present compound exhibited an absorption maximum at 355 mμ, a minimum at 305 μ, and a second, stronger maximum at 280 mμ; the corresponding wave lengths for 5-*t*-butyl-2-hydroxybenzophenone are 347, 300, and 258 mμ, respectively. Introduction of chlorine substituents into 2-hydroxybenzophenones is known to produce bathochromic shifts of about that magnitude.

Fries Rearrangement of 4-*t*-Butyl-2-chlorophenyl Benzoate.—4-*t*-Butyl-2-chlorophenyl benzoate (18 g.) and aluminum chloride (10.5 g.) were intimately mixed in a flask fitted with a reflux condenser and slowly heated by means of a metal bath until the temperature of the reaction mass rose to 140°. This temperature was maintained for approximately 10 min. The reaction mixture was cooled and decomposed with a mixture of ice, dilute hydrochloric acid, and ethyl ether. The ether layer was separated, washed with water, and dried. Evaporation of the ether left a residue which was extracted with carbon tetrachloride. The carbon tetrachloride-insoluble part was recrystallized from ethanol, then from benzene. This procedure gave colorless needles, melting point 179–180°. The melting point of 3-chloro-4-hydroxybenzophenone has been reported by Hayashi[7] to be 180–181°. The ultraviolet absorption spectrum, λ_{max} (log ϵ) = 353 mμ (3.36), 285 mμ (4.04), 235 mμ (4.09), and the infrared spectrum, λ_{max} = 3.0 (s), 6.0 (s), 6.2 (s), 6.3, 6.6, 6.9, 7.1, 7.7 (s), 8.6, 9.5, 10.3, 10.5, 11.1, 12.0, 12.5, 13.5, 14.2 (s), 14.7 μ, were consistent with this structure; yield, 4.0 g., (28%).

Anal. Calcd. for $C_{13}H_9ClO_2$: C, 67.1; H, 3.90; Cl, 15.24; O, 13.75. Found: C, 67.0; H, 3.94; Cl, 15.22; O, 13.86. Molecular Weight Calcd.: 232. Found: 239.

Dinitrophenylhydrazone, m.p. 240°. *Anal.* Calcd. for $C_{19}H_{13}ClN_4O_5$: N, 13.58. Found: N, 13.38.

The carbon tetrachloride solution was evaporated and the tarlike residue was distilled under reduced pressure. The material distilled over a very broad range 80–240°/0.05 mm., and could not be separated into clean fractions even on redistillation of individual cuts. The infrared spectra of some fractions showed some indication of the presence of 2-hydroxybenzophenones, but no pure compound could be isolated.

In another attempt to obtain 5-*t*-butyl-3-chloro-2-hydroxybenzophenone by Fries rearrangement of 4-*t*-butyl-2-chlorophenyl benzoate, 18 g. of the ester was dissolved in 100 ml. of carbon disulfide. The solution was cooled to 0° and saturated with boron trifluoride. The solution was allowed to stand for 3 days and then worked up. Unchanged 4-*t*-butyl-2-chlorophenyl benzoate was recovered quantitatively. Several other experiments showed the same negative result: No reaction occurred under mild conditions; under forcing conditions, a substantial fraction of the *t*-butyl groups were lost and complex mixtures were obtained. Other *t*-butyl substituted phenyl esters behaved in a substantially similar fashion.

Acknowledgment.—The author is indebted to Dr. R. G. Beaman of this laboratory for helpful advice and discussions.

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[7] V. M. Hayashi, *J. prakt. Chem.* [2], **123**, 293.

Tetraphenylcyclobutadiene Derivatives. III. Preparation of Precursors and Some Preliminary Investigations

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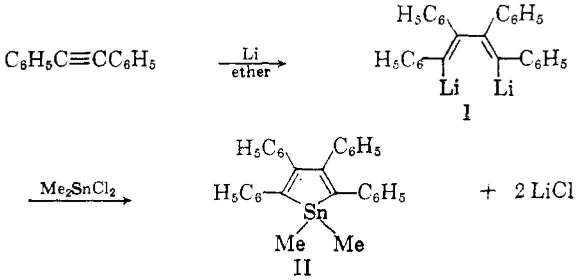
Details are given for the behavior of 1,1-dimethyl-2,3,4,5-tetraphenylstannole (II) toward electrophiles, particularly halogen. The resulting stannole dihalides were converted to 1,4-dihalo-*cis,cis*-1,2,3,4-tetraphenylbutadienes and their utility as intermediates in the synthesis of tetraphenylcyclobutadiene was investigated. A new preparation of 1,2,3-triphenylazulene isreported.

In a previous communication,[1] we have reported that tetraphenylcyclobutadiene derivatives may be conveniently prepared by the thermolysis of (4-bromo - 1,2,3,4 - tetraphenyl - *cis, cis* - 1,3 - butadienyl)dimethyltin bromide (IV); we wish to record here the details of the preparation and chemistry of IV and its homologs and to describe some of our early attempts to convert these compounds to cyclobutadiene derivatives.

