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## New Unsaturated Heterocyclic Systems. I

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The reaction of 1,4-dilithiotetraphenylbutadiene with a metal or metalloid halide yields a number of novel heterocyclopentadienes (Fig. 1) wherein X is Au, Hg, B, Tl, Zr, C, Si, Sn, P, As, Sb, S, Se and Te. With silicon and tin halides spiro compounds (Fig. 2) also can be obtained. The five-membered heterocycles from Hg, N, P, S, Se and Te also have been prepared by treating 1,4-diiodotetraphenylbutadiene with alkali metal derivatives of these elements. Chemical evidence shows that pentaphenylphosphole has little or no aromatic character. Tetraphenyltellurophene, however, closely resembles the corresponding thiophene and selenophene.

## Introduction

The preparation of pentaphenylphosphole (pentaphenylphosphacyclopentadiene) from the reaction between  $\text{PhPCl}_2$  and the complex  $\text{Fe}_2(\text{CO})_6(\text{PhC}_2\text{Ph})_2$  was reported in a previous communication.<sup>1</sup> In order to prove its structure, it also was synthesized by treating 1,4-dilithiotetraphenylbutadiene (I) with  $\text{PhPCl}_2$ . This method (A) also was found independently by other workers<sup>2</sup> who illustrated it by examples of the elements S, P, As, Sb, C, Ge and Sn. We have shown by a systematic study of this reaction that I reacts very readily with a large variety of metal and metalloid halides yielding unusual heterocyclopentadienes not described so far in the literature.

A third method (B) has been found useful for the preparation of some heterocyclopentadienes and consists of the reaction of 1,4-dihalogenobutadienes with a di-alkali derivative of the hetero-element.

The present paper deals with tetraphenylsubstituted heterocycles having the structure shown in Fig. 1 where the element X is Au, Hg, B, Tl, Zr, C, Si, Sn, N, P, As, Sb, S, Se and Te, as well as with spiro-compounds of Si and Sn (Fig. 2). R (Fig. 1)

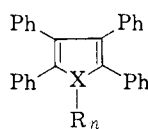


Fig. 1.

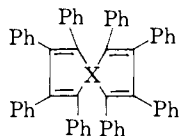


Fig. 2.

depends on the nature of X and may be halogen, alkoxy, alkyl, aryl, cyclopentadienyl, oxygen, sulfur, etc.;  $n$  varies between 0 and 2 according to the valency of the hetero-element.

## Procedures

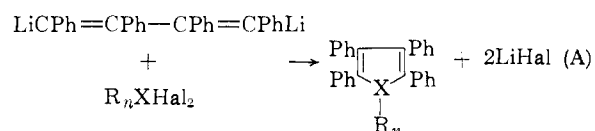
**1,4-Dilithiotetraphenylbutadiene (I)** is obtained by treating diphenylacetylene with lithium as described by Smith and Hoehn.<sup>3</sup> This reaction may lead to a compound which upon hydrolysis yields 1,2,3-triphenyl-naphthalene.<sup>2b,3</sup> The factors responsible for this side reaction have not been elucidated, but it could be shown that neither peroxides of the solvent nor traces of metal salts have an influence on this rearrangement of I. However, experience has shown that this undesired reaction can generally be avoided not only by limiting the reaction time<sup>3</sup> but also by working on

(1) E. H. Braye and W. Hübel, *Chem. & Ind. (London)*, 1250 (1959).(2) (a) F. C. Leavitt, T. A. Manuel and F. Johnson, *J. Am. Chem. Soc.*, **81**, 3163 (1959); (b) F. C. Leavitt, T. A. Manuel, F. Johnson, I. U. Matternas and D. S. Lehman, *ibid.*, **82**, 5099 (1960).(3) I. I. Smith and H. H. Hoehn, *ibid.*, **63**, 1184 (1941).

a larger scale (exceeding 5 g. of  $\text{PhC}_2\text{Ph}$ ). Under such conditions conversions of 85% may be obtained regularly.

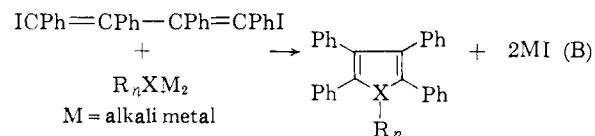
This dimerizing addition of lithium also could be extended to other alkynes. Of particular interest are the results obtained with unsymmetrical substituted acetylenes which lead to conclusions concerning the reaction mechanism. Compounds of the symmetrical configuration  $\text{LiCR}'=\text{CR}-\text{CR}=\text{CR}'\text{Li}$  are formed, which is most readily explained by the dimerization of the radicals  $\text{LiCR}'=\dot{\text{C}}\text{R}$  as suggested by Leavitt, *et al.*<sup>2b</sup> On the other hand, these new 1,4-dilithiobutadienes overcome the limitation of procedures A and B to phenyl-substituted heterocycles. These results will be reported in a subsequent paper.

1,4-Dilithiotetraphenylbutadiene (I) usually reacts rapidly even at low temperatures according to the equation



with formation of heterocyclopentadienes. Though ring closure is always favored, linear products are occasionally obtained. The formation of silicon heterocycles can be achieved only at higher temperatures, using higher boiling solvents, such as tetrahydrofuran, dioxane or 1,2-dimethoxyethane, instead of diethyl ether.

In the course of this work it has been found that 1,4-diiodotetraphenylbutadiene (II) also leads to the formation of heterocyclopentadienes as



The reaction proceeds slowly and has to be carried out at higher temperatures using boiling mesitylene or 2-( $\beta$ -ethoxyethoxy)-ethanol as solvent. Procedure B is limited by the availability of 1,4-dihalogenobutadienes. In fact, 1,4-dichlorobutadiene<sup>4</sup> so far has been, to the best of our knowledge, the only representative of this class. Compound II has been obtained in good yields by treating I with the stoichiometric amount of iodine. Furthermore, the compounds  $\text{R}_n\text{XM}_2$  exist only

(4) R. Criegee, W. Hörauf and W. D. Schellenberg, *Ber.*, **86**, 126 (1953).

TABLE I  
 HETEROCYCLIC COMPOUNDS SYNTHESIZED ACCORDING TO PROCEDURES A AND B

Reactants	Products	Yield, %	M.p., °C. <sup>b</sup>	Color
I + AuCl <sub>3</sub>	1-Hydroxy-2,3,4,5-tetraphenylaura-cyclopentadiene (III)	25	190-195 d.	Yellow
I + HgCl <sub>2</sub> or HgI <sub>2</sub>	Tetraphenylmercurole (IV) and (C <sub>28</sub> H <sub>20</sub> ) <sub>2</sub> Hg <sub>2</sub> (V)	34	188-190 d.	Pale yell.
		7	355 d.	Pale yell.
II + Na(Hg)	Tetraphenylmercurole (IV)	65	188-190 d.	Pale yell.
I + PhBCl <sub>2</sub>	Pentaphenylborole (VI)	66	175 d.	Colorless
I + CBr <sub>4</sub>	1,1-Dibromotetraphenylcyclopentadiene (VII)	39	151-153	Colorless
	(CBr <sub>4</sub> )			
I + PhCHCl <sub>2</sub>	Pentaphenylcyclopentadiene (VIII)	24	255	Colorless
I + Ph <sub>2</sub> SiCl <sub>2</sub>	Hexaphenylsilole (IX)	50	191	Greenish-yellow
I + SiCl <sub>4</sub>	Octaphenyl-1,1'-spirobisilole (X)	1	288-295 d.	Yellow
	(SiCl <sub>4</sub> )			
I + Ph <sub>2</sub> SnCl <sub>2</sub>	Hexaphenylstannole <sup>c</sup> (XI)	40	174	Greenish-yellow
I + SnCl <sub>4</sub>	Octaphenyl-1,1'-spirobistannole <sup>c</sup> (XII)	40	275-280	Yellow
	(SnCl <sub>4</sub> )			
I + (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ZrCl <sub>2</sub>	1,1-Bis-( $\pi$ -cyclopentadienyl)-2,3,4,5-tetraphenyl-zircona-cyclopentadiene (XIII)	53	140-170 d.	Orange
II + PhNNa <sub>2</sub>	Pentaphenylpyrrole <sup>c</sup> (XIV)	9	291	Colorless
I + PhCl <sub>2</sub>	Pentaphenylphosphole <sup>c</sup> (XV)	84	255-256	Greenish-yellow
II + PhPNa <sub>2</sub>	Pentaphenylphosphole (XV)	88		
I + PhCH <sub>2</sub> PCl <sub>2</sub>	P-Benzyl-tetraphenylphosphole (XXII)	38	203-213	Greenish-yellow
I + MePI <sub>2</sub>	P-Methyl-tetraphenylphosphole oxide (XXIII)	10	240-241	Yellow
I + PhP(S)Cl <sub>2</sub>	Pentaphenylphosphole <sup>c</sup> (XV)	45	255-256	Greenish-yellow
	Pentaphenylphosphole sulfide (XVII)	1	197-198	Yellow
I + PhAsCl <sub>2</sub>	Pentaphenylarsole <sup>c</sup> (XXIV)	56	214	Greenish-yellow
I + PhSbCl <sub>2</sub>	Pentaphenylstibole <sup>c</sup> (XXV)	21	162-170 d.	Greenish-yellow
II + Li <sub>2</sub> S	Tetraphenylthiophene <sup>c</sup> (XXVI)	90	184-185	Colorless
I + SO <sub>2</sub> Cl <sub>2</sub>	Tetraphenylthiophene-1,1-dioxide <sup>c</sup> (XXVII)	7	286-287	Yellow
	1,4-Bis-(chlorosulfonyl)-tetraphenylbutadiene (XXVIII)	13	157-159 d.	Colorless
I + Se <sub>2</sub> Br <sub>2</sub>	Tetraphenylselenophene (XXIX)	65	183-184	Colorless
II + Li <sub>2</sub> Se	Tetraphenylselenophene (XXIX)	98		
I + TeCl <sub>4</sub>	Tetraphenyltellurophene (XXX)	56	239.5	Orange-yellow
	(TeCl <sub>4</sub> )			
II + Li <sub>2</sub> Te	Tetraphenyltellurophene (XXX)	82		

