343. *Cyclobutadienes. Part II.*[1,2] *Palladium Complexes from Diphenylacetylene: Reactions of Tetraphenylcyclobutadiene*

By R. C. COOKSON and D. W. JONES

Malatesta's ethoxychloropalladium complexes from diphenylacetylene, considered to be stereoisomeric π-cyclobutenylpalladium compounds (XXX) and (XXXI), are converted by hydrogen chloride into (tetraphenylcyclobutadiene)palladium dichloride. Reaction of each complex with a tertiary phosphine gives a solution with the same electron spin resonance spectrum. In the absence of another reactant the solution from the butadiene complex yields only the high-melting tetraphenylcyclobutadiene dimer. Adducts (XVI) and (XXa) are formed in the presence of methyl phenylacetylene-carboxylate and cyclopentadiene, respectively. The solution from the ethoxychloropalladium complex and a phosphine (although it gives the same electron spin resonance spectrum) does not yield an adduct with cyclopentadiene: 1,2,3-triphenylazulene, tetraphenylfuran, and, in presence of oxygen, 1-ethoxy-2,3,4-triphenylnaphthalene are produced.

IN seeking a simple synthesis of tetraphenylcyclobutadiene derivatives [2] our attention was caught by the preliminary announcement [3] of a remarkably easy way of making the palladium chloride complex from diphenylacetylene and palladium chloride, and we adopted this complex as a convenient precursor of tetraphenylcyclobutadiene (I). After completion of most of the work to be described in this Paper, others also reported [4-6] investigation of Malatesta's complexes. Where our work overlapped the results agree fairly well, with the exceptions noted below.

As reported by Malatesta,[3] reaction of diphenylacetylene with palladium chloride (or its benzonitrile complex [4]) in ethanol at room temperature affords a soluble yellow complex (A) $[2Ph_2C_2,EtOH,PdCl_2,HCl]$ in high yield. If the mixture is heated an insoluble, orange complex (D) is formed instead, together with hexaphenylbenzene. Treatment of complex (A) or (D) with hydrogen chloride in chloroform gives a deep red solution from which orange-red crystals of a complex (B) $[2Ph_2C_2,PdCl_2]$ separate as the hydrogen chloride is evaporated. [Chloroform containing 2% of ethanol is essential for this experiment (*e.g.*, AnalaR chloroform). In the absence of ethanol an amorphous, orange complex is thrown down, which redissolves, however, on addition of ethanol and passage of hydrogen chloride to give the same complex (B).]

Our first experiments were intended to prove the structure of complex (B), for the available information [3] established only its empirical formula. Pyrolysis *in vacuo* at

[1] Preliminary note, Cookson and Jones, *Proc. Chem. Soc.*, 1963, 115.
[2] Part I, *J.*, 1965, 194.
[3] Malatesta, Santarella, Vallarino, and Zingales, *Angew. Chem.*, 1960, **72**, 34.
[4] Blomquist and Maitlis, *J. Amer. Chem. Soc.*, 1962, **84**, 2329.
[5] Maitlis and Stone, *Proc. Chem. Soc.*, 1962, 330.
[6] Maitlis and Games, *J. Amer. Chem. Soc.*, 1963, **85**, 1887.

330—360°, or over a free flame, gave a mixture of two isomers, $C_{28}H_{20}Cl_2$, with a smaller amount of the indenoindene (II).*   The isomer with the lower m. p. was reduced with sodium and n-pentanol to 1,2,3,4-tetraphenylbutane: since the other one had a very similar ultraviolet spectrum they must be two of the three possible isomers of 1,4-dichloro-1,2,3,4-tetraphenylbuta-1,3-diene (III; X = Cl).   Extraction of complex (A) or (B) with boiling ethanol yielded tetraphenylfuran (IV) and a compound formulated as (III; X = OEt) on the basis of analysis, spectra, and conversion by acid into tetraphenylfuran (IV) [(B) probably reacting through (C)].