A secondary objective of this communication (and one from which this research originally stemmed) is the presentation of some evidence bearing on the potential aromaticity of 1,1-dimethyl-2,3,4,5-tetraphenylstannole (II), a member of an unusual new group of metal heterocycles originally prepared by other workers in this laboratory.[2] The stannole II was prepared by modifications of the previously reported[2] technique involving the lithium dimerization of diphenylacetylene to 1,4-dilithio-1,2,3,4-tetraphenylbutadiene (I) and the reaction of I with dimethyltin dichloride.



The stannole II appeared to be particularly suited for a study of its aromatic properties inasmuch as the chemistry of organotin compounds has been extensively explored and any modification of the ex-

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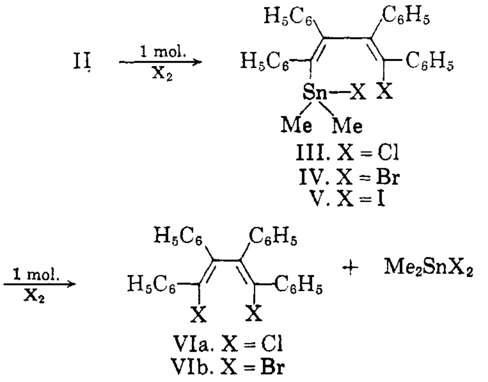
[1] For parts I and II, see H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2194, 2195 (1961).

[2] F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternas, and D. S. Lehman, *ibid.*, **82**, 5099 (1960).

pected reactivity of the carbon-tin bonds of II could provide evidence for the presence or absence of aromatic character, however slight. Accordingly, its stability toward electrophiles was investigated. Brief exposure of II to a dilute solution of glacial acetic acid in alcohol rapidly cleaved the unsaturated ring-carbon to tin bonds with the quantitative product of 1,2,3,4-tetraphenylbutadiene, identical to that obtained by hydrolysis of I.[3] Similarly, as will be discussed in detail below, halogenation of II occurred rapidly and quantitatively, again with cleavage of the alkene-tin bond. Therefore, if ring stability toward electrophiles is a reliable indication of resonance stabilization of II, (analogous to that found in thiophene, for example), then there can be little doubt that the stannole possesses little, if any, such stability.

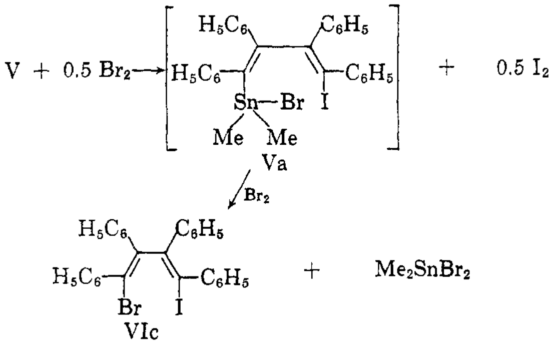
The rapid absorption of one mole of halogen is characteristic of the stannole II and at room temperature in carbon tetrachloride solution this reaction occurs with extreme facility with chlorine, bromine, and iodine. Halogenation takes place with cleavage of the ring rather than 1,2- or 1,4-addition to the conjugated double bonds, with the production of the stannole dihalides, III, IV, and V, respectively. This is substantiated by the cleavage of the remaining olefinic-carbon to tin bond of III with chlorine, or that of IV with bromine to yield, respectively, the 1,4-dichlorobutadiene VIa and 1,4-dibromobutadiene VIb. Alternatively, VIa and VIb can be prepared directly from the stannole II by the addition of two moles of the required halogen without the necessity of isolating the intermediaries, III and IV. With the weaker electrophile, iodine, further reaction of the stannole dihalides III–V does not take place at temperatures up to 100° and since decomposition occurs at higher temperatures, the diiodobutadiene VId was not prepared by this method.