<sup>a</sup> Yields are based on diphenylacetylene or II, respectively, except when otherwise stated. <sup>b</sup> All melting points are uncorrected. <sup>c</sup> Literature references are given in the Experimental part.

when X belongs to group IV, V or VI. However, alloys also have been found useful as could be demonstrated by the preparation of tetraphenylmercuracyclopentadiene from II with sodium amalgam at room temperature.

### Discussion

The heterocyclopentadienes so far synthesized according to procedures A and B are listed in Table I. They are all crystalline compounds, thermally quite stable and obtainable in fairly good yields, with the exception of the spiro-derivative of silicon. 1,1-Bis-( $\pi$ -cyclopentadienyl)-2,3,4,5-tetraphenyl-zirconacyclopentadiene (XIII) is the only substance which is sensitive to light; it hydrolyzes readily to tetraphenylbutadiene, cyclopentadiene and zirconium oxide hydrate.

**Tetraphenylmercurole (IV)** can be obtained by both methods A and B and is the starting material for the preparation of further mercury compounds which will be discussed in a later communication. The olefinic character of tetraphenylmercuracyclopentadiene (IV) is demonstrated by its reaction with maleic anhydride which readily yields tetraphenyl-1,2-dihydrophthalic anhydride and mercury. Thermal decomposition of IV leads to metallic mercury and a nearly insoluble hydrocarbon of

m.p. 421°<sup>5</sup> which also could be obtained in several other reactions, *e.g.*, by heating II in 2-ethoxyethanol at 200° or by treating I with cupric bromide. The latter reaction is analogous to the known dimerization of the organic part of a Grignard reagent in the presence of copper halides.<sup>6</sup> The manner of formation of this hydrocarbon together with its physical properties such as its high melting point and very low solubility leads to the assumption that the compound is octaphenylcyclooctatetraene. This also is supported by its ultraviolet spectrum in tetrahydrofuran:  $\lambda_{\max}$  267 m $\mu$ ,  $\epsilon$  44600; the observed value  $\epsilon/4 = 11150$  corresponds fairly well with the value for *cis*-stilbene ( $\epsilon$  10450).<sup>7</sup> It also was found that trimethyl borate reacts readily with I forming in good yields a colorless compound of composition C<sub>30</sub>H<sub>27</sub>BO<sub>2</sub>, m.p. 145° dec. Its structure has not yet been ascertained. Strong evidence was obtained for the formation of pentaphenylthallole from I and PhTlCl<sub>2</sub>.

(5) After this paper was submitted, a paper by H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2195 (1961), appeared dealing with a hydrocarbon of m.p. 425-427° which seems to be identical with ours. However, on the basis of preliminary X-ray work, no definite conclusions can be drawn about the structure of this substance.

(6) J. Krzewski and E. E. Turner, *J. Chem. Soc.*, **115**, 559 (1919); see also H. Gilman and H. H. Parker, *J. Am. Chem. Soc.*, **46**, 2823 (1924).

(7) R. N. Beale and E. M. F. Roe, *J. Chem. Soc.*, 2755 (1953).

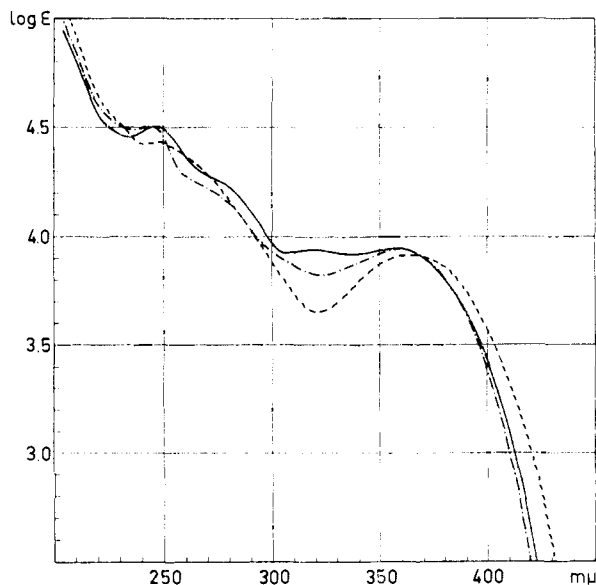


Fig. 3.—Ultraviolet spectra in cyclohexane: —, pentaphenylphosphole; ---, pentaphenylarsole; - · - ·, hexaphenylsilole.

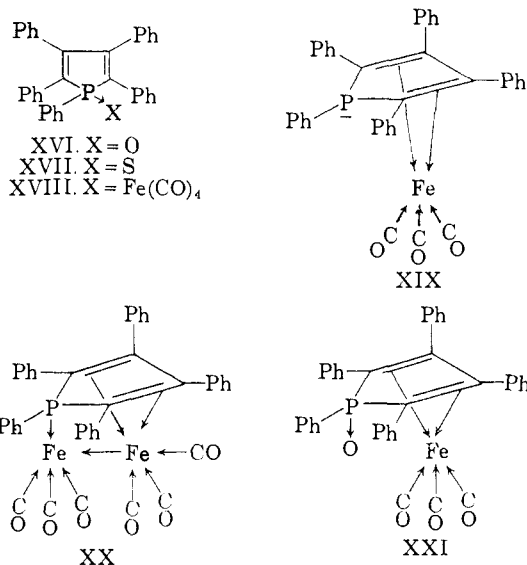
In contrast to the other heterocyclopentadienes prepared according to A, the **sila-cyclopentadienes** can be obtained only at higher temperatures. Further, the type of ether used as solvent was found to be of importance:  $\text{SiCl}_4$  and I yield in boiling dioxane the spiro-compound X, but in boiling 1,2-dimethoxyethane only a brownish compound of formula  $(\text{C}_{28}\text{H}_{20})_3\text{Si}_2$  (m.p.  $215^\circ$ ) could be isolated. One of the most interesting physical properties is the strong fluorescence of the siloles prepared. Hexaphenylstannole (XI) shows only a slightly greenish fluorescence.

**Phospholes.**—It was of particular interest to investigate the possible aromatic properties of this class of heterocycles, which has the same electronic configuration as the pyrroles.

Pentaphenylphosphole (XV) is oxidized relatively slowly in solution by the action of air to pentaphenylphosphole oxide (XVI). P-Alkyl substituted phospholes take up oxygen quite readily; in the case of P-methyltetraphenylphosphole only the oxide XXIII was isolated (Table I). Compound XV also reacts easily with sulfur and selenium yielding pentaphenylphosphole sulfide (XVII) or selenide, respectively. This sulfide also is formed in small amounts by treating I with  $\text{PhP(S)Cl}_2$ ; however, the main product is XV, showing the ease of splitting off the S atom of XVII.

The high affinity of XV toward O, S and Se shows that the phosphorus atom in phospholes possesses a reactive lone electron pair. This is further supported by the formation of the complex pentaphenylphosphole-iron tetracarbonyl (XVIII) from XV and iron pentacarbonyl. The infrared spectrum of XVIII indicates clearly that it has a structure similar to that of iron tetracarbonyl phosphines.<sup>8</sup> On the other hand, the reaction of XV with  $\text{Fe}_3(\text{CO})_{12}$  yields, in addition to XVIII, pentaphenylphosphole-iron tetracarbonyl (XIX) and oc-

asionally pentaphenylphosphole-iron tetracarbonyl (XX). In XIX the four  $\pi$ -electrons of the conjugated double bonds of XV are donated to the iron atom. Phospholes thus resemble a great variety of non-aromatic conjugated dienes which react very easily with iron carbonyls.<sup>9</sup> This easy complex formation together with the nature of the compounds obtained point against the assumption that the lone electron pair of the phosphorus participates in an aromatic sextet. On the contrary, no complexes from pyrroles, which are known to have a certain amount of aromatic character, have been reported yet and the reaction<sup>10</sup> between thiophene and iron carbonyls is very difficult.



