4 cps), which must be the proton *ortho* to both iodine and the carbomethoxy group in VII, indicated that this was the major isomer. The ratio for the areas of Ar–H (7.05–8.32 ppm), O–CH_3 (3.86 ppm), and the Sn–CH_3 (two peaks at 0.42 ppm, 1 cps apart with relative areas of 2:3) was the expected 1:1:3. The infrared spectrum (CCl_4) consisted of absorptions at 3000–3100 (w), 2990 (m), 2920 (m), 2845 (w), 1735 (s), 1580 (m), 1545 (m), 1460 (m), 1440 (m), 1365 (m), 1290 (vs), 1250 (w), 1195 (m), 1120 (s), 1080 (m), 1020 (m), 1005 (m), 970 (m), 900 (w), 655 (w), and 530 (w) cm^{-1}.

Anal. Calcd for $C_{11}H_{15}O_2ISn$: C, 31.10; H, 3.56. Found: C, 31.26; H, 3.34.

Iodinolysis of (2-Biphenylyl)trimethyltin. A similar experiment carried out with this tin compound on a 2.04-mmole scale gave a nearly quantitative yield of 2-iodobiphenyl, bp 85° (0.06 mm), $n^{25}D$ 1.6577 (lit.[36] $n^{20}D$ 1.6620). The ultraviolet spectrum showed (in *n*-heptane) λ_{max} 227 mμ (ϵ 17,700) [lit.[37] λ_{max} 226 mμ (ϵ 20,000)]. The mass spectrum, moreover, showed a molecular ion, M^+ 280, and a peak (M^+ 153) for biphenyl, among others. The infrared spectrum (CCl_4 and CS_2), which had not been reported, had absorptions at 3150

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[34] Kindly furnished by Dr. A. Musco of this department.

[35] The lowest field proton is the one *ortho* to the iodine by analogy to the spectrum of *o*-diiodobenzene, in which the *ortho* protons occur at 7.84 ppm (J_0 = 7.9 cps): J. Martin and B. P. Dailey, *J. Chem. Phys*, **37**, 2594 (1962).

[36] D. R. Augood, J. I. G. Cadogan, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 3413 (1953).

[37] T. M. Dunn and T. Iredale, *ibid.*, 1592 (1952).

(sh), 3110 (sh), 3085 (sh), 3060 (sh), 3035 (sh), 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 (s), 720 (m), 700 (s), 645 (s), 605 (s), and 555 (s) cm^{-1}. The nmr spectrum (CCl_4) had absorptions at 7.75 ppm (1 H, doublet, J = 7.7 cps with further splitting) and 7.17 and 7.07 ppm (8 H); the low-field absorption is assigned to the proton *ortho* to the iodine.

Monobrominolysis of 1,2-Bis(trimethyltin)benzene. A solution of 1.48 mmoles of the tin compound in 350 ml of a 1:1 ether–methanol mixture was cooled to −75° and then treated dropwise with a solution of 0.2301 g (1.44 mmoles) of bromine in 50 ml of methanol. Instantaneous discharge of the bromine color was observed. Removal of solvent and trimethyltin bromide under vacuum left a slightly colored oil. Glpc (F & M, isothermal at 190° with He flow 60 cc/min, using 7.5% SE-30 on Chromosorb P) showed a single peak with retention time 10.5 min. No *o*-dibromobenzene or starting material (retention times 5 and 22 min, respectively) was evident. Distillation gave 0.410 g (86%) of aromatic, colorless liquid, bp 47° (0.03 mm), $n^{25}D$ 1.5703. An analytical sample collected by glpc had $n^{24}D$ 1.5734. The nmr spectrum of 1-bromo-2-(trimethyltin)benzene (in CCl_4) had absorptions at 7.47 ppm (1 H, probably *ortho* to the bromine), 6.9–7.3 ppm (3 H), and 0.38 ppm ($J_{Sn^{117}-H^1}$ = 53 cps; $J_{Sn^{119}-H^1}$ = 55 cps), with relative areas of 1:3:8.8. The infrared spectrum (liquid film) showed bands at 3055 (m), 2985 (m), 2915 (m), 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 (w) cm^{-1}. The ultraviolet spectrum (EtOH) had absorptions at λ_{max} 258 mμ, λ_{max} 264, λ_{max} 267, and λ_{sh} 275.