III. X = Cl
IV. X = Br
V. X = I

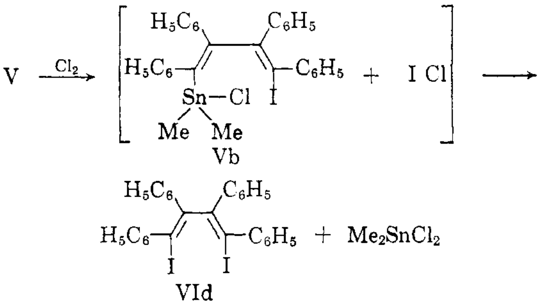
VIa. X = Cl
VIb. X = Br

By a slight variation of the above technique it was possible, within certain limitations, to prepare mixed dihalobutadienes. Thus, the bromoiodobutadiene VIC could be prepared by the cleavage of the stannole diiodide V with bromine. In this case, an additional complication occurs in that the first equivalent of bromine acts not as an electrophile, but as an oxidizing agent, as indicated by the liberation of one equivalent of free iodine. No attempt was made to isolate the intermediate stannole iodobromide Va, but treatment of the resulting iodine-containing solution with an additional mole of bromine yielded the desired bromoiodobutadiene VIc in 90% yield. When V was treated with excess chlorine, in an analogous attempt to prepare the chloroiodobutadiene, there was obtained instead the diiodo compound VId. Inasmuch as the deep iodine color produced on the addition of the first equivalent of chlorine fades on further addition, it was inferred that oxidation of the ionic iodide on the tin by the chlorine was indeed taking place, but that the liberated iodine reacted with additional chlorine to form the interhalogen compound, iodine monochloride. The latter species, which now contains a strongly electrophilic iodine, cleaves the intermediate stannole iodochloride Vb with the production of the diiodide VId. To prepare successfully the iodochlorobutadiene VIe, the above procedure was reversed; one mole of iodine monochloride converted the stannole II to the stannole iodochloride Vb which on treatment with chlorine yielded VIe. Convincing proof that Vb has the structure indicated, and not the one in which the chlorine and iodine are interchanged, is found in the fact that it does not liberate free iodine on exposure to chlorine and that treatment with bromine leads to the bromoiodo compound VIc. A pure



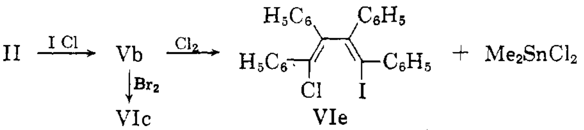
Va

VIc



Vb

VId



VIc

VIe

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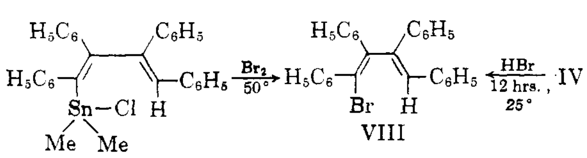
[3] L. I. Smith and H. H. Hoehn, *J. Am. Chem. Soc.*, **63**, 1184 (1941).

sample of the chloroiodobutadiene VIe was not obtained; in common with the iodine containing compounds reported here, it loses iodine on exposure to light, but unlike the other iodides, recrystallization from diverse solvents rendered it less, rather than more, pure.

It is evident from the halogenation reactions discussed above that both the stannole II and the stannole dihalides III–V react as normal tin compounds. Thus, cleavage occurs preferentially at the olefinic carbon-tin bond and not at the methyl-tin bond,[4] and the cleavage occurs stepwise with the ease of reaction paralleling the electrophilicity of the reagent. Further, strongly electronegative atoms on the tin decrease, or even prevent, electrophilic attack, and this is reflected in the increasingly vigorous conditions needed to effect multiple cleavage of tetraaryl or tetraalkyl tin compounds.[4]

These two factors, the strength of the electrophile and the extent of deactivation of the tin compound, adequately explain some apparent discrepancies observed in this work. We have already noted that the weak electrophile, iodine, has no effect on the stannole dihalides, but that the much stronger electrophilic iodine in iodine monochloride will effect a cleavage reaction. Similarly, chlorine cleaves the stannole dichloride III rapidly, but under the same conditions bromine has no effect and the bromochlorobutadiene was, therefore, not prepared. Though bromine is indeed a slightly weaker electrophile than is chlorine, its ready reactivity in some of the previously discussed cleavage reactions would indicate that the factor responsible for its lack of reactivity with III is due in the main to a sharp decrease in the electron density at the site of attack. That this decrease cannot be entirely due to the chlorine atom on the tin, but must also be due to the combined inductive and steric[4a] effect of the terminal chlorine, is evident from the fact that the butadienyltin chloride VII, obtained as a by-product from the preparation of II and differing from Va only in the presence of the 4-chlorine, reacts readily with bromine in carbon tetrachloride to produce the monobromobutadiene VIII. This same bromobutadiene VIII is produced when the stannole dibromide IV is exposed to one mole of hydrogen bromide in carbon tetrachloride at room temperature over a twelve-hour period. Here again, the deactivating effect of the 4-bromine must be invoked inasmuch as the stannole hydrochloride VII is instantly and quantitatively cleaved to tetraphenylbutadiene under conditions in which IV is recovered unchanged.



VII VIII

Thus far, we have not considered the geometrical configuration of the substituted tetraphenylbutadienes III–VIII. Though 1,2,3,4-tetraphenylbutadiene has been known for many years,[5] only recently has it been assigned the *trans,trans* configuration.[6] This assignment appears to be an arbitrary one, and is probably based on the fact that only one isomer has been obtained to date and that the preferred configuration of sterically hindered dienes is the *trans, trans*. An examination of molecular models, however, indicates that all three possible configurations are approximately equally sterically crowded. The results of our chemical investigations lead to the conclusion that the known[3,5,6] 1,2,3,4-tetraphenylbutadiene, m.p. 183–184°, identical with that obtained in our work, has, in fact, the *cis,cis* configuration. This follows logically from (a) the structure of its precursor, the stannole II, which requires a *cis, cis* disposition of its double bonds, and (b) the detailed demonstration by Nesmeyanov and Borisov[7] that electrophilic displacements involving olefinic-carbon to tin bonds proceed with complete retention of configuration. On this basis, we have assigned the *cis, cis* configuration to all of the substituted butadienes mentioned above. An alternative synthetic route, particularly to the mixed *cis,cis*-1,4-dihalobutadienes, is absent from the literature.