Complex (B) was reduced, either by hydrogen over platinum at room temperature and pressure, or by lithium aluminium hydride in ether, to tetraphenylbutadiene (III; X = H) and metallic palladium.   Although this result agrees with the lithium aluminium hydride reduction of (tetraphenylcyclobutadiene)iron tricarbonyl (V),[7] Freedman [8] reported that (tetraphenylcyclobutadiene)nickel dibromide was hydrogenated over platinum at higher temperature and pressure to a hydrocarbon, m. p. 122—123°, thought to be the tetra-phenylcyclobutene (VI) (perhaps a mixture of *cis*- and *trans*-isomers).   It seemed possible that, under these conditions, the butadiene (III; X = H) was still the initial product but
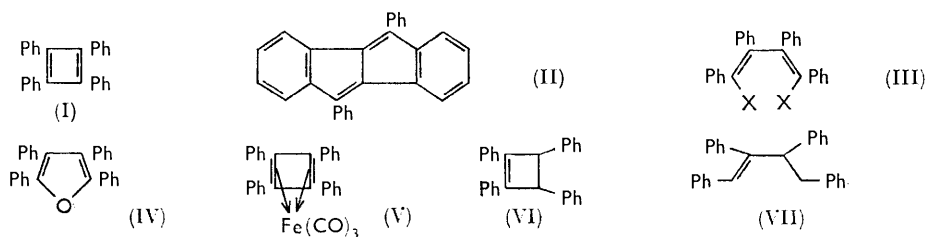
then underwent further reduction to the butene (VI).   If so, Freedman's product, m. p. 122°, should have structure (VII), not (VI).   Indeed, reduction of complex (B) or the butadiene (III; X = H) over platinum under Freedman's conditions did give a hydro-carbon melting at 122° [$\lambda_{max.}$ 293 mμ (ε 15,300)], that on further reduction was converted into 1,2,3,4-tetraphenylbutane.   Were it not that its mass spectrum was said to unequivoc-ally show that it contained two less hydrogen atoms, there would be little doubt that Freed-man's hydrocarbon was really the butene (VII).   Subsequently, Freedman [9] made authentic (VI), which differed from his reduction product.

The chemical evidence so far is consistent with Malatesta's suggestion that complex (B) is (tetraphenylcyclobutadiene)palladium dichloride (VIII), presumably as the dimer with the usual chlorine bridge between the palladium atoms.   The reduction to the diene (III; X = H) may be singled out as of particular significance, since the structure of the iron tricarbonyl complex (V), which gives the same product, has been proved by X-ray analysis.[10] Finally, reaction [6] of the palladium dibromide complex with iron pentacarbonyl converts it into the iron tricarbonyl complex (V).   [In the same way nickel carbonyl [6] converts it into Freedman's (tetraphenylcyclobutadiene)nickel dibromide,[8] and thence, as we had found, into tetraphenylcyclopentadienone.]

Admittedly, the palladium atom has never been removed from the complex to produce a metal-free compound still retaining the four-membered ring, but structures such as (IX), that might therefore be considered, are rendered very unlikely by the almost identical infrared spectra of the palladium dihalide and nickel bromide complexes: isolation of cyclo-butene derivatives from the latter has been achieved.[9]   The complex (B) can, then, be

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* Pyrolysis of (B) over a free flame has subsequently been said [4] to give " solely " (26% isolated yield) a product clearly identical with the higher-melting, less abundant isomer from our experiments.
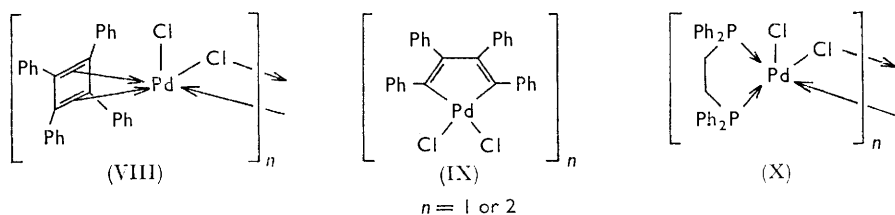
[7] Hübel and Braye, *J. Inorg. Nuclear Chem.*, 1959, **10**, 250.
[8] Freedman, *J. Amer. Chem. Soc.*, 1961, **83**, 2194.
[9] Freedman and Frantz, *J. Amer. Chem. Soc.*, 1962, **84**, 4165.
[10] Dodge and Schomaker, *Nature*, 1960, **186**, 798.

confidently assigned structure (VIII), in which the palladium atom formally attains the configuration of tellurium or xenon, according to the value of n in formula (VIII; $n = 1$

(VIII)   (IX)   (X)

$n = 1$ or 2

or 2). Insolubility prevented determination of the molecular weight of the complex, but bistriphenylphosphinepalladium dichloride, $[Ph_3P]_2,PdCl_2$, was monomeric in chloroform (osmometer), so that perhaps $n = 1$. In its complexes palladium usually seems to be content to acquire a share in only six more electrons rather than the full eight. Complexes (IX), (X), and (XXX) may also be monomeric in solution, although again we have no direct evidence. [A π-4-chlorocyclobutenyl structure (XXVIIIa, or stereoisomer; with Cl instead of EtO) is still not quite ruled out for complex (B).]