Pentaphenylphosphole (XV) also can undergo Diels-Alder reactions; thus with dimethyl acetylenedicarboxylate one obtains dimethyl tetraphenylphthalate whereas maleic anhydride forms the normal adduct. As expected, the oxide reacts more readily with maleic anhydride, but the sulfide has the same reactivity as XV.

From all these chemical properties the conclusion must be drawn that phospholes behave as tertiary phosphines having a conjugated diene system and possess little or no aromatic character.

There is a marked difference between the properties of the oxide XVI and the sulfide XVII. Even under mild conditions the sulfur is split off: treatment of XVII with iron carbonyls gives only pentaphenylphosphole-iron tetracarbonyl (XVIII) while XVI with iron pentacarbonyl yields pentaphenylphosphole oxide-iron tricarbonyl (XXI). Pentaphenylphosphole oxide has a bright yellow fluorescence but the sulfide and the selenide have not. Pentaphenylphosphole itself is strongly fluorescent (green); the intensity, however, decreases

(9) Compare B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 642 (1958); T. A. Manuel and F. G. Stone, *Proc. Chem. Soc.*, 90 (1959); R. Pettit, *J. Am. Chem. Soc.*, **81**, 1266 (1959); E. Weiss and W. Hübel, *J. Inorg. & Nuclear Chem.*, **11**, 42 (1959).

(10) R. Burton, M. L. H. Green, E. W. Abel and G. Wilkinson, *Chem. & Ind. (London)*, 1592 (1958); M. L. H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 993 (1960); see also H. D. Kaesz, R. B. King, T. A. Manuel, L. D. Nichols and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 4749 (1960).

(8) W. Reppe and W. J. Schweckendiek, *Ann.*, **560**, 104 (1948).

when the substituent on the phosphorus atom is benzyl or methyl instead of phenyl.

**Pentaphenylarsole (XXIV)** has similar properties to those of the phosphorus compound XV. Thus, it is greenish, fluorescent and easily forms an oxide; its ultraviolet spectrum closely resembles that of XV (Fig. 3). With iron pentacarbonyl the complex pentaphenylarsole-iron tricarbonyl could be obtained in good yields.

**Tetraphenylselenophene (XXIX)** has been obtained by two other reactions in addition to procedures A and B. Thus, XXIX is formed when either the complex  $\text{Fe}_2(\text{CO})_6(\text{PhC}_2\text{Ph})_2$ <sup>11</sup> or diphenylacetylene itself is heated with selenium.

**Tetraphenyltellurophene (XXX)**.—All attempts reported in the literature<sup>12</sup> to prepare tellurophenes have been unsuccessful. In view of this it was surprising that tetraphenyltellurophene XXX could be readily obtained by both procedures and was found to be very stable. In contrast to the colorless tetraphenylfuran, -thiophene and -selenophene, XXX forms orange-yellow crystals of m.p.  $239.5^\circ$ , which is considerably higher than that of the other three compounds. The ultraviolet spectrum of XXX (Fig. 4) indicates that the yellow color is due to a broadening of the first band; its general shape corresponds closely to those of tetraphenylfuran, -thiophene and -selenophene, suggesting a similar electronic structure. In this connection it was of interest to investigate the chemical behavior of this first tellurophene compound. As with tetraphenylfuran, -thiophene and -selenophene, XXX also failed to undergo the Diels-Alder reaction with maleic anhydride, even under drastic conditions (21 hours at  $220^\circ$ ). Attempts to quaternize it with methyl iodide by heating the components for 19 hours at  $150^\circ$  also were unsuccessful in contrast to diaryltellurides which readily form the corresponding telluronium iodides.<sup>13</sup> Furthermore, complex formation of XXX with metal carbonyls is very difficult, in agreement with the behavior of the other heterocycles of group VI.<sup>10</sup> Only in one experiment with  $\text{Fe}_3(\text{CO})_{12}$  was a small quantity of a complex obtained; its infrared spectrum suggests that it is  $(\text{C}_{28}\text{H}_{20}\text{Te})\text{Fe}(\text{CO})_3$ .

It must be concluded from these results that tellurophenes have an aromaticity similar to that of thiophenes and selenophenes. However, tetraphenyltellurophene readily adds bromine forming tetraphenyltellurophene-1,1-dibromide, due to the more metallic character of tellurium.

**Acknowledgments.**—This work is part of a project supported by Union Carbide Corporation, New York, N. Y., and we acknowledge with thanks their support. We are indebted to Drs. R. H. Gillette and C. E. Sunderlin for their great interest in these investigations, and we wish to express our thanks to Messrs. J. Vandewalle and E. Wittuck for technical assistance and to Drs. J. Kommandeur

(11) W. Hübel and E. H. Braye, *J. Inorg. & Nuclear Chem.*, **10**, 250 (1959).

(12) W. G. Zoellner, *Dissert. Abstr.*, **19**, 3139 (1959); see also F. C. McMahon, T. G. Pearson and P. L. Robinson, *J. Chem. Soc.*, 1644 (1933).

(13) C. Lederer, *Ann.*, **399**, 260 (1913).

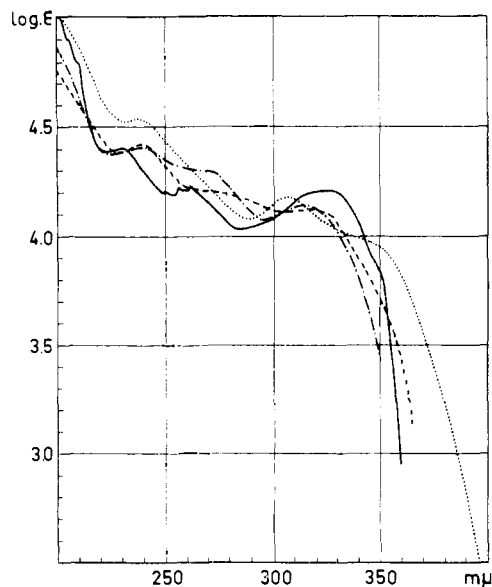


Fig. 4.—Ultraviolet spectra in cyclohexane: —, tetraphenylfuran; ---, tetraphenylthiophene; ·····, tetraphenylselenophene; - · - · - ·, tetraphenyltellurophene.

and H. F. White of the Union Carbide Corporation for measuring the fluorescence spectra.

### Experimental

**Preparation of 1,4-Dithio-1,2,3,4-tetraphenylbutadiene (I).**—A concentrated ethereal solution of diphenylacetylene was shaken with an excess of clean lithium shavings in a stoppered flask. After an induction period, an intense red color developed rapidly. This induction time increased significantly with decreasing toluene concentration and was about 10 minutes for a two to three molar solution. At the beginning the reaction is exothermic and, for batches exceeding 10 g., cooling by means of a stream of air was necessary. Usually, compound I precipitated during the reaction as an orange-yellow powder, which dissolved only slightly on adding more diethyl ether, but which was readily soluble in 1,2-dimethoxyethane giving a deep green solution. After 2 hours, the yield of I was 70 to 85% (determined by hydrolysis to tetraphenylbutadiene). In most cases, a diluted ethereal suspension of I was used for further reactions after mechanical removal of the excess lithium. The reactions must be carried out in an inert atmosphere.

The side reaction, leading to 1,2,3-triphenyl-naphthalene, occurs by subsequent very rapid rearrangement of I into a sticky lithium derivative of brownish-violet color. The speed of this exothermal rearrangement is such that mixtures of tetraphenylbutadiene and triphenyl-naphthalene were found only occasionally after hydrolysis.

**Preparation of 1,4-Diiodotetraphenylbutadiene (II).**—A suspension of I (from 20 g. of diphenylacetylene) in 100 ml. of ether was added dropwise with stirring and cooling to 22.9 g. of iodine suspended in 50 ml. of ether. The yellow precipitate was filtered off and washed with water and alcohol. It consisted of 22.4 g. of II (m.p.  $202^\circ$ ). By working up the filtrate, the yield amounted to 24.1 g. of II (70.5% calcd. on  $\text{PhC}_2\text{Ph}$ ). Compound II was recrystallized from methylene chloride-ethanol; II is fairly soluble in hot benzene, methylene chloride, and tetrahydrofuran (THF), and practically insoluble in boiling petroleum ether. The pure product was slightly yellow and melted at  $203\text{--}204^\circ$  with slow decomposition.