The availability of the *cis,cis*-dihalobutadienes suggested the possibility of exploring a new synthetic route to the elusive cyclobutadienes. All previously attempts to prepare cyclobutadiene and its derivatives have involved elimination reactions, usually of halogen, from a cyclobutane or cyclobutene ring[8]; our approach is fundamentally different in that the cyclobutadiene ring would be formed by the intramolecular elimination of halogen from a *cis,cis*-diene. Further, attempts to prepare the tetraphenyl-substituted cyclobutadiene had not been reported at the time this work was initiated[9] and it appeared likely that the delocalizing effect of the phenyl groups would tend to stabilize the cyclobutadiene ring.

A scheme which appeared particularly attractive involved the addition of one mole of butyllithium to one of the *cis,cis*-dihalotetraphenylbutadienes with the expectation that any 1-halo-4-lithiumtetraphenylbutadiene produced would spontaneously

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[4] R. K. Ingham, S. G. Rosenberg, and H. Gilman, *Chem. Rev.*, **60**, 479 (1960).

[4a] Evidence for the steric effect of the 4-halogen in the stannole dihalides has recently been inferred from the observation that these compounds exhibit *two* methyl bands in their NMR spectra. This will be discussed in detail in a future publication.

[5] A. Orechoff, *Ber.*, **47**, 89 (1914).

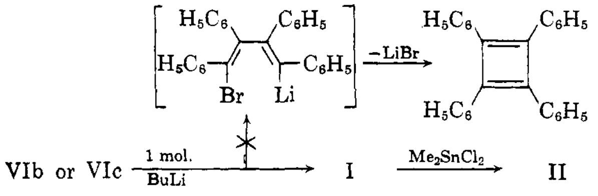
[6] G. J. Hoijtink, *Rec. trav. chim.*, **73**, 895 (1954); **74**, 1529 (1955).

[7] A. N. Nesmeyanov and A. E. Borisov, *Tetrahedron*, **1**, 158 (1957).

[8] For a review of the literature through 1958, see W. Baker and J. F. W. McOmie, in "Non Benzenoid Aromatic Compounds," D. Ginsburg, ed., Interscience Publishers, Inc., New York, N. Y., 1959, pp. 43–105.

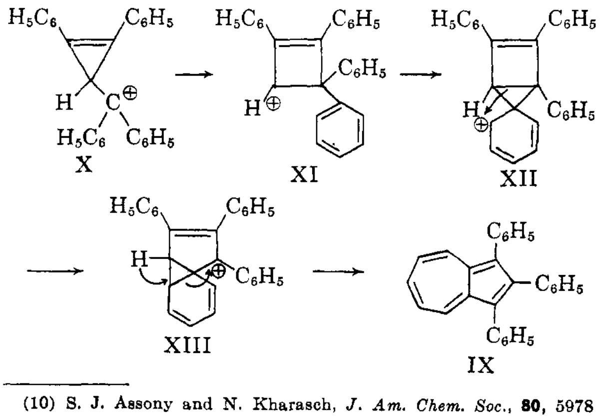
[9] Tetraphenylcyclobutadiene iron tricarbonyl complex has subsequently been reported by W. Hubel, *et al.*, *J. Inorg. Nucl. Chem.*, **9**, 204 (1959).

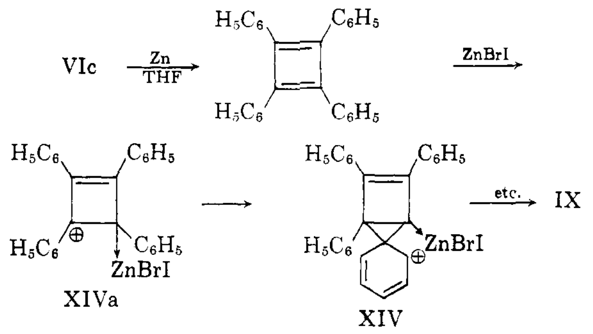
lose lithium halide to form the desired product. This was not realized; both the dibromo- and iodobromobutadienes formed only the dilithio compound I, as could be shown by the isolation of



1,2,3,4-tetraphenylbutadiene upon the addition of alcohol or the formation of the stannole II on the addition of dimethyltin dichloride. It is possible that under the proper conditions the chloroiodobutadiene VIe would succeed where the others did not.