Generation of Tetraphenylcyclobutadiene.—With Malatesta's structure for the palladium complex (VIII) now secure, its suitability as a source of free tetraphenylcyclobutadiene could be explored. When the complex was treated with triphenylphosphine in benzene or chloroform in absence of oxygen, the initially red solution turned green, the colour persisting for many hours (until air was admitted, when it immediately faded). Bistriphenylphos-phinepalladium dichloride and the dimer, m. p. 430° (to be discussed in a later Paper), of tetraphenylcyclobutadiene were formed in high yield. Reaction with 1,2-bisdiphenyl-phosphinoethane [11] proceeded rather faster, to give the analogous phosphine complex (X) and the dimer. If these reactions were conducted in air, tetraphenylfuran (IV) was formed in place of the dimer. As with the elimination of dimethyltin dibromide at 150° from the diene (XIV),[8] it is reasonable to assume that free tetraphenylcyclobutadiene [whether (I), (XI), or (XII)] is liberated, which then adds to itself or to a molecule of oxygen to give

(XI)   (XII)   (XIII)   (XIV)

$Ph-C \equiv C-CO_2Me$

(XV)

(XVI)   (XVII)
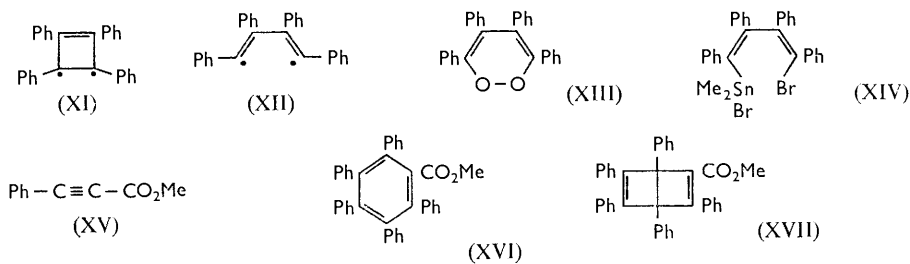
products derived from the peroxide (XIII).* It should be possible to add the unstable intermediate (I), (XI), or (XII) to other molecules, and perhaps to get an indication of whether it reacts in the closed [singlet (I), or triplet (XI)] or open form (XII). At the same

* In the absence of a reducing agent the presumed intermediate peroxide (XIII) [or its valence-tautomer (i)] rearranges to *cis*-dibenzoylstilbene.[8] The formation of tetraphenylfuran (IV) in our experiments can be explained by the faster reaction of the peroxide (XIII) [or (i)] with triphenylphos-phine to give an intermediate such as (ii) or the cyclobutene equivalent, which breaks down to triphenyl-phosphine oxide and the furan (IV). (*cis*-Dibenzoylstilbene did not react with triphenylphosphine under these conditions).


(i)   (ii)

[11] Chatt and Hart, *J.*, 1960, 1378.

time we hoped that reaction of the former with an acetylene might produce a Dewar isomer of tetraphenylbenzene (see refs. 2 and 12), unstable but perhaps isolable.

Some reactive molecules that might have been used to catch the cyclobutadiene (I) were unsuitable because they also react with tertiary phosphines, for example maleic anhydride,[13] dimethyl acetylenedicarboxylate,[14] and diethyl azodicarboxylate.[15] [This difficulty might be overcome by displacing (I) from the complex (VIII) with another ligand, *e.g.*, PhS·CH₂·CH₂·SPh.] Methyl phenylacetylenecarboxylate (XV) and cyclopentadiene, however, do not react with the phosphines. When the reaction was carried out in the presence of the former, the dimer was accompanied by methyl pentaphenylbenzoate (XVI), identical with a sample made by addition of the ester (XV) to tetraphenylcyclopenta-dienone.[16] This result leaves open the question of whether the open form (XII) of the cyclobutadiene adds to give the aromatic structure (XVI) directly, or whether a cyclic form (I) or (XI) first gives the bicyclohexadiene (XVII) which then isomerises. No adduct was isolated from reaction with but-2-yne, although it does add to tetramethylcyclobutadiene generated by reduction of the dichloride with zinc.[2,12] This accords with the lower reactivity, and therefore greater selectivity, expected for the tetraphenyl compound (or its zinc derivative).