*Anal.* Calcd. for  $\text{C}_{28}\text{H}_{20}\text{I}_2$ : C, 55.10; H, 3.30. Found: C, 55.17; H, 3.34.

Compound II also was formed at  $-40^\circ$  from I and  $\text{Fe}(\text{CO})_5\text{I}_2$  (molar ratio) in ether in 74% yield.

**Hydrocarbon of Formula  $(\text{C}_{14}\text{H}_{10})_2$  (Assumed to be Octaphenylcyclooctatetraene).**—Heating 2 g. of II in 50 ml. of 2-ethoxyethanol for 7 hr. at  $200^\circ$  in a sealed tube flushed with nitrogen gave 0.05 g. of needles, m.p.  $421^\circ$ , nearly in-

soluble in all organic solvents tried, including boiling nitrobenzene. Purification may be achieved by extraction with THF in a Soxhlet apparatus during several days. From the mother liquor, tetraphenylfuran<sup>14</sup> (m.p. 174°, 1.05 g., 85%) was isolated.

*Anal.* Calcd. for (C<sub>14</sub>H<sub>10</sub>)<sub>4</sub>: C, 94.34; H, 5.66. Found: C, 93.80; H, 5.72.

A solution of I (from 4 g. of PhC<sub>2</sub>Ph in 10 ml. of ether) in 50 ml. of 1,2-dimethoxyethane was added during 35 min. to a suspension of 5.1 g. (22.2 mmoles) of CuBr<sub>2</sub> in 100 ml. of ether. The dark green mixture was refluxed for half an hour and filtered. The precipitate was washed with ethanol and the copper salts were removed with concentrated ammonia leaving 0.6 g. (15%) of the hydrocarbon, m.p. 421°. The filtrate contained small amounts of tetraphenylbutadiene.

**Preparation of 1-Hydroxy-2,3,4,5-tetraphenyl-aura-cyclopentadiene (III).**—An ethereal solution of I, prepared from 3 g. of diphenylacetylene in 10 ml. of ether, was added to a solution of 2.1 g. of AuCl<sub>3</sub> in 200 ml. of ether. The reaction is slightly exothermic. After refluxing for 1 hr., the brown reaction mixture was filtered and the precipitate extracted with methylene chloride. Benzene was added to the concentrated extracts yielding yellow needles, m.p. 190–195° dec. (25% yield). The compound did not contain chlorine and its infrared spectrum showed a sharp band at 2.78μ, ascribed to an OH group.

*Anal.* Calcd. for C<sub>28</sub>H<sub>21</sub>AuO: C, 58.95; H, 3.71; Au, 34.53; O, 2.81. Found: C, 58.50; H, 3.64; Au, 35.1, 33.70; O, 2.61.

**Preparation of Tetraphenylmercuriole (IV) and (C<sub>28</sub>H<sub>20</sub>)<sub>2</sub>Hg<sub>2</sub> (V).** **Method A.**—The suspension of I, prepared from 30 g. of PhC<sub>2</sub>Ph in 100 ml. of ether, and diluted with 700 ml. of dry ether, was introduced in a 3-necked vessel. Over a period of 1 hour 18.3 g. of HgCl<sub>2</sub>, dissolved in 1 l. of ether, was added at room temperature. After refluxing for 0.5 hr., the precipitate was filtered off, the washed and dried ethereal layer of the filtrate was evaporated to dryness and the residue, taken up in benzene, chromatographed over silica gel. The first fraction (colorless), eluted with a mixture of benzene and petroleum ether, contained 0.54 g. of tetraphenylbutadiene; elution with C<sub>6</sub>H<sub>6</sub> or CH<sub>2</sub>Cl<sub>2</sub> yielded a first yellow band containing 3.27 g. of V and a second yellow band containing 4.48 g. of IV. The raw precipitate of the reaction mixture, washed with water, amounted to 34.5 g. and was extracted successively with 1 l. of warm benzene (yielding 9.1 g. of IV), warm THF (giving 1.44 g. of IV) and CH<sub>2</sub>Cl<sub>2</sub> (0.89 g. of IV). The total yield of IV amounted to 15.91 g. (34% based on diphenylacetylene) in addition to 3.27 g. (7%) of V.

Compound IV is a slightly yellow compound which was difficult to purify and to crystallize; chromatography on silica gel was found to be the best method for its purification. It is fairly soluble in C<sub>6</sub>H<sub>6</sub>, CH<sub>2</sub>Cl<sub>2</sub>, less in ether and insoluble in alcohol and petroleum ether. Diethyl ether was the most suitable solvent for its crystallization. It was observed that the melting points vary considerably and reach 190° dec.

*Anal.* Calcd. for C<sub>28</sub>H<sub>20</sub>Hg: C, 60.27; H, 3.62; Hg, 36.11; mol. wt., 557.08. Found: C, 60.17; H, 3.74; Hg, 36.33; mol. wt. (cryoscopic in C<sub>6</sub>H<sub>6</sub>), 450, 686.

In contrast to IV, (C<sub>28</sub>H<sub>20</sub>)<sub>2</sub>Hg<sub>2</sub> (V) readily crystallizes from benzene-ether and forms large yellow crystals which melt at 355° dec. Its infrared spectrum is similar to that of IV.

*Anal.* Calcd. for C<sub>56</sub>H<sub>40</sub>Hg<sub>2</sub>: C, 60.27; H, 3.62; Hg, 36.11; mol. wt., 1114.16. Found: C, 60.13; H, 3.50; Hg, 35.68; mol. wt. (cryoscopic in C<sub>6</sub>H<sub>6</sub>), 1172, 1148.

**Method B.**—A solution of 2 g. of 1,4-diiodotetraphenylbutadiene (II) in 50 ml. of toluene, was shaken for 19 hr. at room temperature with liquid sodium amalgam, prepared from 1 g. of Na and 136 g. of Hg. The organic layer was washed with water, concentrated, and the residue crystallized from a small amount of ether. The yield of IV was 65% (raw).

**Preparation of Pentaphenylborole (VI).**—Phenylboron-dichloride (1.6 ml.) diluted with 20 ml. of ether was slowly added to a suspension of I, prepared from 3.6 g. of PhC<sub>2</sub>Ph in 8 ml. of ether. After the exothermic reaction had ceased, the mixture was refluxed for 20 min. and water added. The organic products were extracted with benzene and worked up

(14) K. Bernhauer, P. Müller and F. Neiser, *J. prakt. Chem.*, **145**, 301 (1936).

by chromatography on silica gel. Compound VI (2.93 g.; 66%) was eluted with mixtures of petroleum ether and benzene. Crystallized from C<sub>6</sub>H<sub>6</sub>/EtOH, the pale yellow compound melted at about 175° (dec.). Boron (2–3%) was estimated by emission spectroscopy.

*Anal.* Calcd. for C<sub>34</sub>H<sub>23</sub>B: C, 91.89; H, 5.67. Found: C, 91.41; 92.16; H, 6.04.

**Preparation of 1,1-Dibromo-tetraphenylcyclopentadiene (VII).**—Carbon tetrabromide (3.75 g., 11.25 mmoles) dissolved in 50 ml. of ether was added to a suspension of I, prepared from 10 g. (51 mmoles) of PhC<sub>2</sub>Ph in 25 ml. of ether. After refluxing for 0.5 hr. the reaction mixture was worked up by chromatography on silica gel. Besides 2.87 g. (15.7% based on PhC<sub>2</sub>Ph) of tetraphenylbutadiene, VII was obtained as colorless plates, m.p. 151–153°, yield 2.35 g. (39% based on CBr<sub>4</sub>).

*Anal.* Calcd. for C<sub>28</sub>H<sub>20</sub>Br<sub>2</sub>: C, 65.92; H, 3.81. Found: C, 66.56; H, 3.85.

**Preparation of Pentaphenylcyclopentadiene (VIII).**—This hydrocarbon was prepared according to the procedure used for preceding examples from I and benzyldiene chloride in a 24% yield. It melted at 255° (lit. 250°, 258–259°<sup>2b</sup>).

**Preparation of Hexaphenylsilole (IX).**—Compound I was prepared from 9 g. (50 mmoles) of PhC<sub>2</sub>Ph in 40 ml. of ether and diluted with 300 ml. of THF; 5.2 ml. (6.3 g., 25 mmoles) of Ph<sub>2</sub>SiCl<sub>2</sub> was added and the ether distilled off until the boiling point of THF was reached. After refluxing for 4 hours, the cooled reaction mixture was treated with dilute HCl and extracted with benzene. The products, dissolved in CS<sub>2</sub>, were chromatographed over alumina. Elution with petroleum ether-benzene (1:1) gave 6.8 g. (50%) of IX, m.p. 180°. Recrystallized from isopropyl alcohol, the faintly greenish-yellow compound melted at 190–191°. In the solid state it exhibits a strong blue fluorescence in ultraviolet light (emission max. 468 mμ); ultraviolet spectrum: absorption maxima in mμ (log ε): 365 (3.915), 249 (4.435).