When VIc was treated with activated zinc in boiling tetrahydrofuran, it was completely dehalogenated over a twelve-hour period. Resolution of the resulting oily product mixture on neutral alumina was only partially successful and yielded three crystalline fractions, two of which were colorless hydrocarbons, $C_{28}H_{22}$, of m.p. 181° and 149°, respectively. The first of these, obtained in 40% yield, proved to be *cis, cis*-1,2,3,4-tetraphenylbutadiene while the identity of the second isomer has not yet been established. The third crystalline product was most unusual in that it was eluted as a blue band, which on crystallization yielded a blue hydrocarbon, m.p. 211°. Fortunately, blue hydrocarbons are relatively rare and there was little difficulty in establishing its identity as the known 1,2,3-triphenylazulene (IX). This azulene has been prepared and its structure proved by Assony and Kharasch[10] and the properties of our compound were identical to the reported properties in every respect.[11] The formation of IX takes on added significance in the light of a recent report by Breslow and Battiste[12] that the cyclopropylcarbinyl cation X also forms the azulene IX, and that a reasonable path for its formation is *via* the indicated intermediates X–XIII. If we assume that tetraphenylcyclobutadiene results from the zinc dehalogenation of VIc, then the ZnBrI may form a carbonium ion[12a] (XIVa) which by a similar sequence of rearrangements leads to XIV and eventually to IX.





Intermediate XII, or its analog XIV, may alternatively rearrange to 1,2,3-triphenylnaphthalene. However, this was not observed either in our work or in that of Breslow and Battiste,[12] though these authors did report the formation of 1,2,4-triphenylnaphthalene, a rearrangement product which is not possible with our symmetrical intermediate. Consideration was given to the possibility that the hydrocarbon, m.p. 148–149°, mentioned above was 1,2,3-triphenylnaphthalene, but this was disproved by comparison with an authentic sample prepared by the method of Smith and Hoehn.[3] When VIb or VIc was shaken with lithium amalgam in tetrahydrofuran for eighteen hours, this same 149°-melting hydrocarbon was obtained in 50% yield. Lithium amalgam was used by Criegee[13] to dehalogenate tetramethyl-3,4-dichlorocyclobutene to tetramethylcyclobutadiene which dimerized spontaneously to octamethyltricyclooctadiene. A molecular weight determination proved that our compound is not a dimer and probably does not arise *via* a cyclobutadiene intermediate.[14] It is interesting to note that Assony and Kharasch[10] report the isolation of a colorless hydrocarbon, m.p. 155°, which invariably accompanied their triphenylazulene and that Balaban[15] has subsequently proposed a mechanism for the Assony and Kharasch reaction and has suggested that the 155° hydrocarbon is tetraphenylcyclobutadiene. The possibility exists that both Kharasch's and our hydrocarbons are identical, but this notwithstanding, our subsequent researches leave little doubt that neither Kharasch's nor our compound is tetraphenylcyclobutadiene. Chemical and physical investigations bear-

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[10] S. J. Assony and N. Kharasch, *J. Am. Chem. Soc.*, **80**, 5978 (1958).

[11] We are grateful to G. Buchi for the sample of IX used for comparison purposes. Professor Buchi reports that he obtained IX by the irradiation of solutions of diphenylacetylene.

[12] R. Breslow and M. Battiste, *J. Am. Chem. Soc.*, **82**, 3626 (1960).

[12a] I am indebted to a referee for pointing out this carbonium ion complex.

[13] R. Criegee and G. Louis, *Ber.*, **90**, 417 (1957).

[14] We have since prepared three authentic tetraphenylcyclobutadiene dimers; these will be described in future publications.

[15] A. G. Balaban, *Tetrahedron Letters*, No. **5**, 14 (1959).

ing on the structure of the 149° hydrocarbon are currently in progress.

In a further attempt to obtain evidence for cyclobutadiene formation, we investigated the ultraviolet irradiation of the stannole dihalides, III–V. The assumption that the tin-carbon bond of these compounds would be readily subject to homolytic cleavage on photolysis proved to be correct; irradiation of the stannole diiodide V in benzene led to the gradual release of iodine and the production of the azulene, IX, in 30% yield.[16] Though, as before, the route to the azulene, IX, remains highly speculative, it seems not unreasonable to call once more upon a similar intermediate, though in this case, radical rather than ionic intermediates may be more appropriate. These results prompted an investigation of further homolytic reactions of the stannole dihalides and eventually resulted in the discovery of their thermolytic decomposition.[1] This technique offers a simple and direct entry into tetraphenylcyclobutadiene chemistry, and a detailed discussion of this will form the substance of future publications.

Experimental

All melting points are uncorrected. Analyses were performed by Dr. C. K. Fitz (reported in tenths) or by Schwarzkopf Microanalytical Laboratory (reported in hundredths).