Since, until the completion of our work, no Dewar bicyclohexadienes, *e.g.*, (XVII), were known,[17] one could not tell whether such a primary adduct (XVII) would have survived the experiment. Certainly bicyclohexenes, *e.g.*, (XXb),* would be expected to undergo valence-tautomerism to the cyclohexadienes much more slowly, and indeed several bicyclohexenes have subsequently been made.[18] Also, it seemed possible that the heavy phenyl substitution might favour the bicyclic structure.
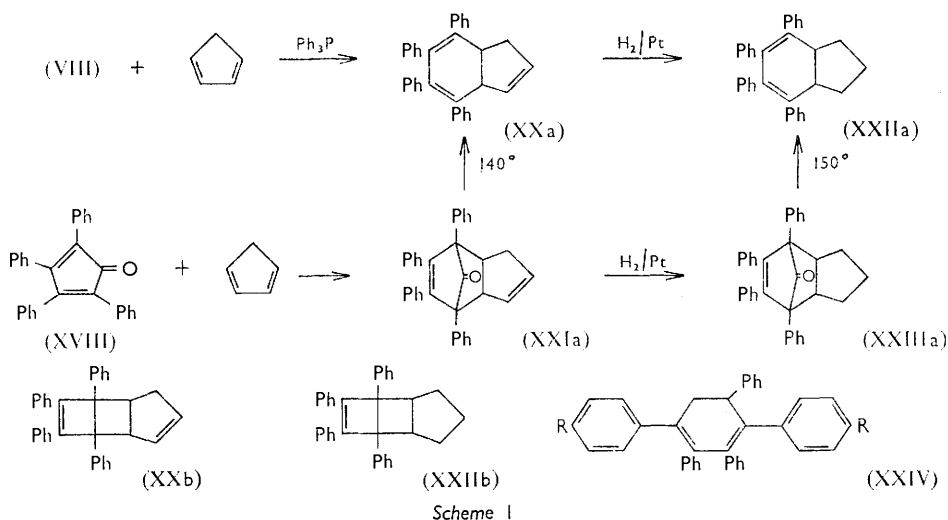
Scheme 1

Tetraphenylcyclobutadiene was therefore generated in the presence of cyclopentadiene. The gross structure of the resulting adduct, $C_{33}H_{26}$, was established by the reactions in Scheme 1, but whether it had the cyclohexadiene (XXa) or bicyclohexene structure (XXb)

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* In formulæ (XX) to (XXIII) (*a*) indicates the cyclohexadiene isomer and (*b*) the bicyclohexene isomer.

[12] Berkoff, Cookson, Hudec, and Williams, *Proc. Chem. Soc.*, 1961, 312.
[13] Aksnes, *Acta Chem. Scand.*, 1961, **15**, 692.
[14] Johnson and Tebby, *J.*, 1961, 2126.
[15] Morrison, *J. Org. Chem.*, 1958, **23**, 1072; Cookson and Locke, *J.*, 1963, 6062.
[16] Dilthey, Thewalt, and Trösken, *Ber.*, 1934, **67**, 1959.
[17] von Tamelen and Pappas, *J. Amer. Chem. Soc.*, 1962, **84**, 3789; 1963, **85**, 3297.
[18] *E.g.*, Kristinsson, quoted by Criegee, *Angew. Chem.*, 1962, **74**, 703; Dauben and Fonken, *J. Amer. Chem. Soc.*, 1959, **81**, 4060.

remained in doubt. Others have always assumed, without proof, that decarbonylation of tetraphenylcyclopentadienone adducts gives the diene. Since addition of the cyclobutadiene in the closed form (XI) would initially give (XXb), a distinction between the two alternative structures was essential.

Both (XXa or b) and the adduct from styrene (XXIVa or b; R = H) must have analogous structures, for their ultraviolet spectra are very similar. Their proton magnetic

(XXV) (XXVI) (XXVII)
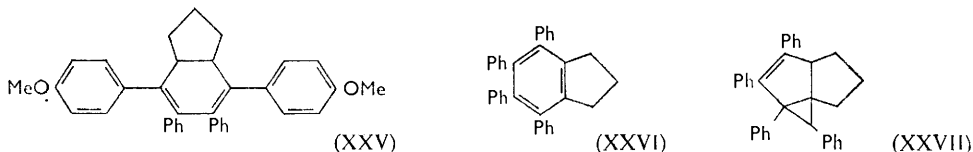
resonance spectra did not distinguish between the two alternative types of structure (a or b). The methoxy-derivatives (XXIV; R = OMe) and (XXV) were then made by similar methods and their spectra were compared with those of the parent hydrocarbons (see Table).

Ultraviolet spectra of some tetraphenylcyclobutadiene adducts

Compound	(XXIV; R = H)	(XXIIa)	(XXIV; R = OMe)	(XXV)
$\lambda_{max.}$ (mμ)	318·5	320	336	333
ε	13,400	13,100	17,800	13,900

The shift of about 15 mμ to longer wavelengths on introduction of two methoxy-groups is consistent only with the cyclohexadiene formulation (a). [The unconjugated double bond in (XXa) moves $\lambda_{max.}$ 8 mμ to shorter wavelengths.] This was confirmed by the dehydrogenation of the dihydro-adduct (XXIIa) with *N*-bromosuccinimide at room temperature to the aromatic compound (XXVI).

Also the ultraviolet maximum of tetraphenylcyclobutene which has since been reported [10] is at a significantly shorter wavelength [303 mμ (ε 19,500)] than that of (XXa).