Anal. Calcd for $C_9H_{13}BrSn$: C, 33.79; H, 4.10. Found: C, 33.98; H, 4.43.

Dibrominolysis of 1,2-Bis(trimethyltin)benzene. A solution of 0.75 mmole of the tin compound in 30 ml of chloroform at room temperature was treated dropwise with a solution of 0.315 g (1.97 mmoles) of bromine in chloroform until the bromine color persisted in the reaction mixture. Removal of solvent left a liquid which was examined by glpc (F & M, isothermal at 170°, 7.5% SE-30 on Chromosorb P) and found to contain trimethyltin bromide and 1,2-dibromobenzene. The latter was identified by comparison of its glpc retention time and its infrared spectrum with those of an authentic sample (Aldrich Chemical Co.)

Thermal Decomposition of 1-Iodo-2-(trimethyltin)benzene. A 25-ml, pear-shaped flask containing 4.241 g (11.5 mmoles) of the tin compound was connected to a trap cooled to −75° which in turn was connected to a vacuum pump. The entire apparatus then was evacuated to 0.04 mm and filled with nitrogen (repeated three times). With the apparatus under a positive pressure of nitrogen, the pot was heated to 235 ± 5° for 3.5 hr. A colorless distillate collected in the cold trap during this period. The system was cooled to room temperature and a trap-to-trap [30° (0.1 mm)] and direct [50° (0.1 mm)] distillation were carried out. The total distillate, 0.547 g, was examined by nmr spectroscopy (CCl_4) and found to exhibit only two absorptions, 0.85 and 0.08 ppm, 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 (CH_3 at 0.3 ppm) or iodobenzene appeared to be present; this was confirmed by glpc analysis of the distillate. No attempt was made to determine the yields of the volatiles by glpc since previous attempts at quantitative glpc with trimethyltin iodide had been unsuccessful. Using the ratios obtained by nmr, the yields of trimethyltin iodide and tetramethyltin were 1.63 mmoles (28%) and 0.41 mmole (7%), respectively. These two products were identified by infrared spectroscopy and glpc in other runs under identical conditions.

The distillation residue was examined by tlc (silica gel–pentane) and found to contain a major component with R_f identical with that of starting material. Four products, all with lower R_f, also were evident, the major product being the one with the highest R_f after starting material. Distillation of the residue gave 1.369 g of liquid, bp 80 (0.15 mm) to 91° (0.08 mm), $n^{25}D$ 1.6072 (starting material had $n^{25}D$ 1.6031). Examination of the distillate by tlc showed it to be nearly pure starting material.

The residue from this distillation then was chromatographed on a 7 × $^7/_8$ in. column of Silica Gel G using hexane as eluent. Initial fractions contained 0.474 g of starting material, pure by tlc. The remaining fractions, which contained mixtures of 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: 1.955 g, 46%). Intermediate fractions, 0.75 g, contained less than 10% of starting material on the basis of tlc. Examination of the intermediate fractions by nmr (in CCl_4) showed absorption at 7.6–7.95, 6.8–7.4, 0.80, and +0.04 ppm with relative areas of about 1:5:2:4. Examination of these fractions by glpc (at 230°) revealed the presence of two products (retention times 10 and 33 min) and small amounts of starting material (retention time 7.5 min). The highest boiling and major product (estimated yield of 15–20% based on nmr spectroscopy and glpc data) was collected by glpc, repassed, and then distilled with a micro-Hickman still, bp ~100° (0.02 mm). The compound had the properties expected for 2-iodo-2′-(trimethyltin)biphenyl. The infrared spectrum (liquid film) had absorptions at 3165 (sh), 3050 (m), 2975 (m), 2915 (m), 2850 (w), 1585 (w), 1555 (w), 1495 (w), 1450 (s), 1430 (m), 1260 (w), 1250 (w), 1200 (w), 1190 (w), 1160 (w), 1110 (w), 1080 (w), 1075 (w), 1050 (w), 1020 (m), 1000 (s), 955 (w), 870 (w), 765 (s),755 (s), 725 (w), 710 (w), 675 (w), 660 (w), 640 (w), 620 (w), and 530 (w) cm^{-1}. Bands at 1050, 1020, and 1000 cm^{-1} appear in the spectrum of 2-iodobiphenyl and apparently are characteristic of 2-substitued biphenyls.[38]