1,1-Dimethyl-2,3,4,5-tetraphenyl Stannole (II).—A solution of 54 g. (0.3 mole) of diphenylacetylene in 150 ml. of anhydrous ether was stirred vigorously under a nitrogen atmosphere in the presence of 6 g. of clean lithium shavings. The red dilithiobutadiene I formed rapidly and the reaction was mildly exothermic. After 2 hr. of stirring, the thick slurry was added rapidly to an ice-cold solution of 33 g. (0.15 mole) of dimethyltin dichloride (Metal and Thermit) dissolved in 250 ml. of anhydrous ether. Additional ether was used as needed to facilitate the addition and a Büchner funnel under a nitrogen blanket was used to introduce the dispersion of I and to retain the unchanged lithium. The resulting yellow solution was filtered through Celite to remove lithium chloride, the ether evaporated and replaced by methylene chloride (250 ml.), and the remainder of the lithium chloride removed by a second filtration. The methylene chloride was replaced by anhydrous ethanol and the product allowed to crystallize in the refrigerator overnight. The crude product weighed 57.6 g. (77%) and consisted of large yellow prisms of m.p. 185–195°. This material is pure enough for most purposes, but may be quantitatively converted to an analytically pure sample of almost white crystals, m.p. 193–195° (lit.,[2] m.p. 192–193°) by an additional recrystallization from methylene chloride–alcohol (charcoal).

In one experiment, carried out on the same scale and under the same conditions of those described above, there was obtained in addition to 30 g. of the stannole II, 20 g. of **(1,2,3,4-tetraphenyl-*cis*,*cis*-1,3-butadienyl)dimethyltin chloride (VII).** Two recrystallizations from alcohol afforded large white prisms, m.p. 201–202°.

Anal. Calcd. for $C_{30}H_{27}ClSn$: C, 66.51; H, 5.02; Cl, 6.55; Sn, 21.91. Found: C, 66.28; H, 4.99; Cl, 6.52; Sn, 22.15.

When 0.8 g. of VII was refluxed briefly in 20 ml. of alcohol containing 2 ml. of glacial acetic acid, the cooled solution deposited 0.5 g. (95%) of 1,2,3,4-tetraphenylbutadiene, m.p. 183–184° (lit.,[3] 183–184°).

(4-Bromo-1,2,3,4-tetraphenyl-*cis*,*cis*-1,3-butadienyl)-dimethyltin Bromide (IV).—To a solution of 25.3 g. (0.05 mole) of II in 250 ml. of methylene chloride was added dropwise with vigorous stirring, 8 g. (0.05 mole) of bromine in 40 ml. of methylene chloride. The bromine color was discharged instantly and the yellow stannole solution became colorless. The methylene chloride was replaced by ethanol and the solution allowed to crystallize overnight in the refrigerator. There was obtained 32.5 g. (97.5%) of pale yellow prisms, m.p. 141–143°. An analytical sample was obtained from methylene chloride–alcohol (charcoal) and consisted of white prisms of m.p. 145–146°.

Anal. Calcd. for $C_{30}H_{26}Br_2Sn$: C, 54.18; H, 3.94; Br, 24.03; Sn, 17.85. Found: C, 54.32; H, 4.13; Br, 24.19; Sn, 17.56.

The stannole dibromide IV could also be obtained in a different crystalline modification of the same melting point and mixed melting point. The infrared spectra of the two forms were vastly different in the solid state and completely identical in solution.

(4-Chloro-1,2,3,4-tetramethyl-*cis*,*cis*-1,3-butadienyl)-dimethyltin Chloride (III).—To a solution of 5 g. (0.01 mole) of the stannole II in 50 ml. of carbon tetrachloride was added 12.0 ml. of an ice-cold solution of 0.86 *M* chlorine in carbon tetrachloride. Evaporation of the solvent and recrystallization of the residual oil from alcohol yielded 5.2 g. (90%) of a pale yellow, crystalline solid, m.p. 148–150°. Two recrystallizations from methylene chloride–alcohol yielded large white prisms, m.p. 152–153°

Anal. Calcd. for $C_{30}H_{26}Cl_2Sn$: C, 62.50; H, 4.51; Cl, 12.31; Sn, 20.61. Found: C, 62.51; H, 4.76; Cl, 12.16; Sn, 20.39.

(4-Iodo-1,2,3,4-tetraphenyl-*cis*,*cis*-1,3-butadienyl)dimethyltin Iodide (V).—This was prepared as above from 1 mole each of the stannole II and iodine. From 5 g. of the stannole II there was obtained 7.4 g. (98.6%) of pale yellow prisms, m.p. 169–171°. Recrystallization from methylene chloride-alcohol (charcoal) afforded colorless prisms, m.p. 175–176° (with resolidification).

Anal. Calcd. for $C_{30}H_{26}I_2Sn$: C, 47.44; H, 3.43; I, 33.45; Sn, 15.64. Found: C, 47.63; H, 3.62; I, 33.34; Sn, 15.64.

When V was first prepared, it was obtained in a lower melting crystalline modification, m.p. 141–142°. The polymorphs had infrared spectra which were different in the solid state and identical in solution. Once the high-melting form was obtained, the lower melting form was no longer observed.