*Anal.* Calcd. for C<sub>30</sub>H<sub>20</sub>Si: C, 89.18; H, 5.61; Si, 5.21. Found: C, 88.97; H, 5.65; Si, 5.22.

**Preparation of Octaphenyl-1,1'-spirobisilole (X).**—To a suspension of I, prepared from 30 g. of diphenylacetylene in 100 ml. of ether, 250 ml. of dry dioxane was added, followed by 3.3 ml. of SiCl<sub>4</sub>. A yellow precipitate was formed with evolution of heat; if at this stage the reaction mixture was worked up, no spiro-compound was isolated. Therefore, the ether was distilled off and the dioxane solution refluxed for 90 minutes. The color became first dark brown and then light brown. The mixture was concentrated under vacuum, water was added and the organic products were extracted with benzene and ether. The combined solutions, dried over K<sub>2</sub>CO<sub>3</sub>, were evaporated to dryness and the residue, dissolved in a minimum amount of benzene, was separated first on alumina into several fractions by means of petroleum ether containing increasing amounts of benzene. Each fraction was rechromatographed on silica gel. Besides some unreacted diphenylacetylene, the following were eluted with petroleum ether-benzene mixtures: 0.52 g. of tetraphenylbutadiene, 1.13 g. of yellow silky needles of 1-benzyldiene-2,3-diphenylindene (m.p. 181–188°),<sup>16</sup> 0.02 g. of 1,4-diphenyldibenzopentalene (m.p. 260°)<sup>17</sup> and 0.01 g. of unidentified orange crystals of m.p. 186–189°. With pure benzene, a yellow band was eluted yielding 0.16 g. of X (0.7% based on SiCl<sub>4</sub>), m.p. 288–295° dec. from benzene-methanol. It showed a weak greenish fluorescence.

*Anal.* Calcd. for C<sub>56</sub>H<sub>40</sub>Si<sub>2</sub>: C, 90.76; H, 5.44; Si, 3.80; mol. wt., 741.03. Found: C, 90.71; H, 5.60; Si (from ash), 3.16; mol. wt. (cryoscopic in C<sub>6</sub>H<sub>6</sub>), 755, 759.

(C<sub>28</sub>H<sub>20</sub>)<sub>2</sub>Si<sub>2</sub>.—The same reaction was carried out using 1,2-dimethoxyethane as solvent and yielded by similar working up 5.5 g. of a brownish diamagnetic crystalline compound of formula (C<sub>28</sub>H<sub>20</sub>)<sub>2</sub>Si<sub>2</sub>. Recrystallized from acetic acid, it melted at 215°.

*Anal.* Calcd. for C<sub>56</sub>H<sub>40</sub>Si<sub>2</sub>: C, 89.63; H, 5.37; Si, 5.00; mol. wt., 1125.58. Found: C, 89.21; H, 5.45; Si, 5.23; mol. wt. (cryoscopic in C<sub>6</sub>H<sub>6</sub>), 1123, 1114.

(15) K. Ziegler and B. Schnell, *Ann.*, **445**, 276 (1925).

(16) P. Ruggli, *ibid.*, **414**, 129 (1918); also A. Orechoff, *Ber.*, **47**, 95 (1914).

(17) K. Brand, *ibid.*, **45**, 3071 (1912).

**Preparation of Hexaphenylstannole (XI).**— $\text{Ph}_2\text{SnCl}_2$  (3 g.) was added to an ethereal solution of 50 ml. of I, prepared from 3 g. of  $\text{PhC}_2\text{Ph}$ . After refluxing for 0.5 hr., water and benzene were added and the mixture was worked up in the usual way; 2.15 g. (40%) of XI was obtained as slightly fluorescent greenish crystals, m.p.  $174^\circ$  from ether-ethanol (lit.<sup>2b</sup>  $173\text{--}174^\circ$ ).

**Preparation of Octaphenyl-1,1'-spirobistannole (XII).**—The spirobistannole prepared from I with  $\text{SnCl}_4$  was obtained as yellow crystals of m.p.  $275\text{--}280^\circ$  (from  $\text{CH}_2\text{Cl}_2\text{--EtOH}$ , lit.<sup>2b</sup>  $280\text{--}282^\circ$ ) with a yield of 40% (based on  $\text{SnCl}_4$ ).

**Preparation of 1,1-Bis-( $\pi$ -cyclopentadienyl)-2,3,4,5-tetra-phenylzirconacyclopentadiene (XIII).**—An ethereal solution of bis-cyclopentadienylzirconium dichloride (1.6 g., 6.2 mmoles) was added to a suspension of I, prepared from 3 g. (16.9 mmoles) of diphenylacetylene. The mixture was refluxed for 0.75 hr. and the orange precipitate, consisting of a mixture of LiCl and XIII, was filtered off, moisture being avoided. Compound XIII was dissolved in a minimum amount of methylene chloride and LiCl was filtered off. Light petroleum ether was added to the filtrate until it became turbid; large orange crystals of m.p.  $140\text{--}170^\circ$  dec. were obtained with a 53% yield. The whole operation had to be carried out rapidly in an inert atmosphere ( $\text{N}_2$ ). When XIII is contaminated with LiCl, water is readily adsorbed and the substance is hydrolyzed to cyclopentadiene (typical smell), tetraphenylbutadiene and hydrated zirconium oxide. Once the crystals are dry and free from LiCl, they may be kept unaltered in air at room temperature for longer periods, but light has to be avoided. Compound XIII is insoluble in ether and petroleum ether and very soluble in  $\text{CH}_2\text{Cl}_2$ ; decomposition by alcohols occurs in a few seconds, but hydrolysis in water is somewhat slower.

*Anal.* Calcd. for  $\text{C}_{35}\text{H}_{30}\text{Zr}$ : C, 78.98; H, 5.23; Zr, 15.79. Found: C, 77.97; H, 5.17; Zr, 15.6.

**Preparation of Pentaphenylpyrrole (XIV).**—Disodium anilide,  $\text{PhNNa}_2$ , was prepared *in situ* according to White, *et al.*<sup>18</sup> Azobenzene (0.5 g., 2.75 mmoles) was dissolved in 100 ml. of liquid ammonia and 0.3 g. (13 mmoles) of sodium was added and the mixture stirred for 2 hours to give a brown solution. To this, 2 g. (3.3 mmoles) of II, dissolved in 100 ml. of mesitylene, then was added. The ammonia was allowed to escape and the reaction mixture was refluxed for 7 hours. After cooling, water was added, the organic layer dried and the solvent removed under diminished pressure. The residue, crystallized from ether-ethanol, gave 0.05 g. of 1,4-diphenyldibenzopentalene.<sup>17</sup> From the mother liquor, 0.04 g. (9%) of XIV was isolated. It melted at  $291^\circ$  and gave no depression with an authentic sample (lit.<sup>19</sup>  $282^\circ$ ).

**Preparation of Pentaphenylphosphole (XV). Method A.**—Raw pentaphenylphosphole of m.p.  $250\text{--}253^\circ$  was obtained from I and  $\text{PhPCl}_2$  in 84% yield by using the general technique. The most important impurity was some pentaphenylphosphole oxide (XVI), which is difficult to remove by crystallization. However, purification was readily achieved by chromatography on silica gel, XV being eluted easily with benzene (greenish-yellow band) and the oxide XVI (strongly yellow) coming only with  $\text{Et}_2\text{O}$  or better with  $\text{AcOEt}$ . The solutions of XV are slowly oxidized by the action of air, but in crystalline form it has been kept unaltered for a year. Compound XV is greenish-yellow, strongly fluorescent and melts at  $255\text{--}256^\circ$  (from  $\text{C}_6\text{H}_6\text{--EtOH}$ ; lit.  $261\text{--}262^\circ$ ,<sup>2a</sup>  $256\text{--}257^\circ$ <sup>2b</sup>); ultraviolet spectrum: absorption maxima in  $m\mu$  ( $\log \epsilon$ ): 357.5 (3.945), 320 (3.94), 247.5 (4.51); fluorescence spectrum:  $\lambda_{\text{max}}$  480  $m\mu$ .

**Method B.**—Disodium phenylphosphide was prepared according to Horner, *et al.*<sup>20</sup>; 1.17 g. (6.55 mmoles) of  $\text{PhPCl}_2$  was added to a dispersion of 0.6 g. (26.2 mmoles) of sodium in 50 ml. of mesitylene, heated at  $100^\circ$ . After the mixture has been refluxed for 1 hour (b.p.  $164^\circ$ ), 4 g. (6.55 mmoles) of II was added and refluxing was continued for 7 hours. The reaction mixture was washed with water and the products were purified by chromatography (silica gel); 2.2 g. (88%) of pure XV and 0.125 g. (4%) of XVI were obtained.