The ultraviolet spectrum (EtOH) had λ_{sh} 240 mμ (ϵ 18,000), λ_{sh} 248 mμ (ϵ 9500), and λ_{max} 257 mμ (ϵ 9100). The nmr spectrum was particularly characteristic, consisting of a doublet J (= 8.0 cps) with secondary splitting at 7.85 ppm (1 H), a complex band at 6.77–7.6 ppm (7 H), and a singlet at 0.04 ppm (9 H) upfield from TMS. The low-field aromatic absorption is analogous to that of the 3-hydrogen in 2-iodobiphenyl, which appears at 7.8 ppm (J = 7.7 cps). The trimethyltin absorption appears at the same place as it does in (2-biphenylyl)trimethyltin. The mass spectrum showed a weak molecular ion peak, M^+ 444, and a very strong stannonium ion resulting from loss of a methyl group, M^+ 429, which is in complete agreement with the fragmentation expected for this molecule on the basis of Glockling's studies of alkylaryltin compounds.[39]

Anal. Calcd for $C_{15}H_{17}ISn$: C, 40.67; H, 3.87; I, 28.66. Found: C, 41.28; H, 3.96; I, 29.00.

The presence of dimethylbis(*o*-iodophenyl)tin in the reaction mixture is derived from spectroscopic evidence and from a cleavage study of the reaction products. A pure sample could not be obtained since it could not be freed from 2-iodo-2′-(trimethyltin)biphenyl by thin layer or column chromatography; glpc also was not successful in its isolation. Its presence is implied by the following data. The intermediate chromatography fractions, mentioned above, showed two kinds of Sn–CH_3 absorption in their nmr spectra. The high-field absorption at +0.04 ppm is due to 2-iodo-2′-(trimethyltin)biphenyl; the absorption at 0.8 ppm occurs at the same place as the protons in a compound similar to dimethylbis(*o*-iodophenyl)tin, namely dimethylbis(2,3,4,5-tetrachlorophenyl)tin. Such a chromatographic fraction of 0.051 g, which contained less than 2% of starting material (no absorption at 0.4 ppm in the nmr spectrum) and which contained 95% of the components with the highest R_f in tlc after starting material, was treated with methanolic hydrogen chloride. Removal of the solvent under vacuum left a yellow oil which was examined by glpc. The chromatogram showed three components in addition to trimethyltin chloride. The highest boiling (retention time of 20 min on a 6 ft × 5 mm column of 7.5% SE-30 on Chromosorb P programmed from 170 to 222° at 7.5°/min with a 60 cc/min flow of helium) was identified as 2-iodobiphenyl by comparison of its retention time and infrared spectrum with those of authentic material. The next highest boiling component trailed very badly and could not be collected. The third component was iodobenzene (implying iodophenyl groups had been attached to tin). It was identified by means of its retention time and infrared spectrum. The peak areas of 2-iodobiphenyl and iodobenzene in the chromatogram were about equal; the ratio of the areas of the nmr absorptions at 0.8 and +0.04 ppm in the mixture of starting materials was 3:4.

Concerning Infrared Spectra of Trimethyltin Derivatives. Characteristic bands associated with Me_3Sn groups in the compounds studied are: 1190–1195 cm^{-1}, Sn–CH_3 deformation; 765–775 cm^{-1}, Sn–CH_3 rock; 520–535 cm^{-1}, Sn–CH_3 symmetrical and/or asymmetrical stretch. Lohmann[40] in his compilation lists 1180–1210 cm^{-1} (Sn–CH_3 deformation), 770–790 cm^{-1} (Sn–CH_3 rock),

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(38) C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press Inc., New York, N. Y., 1963.

(39) D. B. Chambers, F. Glockling, J. R. C. Light, and M. Weston, *Chem. Commun.*, 281 (1966).

(40) D. H. Lohmann, "Group Absorption Frequencies of Tin-Containing Compounds," Tin Research Institute, Oct 1965.

520–570 cm^{-1} (Sn–CH$_3$ asymmetrical stretch), and 506–525 cm^{-1} (Sn–CH$_3$ symmetrical stretch) as limits for these absorptions.