1,4-Dichloro-*cis*, *cis*-1,2,3,4-tetraphenylbutadiene (VIa).—Gaseous chlorine was bubbled through a solution of 1.5 g. of the stannole II in 50 ml. of chloroform. The yellow solution was evaporated to dryness and the resulting brown oil crystallized from ethanol to yield 0.7 g. of pale yellow prisms (65%) which on recrystallization from methylene chloride–methanol yielded white prisms of m.p. 164–165°.

Anal. Calcd. for $C_{28}H_{20}Cl_2$: C, 78.7; H, 4.7; Cl, 16.6. Found: C, 78.8; H, 4.6; Cl, 16.7.

1,4-Dibromo-1,2,3,4-tetraphenyl-*cis*, *cis*-butadiene (VIb).—The stannole II (5 g.) in 50 ml. of chloroform was treated with 2 moles of bromine in carbon tetrachloride. The first mole of bromine reacted instantly yielding a colorless solution, while the second mole required occasional warming to affect complete reaction. The yellow-orange solution was taken to dryness and the resulting oil crystallized by the addition of ethanol, yielding 5 g. (98%) of yellow prisms, m.p. 146–152°. Two recrystallizations from alcohol–methylene chloride afforded white prisms, m.p. 151–152°. On occasion, this compound is obtained in an alternate crystalline modification, consisting of short rods of m.p. 147–148°. These polymorphic modifications have identical infrared

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(16) Similar results were obtained with the stannole dibromide, Vb, though in these earlier experiments the yield of azulene was considerably smaller, presumably due to its rapid destruction on non-neutral alumina columns or on exposure of its solution in a halogenated solvent to light.

spectra in solution, and the lower melting form reverts to the higher melting when an alcohol slurry is left overnight at room temperature.

Anal. Calcd. for $C_{28}H_{20}Br_2$: C, 65.1; H, 3.9; Br, 31.0. Found: C, 65.2; H, 3.5; Br, 31.0.

VIb may also be prepared in comparable purity and yield by treatment of the stannole dibromide IV with one mole of bromine. By either technique, evaporation of the alcohol filtrate after crystallization of VIb, yields a brown glassy solid which can be converted by sublimation from a steam bath to white shiny platelets of **dimethyltin dibromide**, m.p. 76–77° (lit.,[4] m.p. 74°).

1-Bromo-4-iodo-1,2,3,4-tetraphenyl-*cis,cis*-butadiene (VIc).—The stannole diiodide V in chloroform was treated with 1.5 moles of bromine in carbon tetrachloride at room temperature. The deep iodine color which appeared and persisted after the addition of the first half mole of bromine was removed by washing with concentrated aqueous potassium iodide solution, the organic layer separated, dried, and the solvents removed by distillation. Crystallization of the residue from ethanol yielded white platelets of m.p. 182–184° in 76% yield. Repeated crystallizations from methylene chloride–methanol raised the melting point to 192–193° but an analytically pure sample was not obtained, and its tendency to decompose was manifested by its rapid discoloration both in the solid state and in solution. It is also possible that our product was contaminated with some diiodobutadiene VId arising from the formation of iodine monobromide during the course of the reaction.

Anal. Calcd. for $C_{28}H_{20}BrI$: C, 59.7; H, 3.6; Br, 14.2; I, 22.5. Found: C, 57.3; H, 3.2; Br, 15.2; I, 24.1.

(4-Iodo-1,2,3,4-tetraphenyl-*cis,cis*-1,3-butadienyl)dimethyltin Chloride (Vb).—A solution of 2 g. (4 mmoles) of the stannole II in 50 ml. carbon tetrachloride was added to 0.65 g. (4 mmoles) of iodine monochloride in 10 ml. carbon tetrachloride at room temperature with rapid stirring. Evaporation of the solvent and crystallization of the residue from alcohol yield 2.3 g. (85%) of yellow prisms, m.p. 118–121°. An additional crystallization from ethanol (charcoal) yielded yellow prisms of melting point 119–122°, and no further improvement in melting point was obtained on additional recrystallizations from various solvents.

Anal. Calcd. for $C_{30}H_{26}ClISn$: C, 53.97; H, 3.92; Cl, 5.31; I, 19.01; Sn, 17.78. Found: C, 54.91; H, 4.55; Cl, 4.98; I, 17.93; Sn, 17.03.

When 0.1 g. of Vb in 1 ml. of carbon tetrachloride was warmed with bromine until the bromine color persisted, there was obtained after the usual work-up, 70 mg. (85%) of VIc.