In the hope of preparing the isomer (XXIIb), to check whether it was stable to the conditions of the cyclobutadiene addition and thus whether compound (XXb) could have been an intermediate, the diene (XXIIa) was irradiated in benzene solution. However, the product, obtained in good yield, had $\lambda_{max.}$ 278 mμ (ε 12,700), in better agreement with (XXVII) or (V) than (XXIIb), [tetraphenylcyclopentene has $\lambda_{max.}$ 270 mμ (ε 10,000) [19] and tetraphenylcyclobutene $\lambda_{max.}$ 303 mμ (ε 19,500) [10]]. An effort to extend this photo-reaction [20] to the synthesis of the bicyclopentene system failed: 2,3,4,5-tetraphenylcyclopenta-2,4-diene and its 1-ethyl derivative (iii) were unchanged by prolonged irradiation. Even had the product (iv) reverted to the monocyclic form reversibly it should have given a mixture of tautomeric cyclopentadienes. This result is consistent with the isomerisation of the bicyclononadiene (XXIIa) to structure (v) through re-cyclisation of the cyclononatriene.


(iii) (iv) (v)
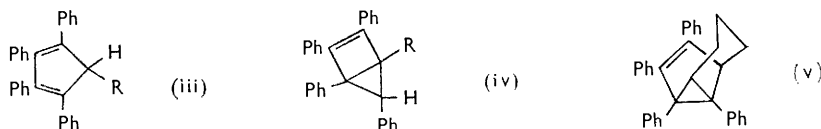
The Structures of Complexes (A) *and* (C).—Malatesta *et al.*[3] formulated complex (A) as (XXVIII), although the symmetrical π-allyl structure would now be preferred.[21] Blomquist and Maitlis [4] rejected Malatesta's structure (XXVIII) or (XXVIIIa) in favour of " an acyclic structure such as (XXIX)," mainly because they wished to use the former to represent the different complex (C), formed by reaction of the butadiene complex (VIII)

[19] Sonntag, Linder, Becker, and Spoerri, *J. Amer. Chem. Soc.*, 1953, **75**, 2283.
[20] Evanega, Bergmann, and English, *J. Org. Chem.*, 1962, **27**, 13.
[21] Cf. Robinson and Shaw, *J.*, 1963, 4806.

with ethanol. Structure (XXIX), however, seems most unlikely, whether or not the butadiene unit and the palladium atom are intended to be in one plane. In the planar arrangement there are no empty palladium *d*-orbitals to overlap with the double bond and the π^* orbitals have the wrong symmetry for back-donation. (In such a planar molecule co-ordination of palladium to the oxygen atom is more likely than to the double bond.) The skew overlap from a twisted diene unit in (XXIX) is little better.

(XXVIII)　　　　　　(XXVIIIa)　　　　　　(XXIX)

(XXX)　　　　　　(XXXI)　　　　　　(XXXII)