**Preparation of P-Benzyl-tetraphenylphosphole (XXII).**—Benzylchlorophosphine and I were treated in the usual

(18) G. F. White and K. H. Knight, *J. Am. Chem. Soc.*, **45**, 1780 (1923).

(19) W. Dilthey, G. Hurtig and H. Passing, *J. prakt. Chem.*, **156**, 27 (1940).

(20) L. Horner, P. Beck and H. Hoffmann, *Ber.*, **92**, 2091 (1959).

manner and the mixture worked up by chromatography on alumina; XXII was eluted with benzene and was obtained as fluorescent yellow leaflets, m.p.  $203\text{--}213^\circ$ , 38% yield. Small amounts (0.02 g.) of P-benzyl-tetraphenylphosphole oxide were eluted with ethyl acetate and obtained as yellow fluorescent needles, m.p.  $228\text{--}230^\circ$  (from  $\text{CH}_2\text{Cl}_2\text{--MeOH}$ ).

*Anal.* Calcd. for  $\text{C}_{35}\text{H}_{27}\text{P}$ : C, 87.86; H, 5.27. Found: C, 87.06; H, 5.56. Calcd. for  $\text{C}_{35}\text{H}_{27}\text{OP}$ : C, 85.01; H, 5.10. Found: C, 84.35; H, 5.43.

**P-Benzyl-tetraphenylphosphole oxide** also was obtained (10% yield) by heating a mixture of 1 g. of  $\text{Fe}_2(\text{CO})_9(\text{PhC}_2\text{Ph})_2$ <sup>11</sup> and 0.4 ml. of  $\text{PhCH}_2\text{PBr}_2$  in 20 ml. of benzene at  $170^\circ$  for 16 hours in a sealed tube. The reaction mixture was worked up by chromatography and yielded besides the oxide: tetraphenylcyclobutadiene-iron tricarbonyl<sup>11</sup> (18%), tetraphenylcyclopentadienone<sup>15</sup> (10%) and some 1,2,3,4-tetraphenylcyclopenten-2-one.<sup>21</sup>

**Preparation of P-Methyl-tetraphenylphosphole Oxide (XXIII).**—An ethereal solution containing 1 ml. of  $\text{MePI}_2$ <sup>22</sup> was added to a suspension of I, prepared from 2 g. of  $\text{PhC}_2\text{Ph}$ . After about half an hour, the mixture was worked up by chromatography on alumina. Elution with a mixture of benzene and methanol and crystallization from ether-ethanol gave about 10% of pale yellow, slightly fluorescent crystals, m.p.  $240.5\text{--}241.5^\circ$ . The easy oxidation of alkyl substituted phospholes led only to the isolation of the oxide.

*Anal.* Calcd. for  $\text{C}_{29}\text{H}_{23}\text{OP}$ : C, 83.22; H, 5.54. Found: C, 82.79; H, 5.44.

**Preparation of Pentaphenylphosphole Oxide (XVI).**—Compound XV (1 g.), suspended in 200 ml. of acetone, was refluxed with an excess of  $\text{H}_2\text{O}_2$  for 2 hours. The reaction mixture was diluted with  $\text{H}_2\text{O}$ ; extraction with  $\text{CH}_2\text{Cl}_2$  yielded quantitatively XVI. It forms yellow crystals, m.p.  $284\text{--}285^\circ$  from benzene-ether (lit.<sup>2b</sup>  $292\text{--}293^\circ$ ); ultraviolet spectrum: absorption maxima in  $m\mu$  ( $\log \epsilon$ ): 385 (4.602), 272 (4.927), 260 (4.875). There is a fluorescence emission maximum at 528  $m\mu$ . Oxidation of XV by air in alcohol solution took several days to be complete.

**Preparation of Pentaphenylphosphole sulfide (XVII).**—(a) To a solution of sodium polysulfide, prepared by refluxing 1.2 g. of  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  and 0.6 g. of sulfur in 2-ethoxyethanol, 0.68 g. of XV was added and the reaction mixture refluxed for 4 hours. Dilution with water, extraction with  $\text{CH}_2\text{Cl}_2$ , concentration and addition of ethanol, gave yellow leaflets (0.64 g., 88%) containing one mole  $\text{CH}_2\text{Cl}_2$ . This solvent of crystallization is lost at about  $115\text{--}125^\circ$  (with occasional melting). Unsolvated sulfide melted at  $197\text{--}198^\circ$ .

(b) Compound XV (0.5 g.) and 0.3 g. of sulfur were refluxed for 3 hr. in 50 ml. of benzene. The unreacted sulfur was removed by adding dioxane and  $\text{Na}_2\text{S}$  and refluxing the mixture for 1 hour. By working up as described above, 0.48 g. (90%) of XVII was obtained.

(c) A suspension of I, prepared from 5 g. (28 mmoles) of  $\text{PhC}_2\text{Ph}$ , was added to a solution of 5.4 g. (25.6 mmoles) of  $\text{PhP(S)Cl}_2$  in ether, a vigorous reaction taking place. Chromatography on silica gel yielded only a very small amount of the expected XVII (0.03 g.); besides some XVI, the main product was XV notwithstanding the great excess of  $\text{PhP(S)Cl}_2$  used.

*Anal.* Calcd. for  $\text{C}_{34}\text{H}_{25}\text{PS}$ : C, 82.23; H, 5.08; P, 6.24; S, 6.45. Found: C, 82.11; H, 5.31; P, 6.10; S, 6.41. Calcd. for  $\text{C}_{34}\text{H}_{25}\text{PS}\cdot\text{CH}_2\text{Cl}_2$ : P, 5.33; S, 5.52. Found: P, 5.34; S, 5.44.

**Preparation of Pentaphenylphosphole Selenide.**—Compound XV (0.23 g.) and powdered selenium (0.1 g.) were refluxed for 3 hr. in 150 ml. of benzene. The excess of Se was filtered off, the filtrate concentrated and petroleum ether added. The selenide (0.25 g., 93%) was obtained as yellow leaflets, m.p.  $187\text{--}188.5^\circ$ . From mixtures containing methylene chloride, it crystallized with one mole of  $\text{CH}_2\text{Cl}_2$  which is readily lost at  $60\text{--}70^\circ$  *in vacuo*.

*Anal.* Calcd. for  $\text{C}_{34}\text{H}_{25}\text{PSe}$ : C, 75.13; H, 4.64; P, 5.70. Found: C, 75.14; H, 4.57; P, 5.46.

**Preparation of Pentaphenylphosphole  $\text{Fe}(\text{CO})_4$  (XVIII).**—Pentaphenylphosphole (0.5 g.) and  $\text{Fe}(\text{CO})_5$  (10 ml.) were heated with 20 ml. of iso-octane in a sealed tube for 12 hr. at  $140\text{--}150^\circ$ . The solution was filtered, evaporated to dryness, the residue taken up in warm ethanol and petroleum

(21) W. Dilthey and F. Quint, *J. prakt. Chem.*, **128**, 139 (1930).

(22) L. Maier, *Angew. Chem.*, **71**, 574 (1959).

ether added. The complex XVIII was obtained in almost quantitative yield as red crystals, m.p. 186–188°; the melt recrystallized at about 200° and decomposition occurred at 270–284° with gas evolution; infrared spectrum: bands for terminal carbonyl groups at 4.84, 5.02, 5.10, 5.12  $\mu$  (in  $\text{CCl}_4$  or  $\text{C}_2\text{Cl}_4$ ).

*Anal.* Calcd. for  $\text{C}_{38}\text{H}_{28}\text{FeO}_4\text{P}$ : C, 72.16; H, 3.99; Fe, 8.83; P, 4.91. Found: C, 72.11; H, 3.83; Fe, 8.97; P, 5.00.

**Pentaphenylphosphole  $\text{Fe}(\text{CO})_5$  (XIX) and Pentaphenylphosphole  $\text{Fe}_2(\text{CO})_{12}$  (XX).**—Compound XV (2 g.) and  $\text{Fe}_3(\text{CO})_{12}$  (6 g.) were refluxed for 75 min. in 200 ml. of isoöctane. The filtered mixture was evaporated to dryness and the residue crystallized from ether–ethanol. A crop of 0.21 g. of yellow crystals of XIX was obtained, the mother liquor yielding 0.32 g. of XVIII. Complex XIX decomposed at 210–215° with slight gas evolution; a partial recrystallization was observed at 220° and at 235–245°, gas was evolved again with formation of XV (m.p. 252°); infrared spectrum of XIX: absorption for terminal CO–groups (similar to other diene-iron tricarbonyls) occurs at 4.86, 5.01 and 5.06  $\mu$  (KBr).