1-Chloro-4-iodo-1,2,3,4-tetraphenyl-*cis,cis*-butadiene (VIe).—To 4 mmoles of Vb, generated *in situ* as given above, was added 4.6 ml. of a 0.86 *M* solution of chlorine in carbon tetrachloride. The reddish solution was filtered to remove a small amount of yellow powder, the filtrate evaporated and the reddish oil taken up in ether, washed several times with water, dried, treated with charcoal, and the ether evaporated to leave a greenish oil weighing 2 g. The oil was crystallized from methylene chloride–ethanol and yielded 1.4 g. (70% of pale green prisms, m.p. 135–140°. The infrared spectrum of this compound closely paralleled those of the previously reported dihalobutadienes but was sufficiently distinctive to be differentiated from them. Successive recrystallizations of the crude material from various solvents including ethanol, ligroin, and glacial acetic acid effected a continual elevation of its melting point but an analytically pure sample of sharp melting point was not obtained.

1-Bromo-1,2,3,4-tetraphenyl-*cis,cis*-butadiene (VIII). (a). **From VII.**—Treatment of 0.55 g. (1 mmole) of VII in 10 ml. of chloroform with 1 mmole of bromine in carbon tetrachloride at 50° caused rapid decolorization. Evaporation of the solvent and crystallization of the residual oil from alcohol yielded (90%) of yellow crystals, m.p. 130–132°. An analytical sample was obtained from alcohol (charcoal) as white needles, m.p. 132–133°.

Anal. Calcd. for $C_{28}H_{21}Br$: C, 77.1; H, 4.8; Br, 18.2. Found: C, 76.7; H, 4.8; Br, 18.0.

(b). **From IV.**—When IV was refluxed briefly in glacial acetic acid or treated with a solution of hydrochloric acid in ethanol, the original compound was recovered unchanged. However, when 1.6 g. of IV in 50 ml. of chloroform was left overnight at room temperature in contact with 10 ml. of a 0.25 *N* solution of hydrobromic acid in chloroform, removal of the solvents and crystallization of the oil from methylene chloride–ethanol yielded 1.0 g. (99%) of pale yellow needles, m.p. 128–130°. Its identity to the product obtained from (a) was established by mixed melting point and superimposability of their infrared spectra.

Reaction of VIc with Butyllithium.—One equivalent of butyllithium in hexane (Foote Mineral) was added to a cold solution of 140 mg. (0.25 mmole) of VIc in 15 ml. of dry ether maintained at 0°. The resulting clear, yellow solution was allowed to warm to room temperature over a 30-min. period and was then quenched with water. Washing with water, drying and concentration of the ether solution gave 47 mg. (50%) of 1,2,3,4-tetraphenylbutadiene, m.p. 182–183°, identified by its infrared spectrum. From the filtrate was isolated 40 mg. (30%) of starting material.

Reaction of VIc with Zinc.—A solution of 0.4 g. of VIc in 20 ml. of anhydrous THF was refluxed for 18 hr. under nitrogen in the presence of 1 g. of activated zinc. The green solution was filtered through Celite and the solvent removed by distillation. The resulting green pasty solid yielded on the addition of ethanol, 0.1 g. (40%) of 1,2,3,4-tetraphenylbutadiene. After removal of the alcohol, the residue was dissolved in petroleum ether and chromatographed on neutral alumina. Elution with petroleum ether resolved the green band into a yellow and a blue band which were readily separated. The yellow eluent was eventually crystallized from methanol to yield 20 mg. of the hydrocarbon, m.p. 148–149°. The blue fraction yielded a few milligrams of crystals, identical to IX prepared as described below.

Reaction of VIb with Lithium Amalgam.—A solution of 200 mg. of VIb in 25 ml. of anhydrous THF was refluxed for 18 hr. with 3 g. of 0.5% lithium amalgam. The dark solution was filtered, the solvent removed, and the residue taken up in ether. After washing free of halide, drying, and removing the solvent, the residual oily solid gave a negative test for halogen. Crystallization of the oil from petroleum ether–alcohol yielded 70 mg. of tan prisms in two crops. Recrystallization from ethanol (with the help of methylene chloride) or from glacial acetic acid (charcoal) gave white prisms, m.p. 148–149°. A mixed melting point with the hydrocarbon obtained from the reaction of VIc with zinc showed no depression.

Anal. Calcd. for $C_{28}H_{22}$: C, 93.8; H, 6.2; mol. wt. 358. Found: C, 93.8; H, 6.0; mol. wt. (mass spec.) 358.

Ultraviolet Irradiation of Vc.—A solution of 1 g. of Vc in 100 ml. of dry benzene in a Pyrex flask was irradiated for approximately 8 hr. at ambient temperatures by means of a Hanovia Type 7420 light source. The deep iodine color of the solution was removed by washing with thiosulphate and the resulting deep green solution taken to dryness, dissolved in petroleum ether, and chromatographed on a neutral alumina of a moderate activity. The blue band which appeared was eluted with petroleum ether and the evaporated residue crystallized from dry nitromethane. The resulting blue granules (0.19 g., 30%) had m.p. 195–200° and after one additional recrystallization melted at 211°. The blue solid was identified as **1,2,3-triphenylazulene (IX)** by mixed melting point with an authentic sample,[11] and by the fact that its ultraviolet and visible spectrum were identical to that reported by Assony and Kharasch.[10]

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