n = 1 or 2
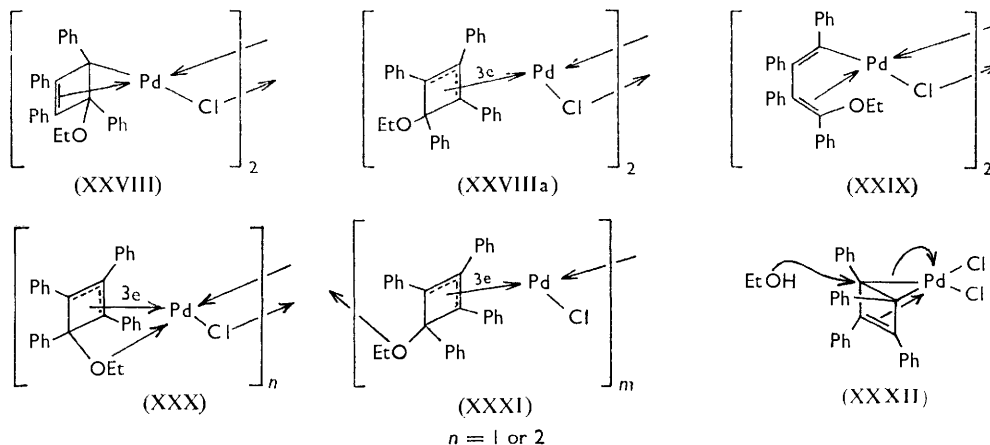
Although there is no conclusive evidence, reasonable structures are (XXX) for complex (A) and (XXXI) for complex (C). The isomeric complexes are conceived as differing only in the configuration of the ethoxy-group: in the *cis*-isomer (A) the oxygen atom can form a chelate ring with the palladium, whereas in the *trans*-isomer (C) it might be available for co-ordination to the palladium atom of another π-allyl group, so as to build up a polymeric network. Admittedly, the only evidence for the latter suggestion is the insolubility of complex (C), but the stereoisomeric structures do give a rational account of the formation and interconversion of the three complexes. Co-ordination of two molecules of diphenyl-acetylene on to ethoxypalladium chloride or its equivalent might well lead to the *cis*-isomer (A) (XXX). Then loss of ethanol from the *O*-protonated complex, followed by attack of Cl^- on palladium, would yield the cyclobutadiene complex. On the other hand, reaction of the cyclobutadiene complex (VIII) with ethanol would consist of nucleophilic displacement, on carbon, of palladium by ethanol, with the usual inversion of configuration, as indicated diagramatically (without implying necessarily only one step) in formula (XXXII). Again, we have no evidence on whether there are chlorine bridges or not: in its simple alkyl derivatives palladium often obtains a share in only six rather than eight more electrons.[22]
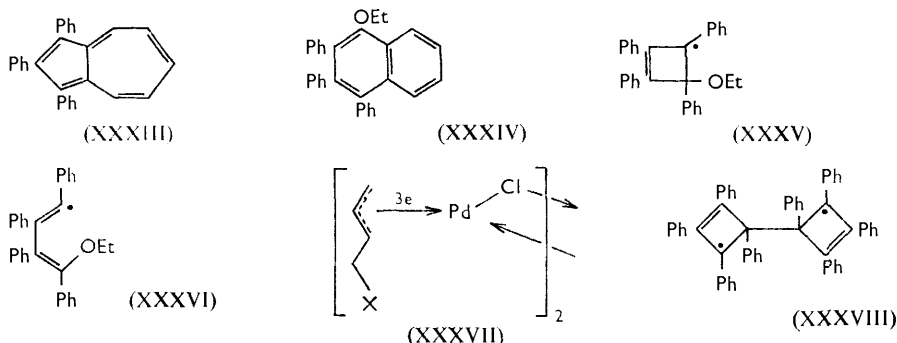
Reaction of Complex (A) *with Triphenylphosphine.*—Treatment of complex (A) with triphenylphosphine in benzene or toluene gave a dark green solution. The colour persisted during 18 hours' boiling, but disappeared as soon as air was admitted. The palladium was isolated as bistriphenylphosphinepalladium dichloride and a series of hydrido-palladium–phosphine complexes, the structures of which we intend to discuss in a later Paper. The crystalline, metal-free products were 1,2,3-triphenylazulene (XXXIII), tetraphenylfuran (IV), and, in presence of air, 1-ethoxy-2,3,4-triphenylnaphthalene (XXXIV). The reaction took the same course in the presence of cyclopentadiene, and no adduct could be detected. The diethoxybutadiene (III; X = OEt) resulted from reaction of complex (A) with triphenylphosphine in ethanol.

Presumably loss of palladium † [initially perhaps as $(Ph_3P)_2PdCl$ which dismutates]

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† One can only speculate about the order of steps. It is quite possible, for example, that the ligand reacts while still partly bound to the palladium, which may accept the hydrogen.

[22] Coates, " Organometallic Compounds," Methuen, London, 1960, p. 318.

leaves the radical (XXXV) or (XXXVI), which can substitute the *o*-position of a phenyl group to give the naphthalene (XXXIV), lose an ethyl radical to give the furan (IV), or attack the 1-carbon atom of a phenyl group and rearrange [23] to the azulene (XXXIII).

(XXXIII)   (XXXIV)   (XXXV)

(XXXVI)   (XXXVII)   (XXXVIII)

Nature of the Free Radicals.—The green solution produced by reaction of the cyclobutadiene complex (VIII) with triphenylphosphine in benzene or chloroform gave a strong electron spin resonance (e.s.r.) spectrum (see Figure) that lasted for many hours in the absence of oxygen. The spectrum must be caused by an organic radical related to tetraphenylcyclobutadiene for the following reasons. The identical spectrum was produced by

Electron spin resonance spectra of solutions produced by reaction of triphenylphosphine with (A) (tetraphenylcyclobutadiene)palladium dichloride (VIII) and (B) (tetra-*p*-chlorophenylcyclobutadiene)palladium dichloride
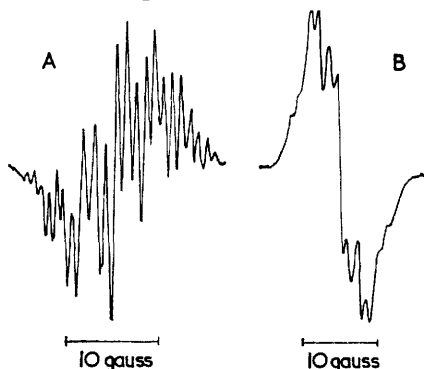
triphenylphosphine and by 1,2-bisdiphenylphosphinoethane, so that the radical is unlikely to contain phosphorus. No e.s.r. spectrum was given by simple π-allylpalladium complexes such as (XXXVII; X = Cl or OMe) [21] and the tertiary phosphines under the same conditions. As a further check, 4,4′-dichlorodiphenylacetylene was converted into a series of complexes exactly analogous to complexes (A), (B), and (C) from diphenylacetylene. Treatment of (tetra-*p*-chlorophenylcyclobutadiene)palladium dichloride [analogous to complex (B) (VIII)] with triphenylphosphine gave a different e.s.r. spectrum (Figure). The spectrum obviously cannot be that of triplet tetraphenylcyclobutadiene itself. Also, the same spectrum is produced by reaction of complex (A) with triphenylphosphine (or the diphosphine), and that reaction yields neither the tetraphenylcyclobutadiene adducts nor dimer.