*Anal.* Calcd. for  $\text{C}_{37}\text{H}_{28}\text{FeO}_3\text{P}$ : C, 73.52; H, 4.18; Fe, 9.24. Found: C, 73.33; H, 3.97; Fe, 9.65.

The formation of XIX was not very reproducible, and in some runs carried out under similar conditions only complex XVIII was obtained. In the following experiment complex XX also was formed:

Compound XV (0.45 g.) and  $\text{Fe}_3(\text{CO})_{12}$  (1.5 g.) were refluxed for 75 min. in 50 ml. of isoöctane. The solution was chromatographed over silica gel. After  $\text{Fe}_3(\text{CO})_{12}$  had been washed out with petroleum ether a brown band was eluted with benzene. The residue of this fraction was taken up in ethanol and petroleum ether was added. The first crop consisted of 0.06 g. of XVIII and from the mother liquor 0.26 g. of orange plates of XX were obtained which decomposed slightly at 178–183°, giving a viscous oil that again evolved gas at 250°. The infrared spectrum of XX has 5 bands (4.79, 4.85, 4.95, 5.01 and 5.16  $\mu$  in  $\text{C}_2\text{Cl}_4$ ) for terminal carbonyl groups, suggesting structure XX. However, the analytical data obtained are equally consistent with a formulation as pentaphenylphosphole  $\text{Fe}_2(\text{CO})_5$ .

*Anal.* Calcd. for  $\text{C}_{40}\text{H}_{28}\text{Fe}_2\text{O}_5\text{P}$ : C, 64.54; H, 3.39. Found: C, 64.94; H, 3.47. (Calcd. for  $\text{C}_{39}\text{H}_{28}\text{Fe}_2\text{O}_5\text{P}$ : C, 65.39; H, 3.52).

**Reaction of XV with Maleic Anhydride.**—Maleic anhydride (0.7 g.) and XV (1.4 g.) were heated with 30 ml. of benzene in a sealed tube for 20 hr. at 150°. A small amount of brown material was filtered off and the filtrate was chromatographed on silica gel. Unreacted XV (1.17 g., 83.5%) was eluted with benzene. Elution with ether gave 0.05 g. of the expected adduct, which was difficult to purify and was obtained as faintly yellow crystals, m.p. 260–264° dec. The values of the analysis were close to those of the adduct of the oxide XVI. However, further investigations have shown that the infrared spectra and the melting points of the two adducts are different. Thus, the compound has to be regarded as the maleic anhydride adduct of XV.<sup>23</sup>

**Reaction of XV with Dimethyl Acetylenedicarboxylate.**—Pentaphenylphosphole (XV, 1 g.) and dimethyl acetylenedicarboxylate (2.8 g.), dissolved in 30 ml. of dioxane, were heated in a sealed tube at 150° for 15 hr. The red-brown solution was evaporated to dryness and the residue recrystallized from ethanol. Dimethyl tetraphenylphthalate, m.p. 261° (no depression by mixture with an authentic sample),<sup>24</sup> was obtained with 88% yield. The PhP–group had been split off, but no well-defined phosphorus compound could be isolated.

No reaction took place when XV was heated with an excess of diphenylacetylene at 200° for 15 hr. in benzene.

**Reaction of XVI with  $\text{Fe}(\text{CO})_5$ .**—Pentaphenylphosphole oxide (1 g.), 5 ml. of  $\text{Fe}(\text{CO})_5$  and 20 ml. of benzene were heated for 15 hr. at 150° in a sealed tube. After cooling, 0.27 g. of the yellow complex XXI crystallized out; concentration of the filtrate and addition of petroleum ether yielded a second crop (0.94 g.) of the complex, giving a total yield of 94%. Recrystallization from ether–petroleum ether gave crystals, m.p. 226–235° dec.; infrared absorption bands for terminal CO–groups: 4.84, 4.95 and 5.02  $\mu$ .

(23) The formulation in an earlier paper<sup>1</sup> was based on the analyses.

(24) W. Dilthey, J. Thewalt and O. Trosken, *Ber.*, **67**, 1959 (1934).

*Anal.* Calcd. for  $\text{C}_{37}\text{H}_{28}\text{FeO}_4\text{P}$ : C, 71.62; H, 4.06; Fe, 9.01; P, 5.01. Found: C, 71.76; H, 3.95; Fe, 9.26; P, 5.05.

**Reaction of XVI with Maleic Anhydride.**—Maleic anhydride (0.2 g.) and 0.5 g. XVI were heated for 18 hr. at 150° in 30 ml. of benzene. Isoöctane (60 ml.) was added and the mixture concentrated to 30 ml. The colorless adduct precipitated in a 67% yield. Recrystallized twice from methylene chloride–isoöctane, the adduct melted at 245–255°, dissociating gradually to give solid yellow XVI. This adduct could not be obtained analytically pure.

**Reaction of XVII with Maleic Anhydride.**—Maleic anhydride (0.8 g.) and XVII (2 g.) were heated with 40 ml. of benzene at 150° for 15 hr. The solution was chromatographed on silica gel; XVII was recovered to the extent of 73% (1.46 g., eluted with benzene). The adduct (0.1 g.) was taken off with ether and formed colorless crystals, m.p. 230–234°, from ether–isoöctane. Its infrared spectrum shows the characteristic absorption bands for cyclic anhydrides and differs from those of the adducts of XV and XVI. This sulfur-containing adduct could not be obtained analytically pure.

**Reaction of XVII with Iron Carbonyls.**—Heating 0.5 g. of XVII with 10 ml. of  $\text{Fe}(\text{CO})_5$  in 20 ml. of benzene for 15 hr. at 150° (sealed tube), yielded exclusively the complex pentaphenylphosphole  $\text{Fe}(\text{CO})_4$  (XVIII, 0.4 g.).

At room temperature, XVII (2.1 g.) reacted with  $\text{Fe}_2(\text{CO})_9$  (6 g.) and after 15 hr. gave 0.7 g. of complex XVIII in addition to 0.25 g. of  $\text{Fe}_3\text{S}_2(\text{CO})_9$ .<sup>25</sup> On heating XVII with  $\text{Fe}_3(\text{CO})_{12}$  in boiling isoöctane (100°) or boiling petroleum ether (b.p. 70–80°) only complex XVIII was obtained in about 70% yield.

**Preparation of Pentaphenylarsole (XXIV).**—By adding  $\text{PhAsCl}_2$  to an ethereal suspension of I, greenish-yellow XXIV was precipitated in a 56% yield (m.p. 210–212°). Two crystallizations from methylene chloride–ether gave a constant m.p. of 213–214.5° (lit.<sup>2b</sup> 215–216°); ultraviolet spectrum:  $\lambda_{\text{max}}$  in  $\text{m}\mu$  ( $\log \epsilon$ ): 360 (3.945), 244 (4.505); fluorescence emission:  $\lambda_{\text{max}}$  480  $\text{m}\mu$ . XXIV sublimes above 180° (1 mm.) forming thin needles.

**Preparation of Pentaphenylarsole Oxide.**—A solution of 1 g. of XXIV and 10 ml. of hydrogen peroxide (30%) in 300 ml. of acetone was refluxed for half an hour, concentrated to a third of its volume under diminished pressure, and diluted with water. The benzenic extracts were dried over  $\text{Na}_2\text{SO}_4$  and evaporated to dryness. Chromatography on silica gel yielded 0.27 g. of unreacted XXIV (eluted with benzene) and 0.61 g. of pentaphenylarsole oxide (eluted with a mixture of benzene–methanol). Recrystallization from benzene yielded yellow needles, m.p. 252°.

*Anal.* Calcd. for  $\text{C}_{34}\text{H}_{28}\text{AsO}$ : C, 77.86; H, 4.81; O, 3.05. Found: C, 77.64; H, 4.73; O, 3.51.

**Preparation of Pentaphenylarsole  $\text{Fe}(\text{CO})_5$ .**—Compound XXIV (0.5 g.),  $\text{Fe}(\text{CO})_5$  (3 ml.) and isoöctane (50 ml.) were heated in a sealed tube at 150° for 15 hr. The filtered solution yielded 0.44 g. (69%) of slightly yellow crystals which melted at 155–170° (dec., from ethanol); infrared absorption bands for terminal carbonyl groups were observed at 4.87, 5.01 and 5.05  $\mu$ .

*Anal.* Calcd. for  $\text{C}_{37}\text{H}_{28}\text{AsFeO}_3$ : O, 7.40; Fe, 8.61. Found: O, 7.43; Fe, 8.20.