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Halomethyl–Metal Compounds. XII.[1] The Action of Sodium Iodide on Phenyl(trihalomethyl)mercury Compounds. A New Method of Dihalocarbene Generation

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Abstract: The action of sodium iodide in acetone or in 1,2-dimethoxyethane (DME) on phenyl(trihalomethyl)mercury compounds results in displacement of trihalomethyl anion from mercury with formation of phenylmercuric iodide. In acetone the CX_3^- species is intercepted by the solvent and the products formed are haloform, dimethyl(trihalomethyl)carbinol, and 3,3,3-trihalo-*t*-butyl isobutyrate. The action of sodium iodide in DME on phenyl(trihalomethyl)mercurials in the presence of olefins provides a new route to *gem*-dihalocyclopropanes. With $C_6H_5HgCCl_3$ these reactions are rapid at 83–85° and slow at room temperature; with $C_6H_5HgCCl_2Br$ they are rapid at room temperature and slow at $-15°$. As yet unknown side reactions limit the product yields when relatively unreactive olefins are used (*e.g.*, tetrachloroethylene, triethylvinylsilane, vinyl acetate), but very good product yields are obtained with the more reactive (toward CCl_2) olefins such as cyclohexene and cyclooctene. A study of the relative reactivities of olefins toward the $C_6H_5HgCCl_3$ + NaI (at 80°) and the $C_6H_5HgCCl_2Br$ + NaI (at $-15°$) systems was carried out. The k_{rel} values obtained at 80° were virtually identical with those obtained at 80° using $C_6H_5HgCCl_2Br$ in benzene (or DME) and CCl_3CO_2Na in DME, and the values obtained at $-15°$ were virtually identical with those obtained at this temperature using $CHCl_3$ + *t*-BuOK as the CCl_2 source.

We have described in some detail the reactions of $C_6H_5HgCCl_2Br$, $C_6H_5HgCClBr_2$, $C_6H_5HgCBr_3$, and $C_6H_5HgCCl_3$ with olefins, in which CX_2 is transferred from the mercurial reagent to the olefin to produce *gem*-dihalocyclopropanes in high yield.[3–6] As noted, such reactions proceed rapidly in refluxing benzene when $C_6H_5HgCCl_2Br$ is used as the CCl_2 source, but much longer reaction times (36–48 hr) are required for $C_6H_5HgCCl_3$. This marked difference in reactivity was attributed to a more favorable elimination of phenylmercuric bromide, as compared with phenylmercuric chloride, owing mainly to steric effects.[6] Since phenyl(trichloromethyl)mercury is cheaper and somewhat more easily prepared than phenyl(bromodichloromethyl)mercury, we were quite interested in the possible "activation" of the former, either *via* a catalytic process or by its conversion, possibly *in situ*, to a more reactive species.

It was the report by Ledwith and Phillips[7] that ethyl(chloromethyl)mercury undergoes extremely rapid and quantitative displacement of Cl by iodide ion in acetone (eq 1) which suggested a possible activation of $C_6H_5HgCCl_3$ to us. If iodide ion would react in a similar fashion with the latter, then generation of $C_6H_5HgCCl_2I$ should be possible. This mercurial would be expected to be less stable, *i.e.*, a more reactive CCl_2 source, than $C_6H_5HgCCl_2Br$, and thus CCl_2 generation *in situ* by the action of iodide ion on $C_6H_5HgCCl_3$ in the presence of an olefin seemed a possibility worth investigating. However, an alternative mode of attack of iodide ion on phenyl(trichloromethyl)mercury had to be considered. Nucleophilic attack at mercury in RHgX compounds, *e.g.*, eq 2, is well known.[8] The trichloromethyl group is quite electronegative[9] and the trichloromethyl anion is a relatively stable species;[10] furthermore, the presence of three chlorine substituents on the carbon atom introduces very severe steric

$$CH_3CH_2HgCH_2Cl + Na^+I^- \xrightarrow{\text{acetone}} CH_3CH_2HgCH_2I + NaCl(s) \quad (1)$$

$$C_6H_5HgCl + Na^+I^- \xrightarrow{\text{acetone}} C_6H_5HgI + NaCl(s) \quad (2)$$

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