Although a unique analysis of the spectrum has not yet been made, it can be interpreted as seven lines of 2·9 gauss, further split into five lines of 0·95 gauss. This tentative analysis, requiring coupling of the electron with sets of six and four equivalent protons, might be compatible with a 1,2,3-triphenylcyclobutenyl radical, provided the splitting by *ortho*- and *para*-protons on the phenyl groups was almost equal and the spin-density on the 2-phenyl

[23] Cf. Breslow and Battiste, *J. Amer. Chem. Soc.*, 1960, **82**, 3626; Freedman, *J. Org. Chem.*, 1962, **27**, 2298.

group was negligible. Neither provision is likely to be quite true. However, on that basis the paramagnetic species in the solution from the cyclobutadiene complex might be the diradical (XXXVIII), formed by dimerisation of the cyclobutadiene (XI) short of final ring-closure. (The high-melting dimer itself is diamagnetic and gives no e.s.r. signal.) The apparently identical spectrum from complex (A) would then arise from the ethoxy-radical (XXXV). Species (XXXVIII) would be expected to exist as a fairly independent diradical rather than as a triplet, although the proximity of the second electron would broaden the lines somewhat [perhaps enough to make the spectrum visibly different from that of (XXXV)]. Although the diradical (XXXVIII) might be in equilibrium with the monomer (XI), which could then add to cyclopentadiene, it is rather surprising that the paramagnetic molecules especially (XXXVIII), last so long if they are really intermediates in forming the main products from (VIII) and (XXX). The e.s.r. may well come from quite different species.

[*Note added in Proof.*—The orange complex (D) has now been shown to be the 2 : 3 complex of tetraphenylcyclobutadiene and palladium dichloride (Hüttel and Neugebauer, *Tetrahedron Letters*, 1964, 3541).]

EXPERIMENTAL

Alumina for chromatography was Spence's Type H. Light petroleum had b. p. 60—80°. Ultraviolet spectra were measured on a Unicam S.P. 700 for ethanol solutions and infrared spectra, for Nujol mulls, on a Unicam S.P. 200 spectrometer.

Preparation of the Tetraphenylcyclobutadiene–Palladium Dichloride Complex (B) (VIII).[3]— Diphenylacetylene (1·3 g.) and palladium dichloride (0·5 g.) were shaken in ethanol solution (25 ml.) for 48 hr., by which time the palladium salt had disappeared. The heavy yellow precipitate which had formed was filtered and recrystallised from chloroform–ethanol as prisms (1·05 g.), m. p. 186° (decomp.). [When the mixture was heated on a steam-bath an orange, rather insoluble complex (D) was thrown down. This complex was not the same as that produced at room temperature.]

The foregoing complex (A) (0·38 g.) in AnalaR chloroform (25 ml.) was saturated with dry hydrogen chloride and set aside for 1 hr. Removal of hydrogen chloride by heating on a water-bath gave the red complex (B) (VIII) as needles (0·32 g.), m. p. 282—285° (decomp.). [Use of chloroform completely free from ethanol and passage of hydrogen chloride caused separation of an amorphous orange complex. This redissolved on addition of ethanol and, on passage of hydrogen chloride, gave tetraphenylcyclobutadienepalladium dichloride (B).]

Thermal Decomposition of Complex (VIII).—The complex (1 g.) was heated at 330—360° *in vacuo* for 5 hr., in a bath containing Wood's metal. The dark coloured sublimate was treated with ethanol and the insoluble solid (193 mg.) was chromatographed on alumina. Elution with light petroleum (400 ml.) gave 1,4-dichlorotetraphenylbutadiene (III; X = Cl) (170 mg.) that crystallised from chloroform–ethanol as prisms, m. p. 185° (Found: C, 78·6; H, 4·6%; M (Rast), 403. $C_{28}H_{20}Cl_2$ requires C, 78·7; H, 4·7%; M, 427).