**Preparation of Pentaphenylstibole (XXV).** From I and  $\text{PhSbCl}_2$ <sup>26</sup> XXV was prepared in a 21% yield; greenish-yellow crystals of m.p. 162–170° (lit.<sup>2b</sup> 160°). Decomposition occurs at 220°.

Oxidation of pentaphenylstibole solutions by air gave the corresponding oxide as a faintly yellow compound, m.p. 250–255° dec.

*Anal.* Calcd. for  $\text{C}_{34}\text{H}_{28}\text{OsSb}$ : C, 71.47; H, 4.41; O, 2.80. Found: C, 72.12; H, 4.65; O, 2.74.

**Preparation of Tetraphenylthiophene (XXVI).**—A solution of 2 g. of 1,4-diodotetraphenylbutadiene (II) in 125 ml. of 2-( $\beta$ -ethoxyethoxy)-ethanol was refluxed for 3 hr. with 0.5 g. of  $\text{Li}_2\text{S}$ . The cooled reaction mixture was diluted with water. Extraction and crystallization yielded 1.15

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g. (90%) of tetraphenylthiophene, m.p. 184–185° (lit.<sup>27</sup> 184°).

**Preparation of Tetraphenylthiophene 1,1-Dioxide (XXVII) and 1,4 - Bis - (chlorosulfonyl) - tetraphenylbutadiene (XXVIII).**—A suspension of I in 60 ml. of ether, prepared from 3 g. of diphenylacetylene, was added dropwise, at –40°, to 2 ml. of sulfur chloride in 80 ml. of ether.

After the reaction mixture had reached room temperature, water was added, the precipitated XXVII (0.25 g., 7%), m.p. 286–287° (lit.<sup>28</sup> 276–278°) was filtered off and the filtrate extracted with benzene. Crystallization of the extracts gave 0.62 g. (13%) of a colorless compound, containing S and Cl. It melted at 157–159° with decomposition, forming tetraphenylthiophene 1,1-dioxide. Its infrared spectrum and analysis showed it to be 1,4-bis-(chlorosulfonyl)-tetraphenylbutadiene (XXVIII).

*Anal.* Calcd. for  $C_{28}H_{20}Cl_2O_4S_2$ : C, 60.54; H, 3.63; O, 11.52. Found: C, 61.94; H, 3.88; O, 11.14.

**Preparation of Tetraphenylselenophene (XXIX). Method A.**—A 50-ml. ethereal suspension of I, prepared from 3 g. (16.9 mmoles) of diphenylacetylene, was cooled at –40° and stirred, while 2.8 g. (8.8 mmoles) of  $Se_2Br_2$  dissolved in 50 ml. of benzene was slowly added, the temperature being allowed to rise to 10°. The red amorphous selenium which was formed crystallized on standing overnight and was filtered off (1.3 g.). Water was added to the filtrate and crystallization of the residue of the organic layer gave 2.39 g. (65%) of XXIX. The thin colorless needles, obtained from methylene chloride–ethanol, had a transition point at 174° on quick heating, or 140–150° on slow heating and a m.p. at 183–184°; XXIX sublimes at 180° (15 mm.).

*Anal.* Calcd. for  $C_{28}H_{20}Se$ : C, 77.24; H, 4.63. Found: C, 77.11; H, 4.56.

**Method B. Preparation of  $Li_2Se$ .**—To a suspension of 16.8 g. (0.215 mole) of powdered selenium in 125 ml. of liquid ammonia, 3.2 g. (0.46 mole) of lithium was added in several portions and the ammonia was allowed to escape overnight. Lithium selenide must be handled in a nitrogen atmosphere.

A solution of 2 g. of II and 0.5 g. of  $Li_2Se$  in 125 ml. of 2-( $\beta$ -ethoxyethoxy)-ethanol was refluxed for 4 hr. The cooled reaction mixture was diluted with water. Extraction with benzene and crystallization from methylene chloride–ethanol yielded XXIX nearly quantitatively (1.4 g.).

**Tetraphenylselenophene (XXIX)** also was obtained by heating an intimate mixture of powdered amorphous selenium (5 g.) and  $Fe_2(CO)_9(PhC_2Ph)_2^{11}$  (1 g.) at 200° for 25 minutes; XXIX was extracted with  $CH_2Cl_2$  and purified by chromatography; yield 0.41 g. (60%).

However, tetraphenylselenophene is obtained most readily by stirring vigorously a mixture of diphenylacetylene (2 g.) with selenium (3 g.) at 250° for 2 hours. After cooling, extraction with hot benzene yielded 2.40 g. (98%) of pure XXIX.

**Preparation of Tetraphenyltellurophene (XXX). Method A.**—To a suspension of I in 100 ml. of ether, prepared from 10 g. (56 mmoles) of diphenylacetylene, 5.3 g. (19.7 mmoles) of tellurium tetrachloride dissolved in 150 ml. dry ether was added at room temperature in the course of about 15 min. The brown color turned yellow and then greenish. The reaction mixture was poured into methylene chloride and

water. After filtering on kieselgur, the organic layer was dried on  $MgSO_4$  and evaporated. The residue was triturated with ether, leaving XXX (5.35 g., 56% based on  $TeCl_4$ ) undissolved. The raw compound was usually green and melted at about 236°. Treatment with charcoal gave yellow-orange crystals; subsequent crystallizations (from methylene chloride–ethanol) or chromatography on silica gel or alumina did not alter the color and the m.p. remained constant at 239–239.5°.

*Anal.* Calcd. for  $C_{28}H_{20}Te$ : C, 69.48; H, 4.17. Found: C, 69.70; H, 4.23.

**Method B.**— $Li_2Te$  was prepared according to the same method as used for  $Li_2Se$ ; the finely divided telluride so obtained is very sensitive to air. Two grams of II and about 1.5 g. of  $Li_2Te$  were refluxed for 8 hours in 125 ml. of bis-( $\beta$ -ethoxyethyl) ether. After cooling, 1 l. of water was added; the benzene extracts yielded 1.3 g. (82%) of XXX.

**Reactions of XXX with Iron Carbonyls.**—Tetraphenyltellurophene (0.75 g.) and  $Fe_3(CO)_{12}$  (2.5 g.) were refluxed in a mixture of 80 ml. of toluene and 40 ml. of benzene (b.p. 94°) for 80 minutes. The filtrate was evaporated to dryness and the residue, dissolved in benzene, was chromatographed on alumina. The first band, eluted with benzene, consisted of 0.5 g. unreacted XXX. A gray band was eluted with ether; crystallization from ethanol yielded 0.02 g. of red crystals which darkened at about 150° and melted at 200–225°. The infrared spectrum has bands at 4.90, 5.09 and 5.16(sh.) $\mu$  which have the general shape observed for iron tricarbonyl complexes; the remaining part of the spectrum closely resembles that of tetraphenyltellurophene itself. The amount available did not permit analysis and the results could not be duplicated. In boiling isooctane (b.p. 99°; 90 minutes) small amounts of tetracyclone<sup>16</sup> and tetracyclone-iron tricarbonyl<sup>11</sup> were formed in this reaction. In boiling benzene (80°; 3 hr. and 9 hr.) the red complex was observed only.

Tetraphenyltellurophene was recovered in 89% yield after heating XXX for 7 hr. at 130° with excess  $Fe(CO)_5$  in benzene. No reaction took place at room temperature with  $Fe_2(CO)_9$  (3 days).

**1,1-Dibromotetraphenyltellurophene.**—Bromine (1.4 g.) was added to a stirred suspension of 2 g. of XXX in 100 ml. of  $CCl_4$  at room temperature. After 15 min., the reaction mixture was evaporated to dryness under diminished pressure and the residue crystallized from methylene chloride–ether. Large brownish-red crystals (2.44 g., 92%) were obtained; they became yellow at 170° and melted with decomposition at 243–245°.

*Anal.* Calcd. for  $C_{28}H_{20}Br_2Te$ : C, 52.23; H, 3.13; Br, 24.82. Found: C, 52.47; H, 3.19; Br, 25.16.

**Reaction of 1,1-Dibromotetraphenyltellurophene with Maleic Anhydride.**—A 0.8-g. sample of the dibromide, 0.25 g. of maleic anhydride and 30 ml. of dry benzene were heated in a sealed tube at 140°. Shiny crystals of tellurium precipitated. After 4.5 hr., 0.18 g. of the dibromide was recovered (conversion 77.5%) and the filtered tellurium amounted to 0.1 g. The filtrate yielded 0.06 g. of 1,4-diphenyl-2,3,5,6-dibenzopentalene<sup>17</sup> and some 1,4-dihydro-1,4-diphenyl-2,3,5,6-dibenzopentalene of m.p. 290–292° (lit.<sup>29</sup> 285–286°).

When the reaction was carried out at 180° (13 hr.) only 81% Te and 41% tetraphenylfuran were obtained.

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