Chromatography of the ethanol-soluble fraction on alumina and elution with light petroleum gave an isomeric dichlorobutadiene (III; X = Cl) (0·36 g.) that, after several crystallisations from ethanol, formed plates, m. p. 150—155° (Found: C, 78·2; H, 4·8; Cl, 16·35. $C_{28}H_{20}Cl_2$ requires C, 78·7; H, 4·7; Cl, 16·6%). Freedman[23] gives m. p. 164—165° for *cis,cis*-1,4-dichloro-tetraphenylbutadiene. Elution with light petroleum–benzene (9 : 1) gave 5,10-diphenylindeno-[2,1-*a*]indene (II) (25 mg.).

Reduction of the Dichlorotetraphenylbutadiene, m. p. 150—155°. The compound (18 mg.) was refluxed in n-pentanol (1 ml.) for 3 hr., whilst small pieces of sodium (total 0·1 g.) were added. The product was diluted with water and extracted into ether. The dried (MgSO$_4$) extract was evaporated to give a yellow oil that crystallised from ethanol as white needles (8 mg.). Recrystallisation from ethanol gave 1,2,3,4-tetraphenylbutane, m. p. and mixed m. p. 180—181°.

Reduction of the Complex (VIII).—(*a*) The complex (0·5 g.) in chloroform (125 ml.) was hydrogenated over PtO$_2$,H$_2$O (150 mg.) at atmospheric pressure until the complex had been destroyed (1 hr.). Filtration of the catalyst and palladium, followed by removal of the solvent, gave an oil that crystallised from ethanol as white needles (70 mg.), m. p. 183—185°, not depressed on admixture with an authentic sample of 1,2,3,4-tetraphenylbutadiene (III; X = H).

(*b*) The complex (1 g.) in 1,1,2,2-tetrachlorethane (150 ml.) was hydrogenated over PtO_2,H_2O (102 mg.) at 70° and 80 p.s.i. for 7 hr. Work-up as in (*a*) gave a yellow oil (0·64 g.) which formed long white needles (0·22 g.), m. p. 120° (from ethanol) (Found: C, 93·8; H, 6·3. Calc. for $C_{28}H_{24}$: C, 93·3; H, 6·7%). When the hydrogenation was allowed to run for 20 hr. the product was 1,2,3,4-tetraphenylbutane.

Reduction of 1,2,3,4-Tetraphenylbutadiene.—Reduced as in (*b*) above, the diene (0·7 g.) gave white needles (0·41 g.), m. p. 120°, identical with the hydrogenation product of the complex.

Reaction of Complex (VIII) *with Ethanol.*—The complex (2 g.) was extracted with ethanol in a Soxhlet apparatus for 60 hr. After filtration to remove palladium the ethanol solution was evaporated. A solution of the yellow oil (1·2 g.) in ethanol deposited tetraphenylfuran (0·43 g.), m. p. 170°. The mother-liquor, on evaporation and crystallisation of the resultant oil from methanol, gave prisms (0·36 g.) of 1,4-*diethoxytetraphenylbutadiene* (III; X = OEt), m. p. 124° [Found: C, 85·65; H, 6·8; O, 7·25; OEt, 20·2%; *M* (Rast), 414. $C_{32}H_{30}O_2$ requires C, 86·1; H, 6·8; O, 7·2; OEt, 20·2%; *M*, 446].

This compound (40 mg.) was refluxed with 50% (v/v) aqueous sulphuric acid (10 ml.) for 12 hr. The white sublimate that collected in the condenser (25 mg.) was taken up in chloroform. The dried, evaporated solution, afforded an oil that crystallised from ethanol as plates, m. p. 170—173°, shown to be tetraphenylfuran (IV) by mixed m. p.

Reaction of Complex (VIII) *with Triphenylphosphine.* (*a*) *In air.* The complex (3 g.) in dry benzene (250 ml.) was treated with triphenylphosphine (6 g.) and the mixture shaken for 3 days in a stoppered flask. During this time, yellow *bistriphenylphosphinepalladium dichloride* precipitated (2·47 g.). This was filtered off and recrystallised from chloroform–ethanol as rods (Found: C, 61·6; H, 4·1. $C_{36}H_{30}Cl_2P_2Pd$ requires C, 61·6; H, 4·3%). This complex was identical with the product obtained by shaking an excess of triphenylphosphine and palladium dichloride in chloroform solution for 24 hr.

The filtrate obtained after removal of the yellow complex was passed down an alumina column, constructed in benzene, to remove any remaining complex. The eluate gave an oil (1·64 g.) that was taken up in light petroleum and chromatographed on alumina. Elution with light petroleum (7 × 250 ml.) gave a white solid (0·53 g.) that crystallised from chloroform–ethanol as plates, m. p. 170—172°, with an i.r. spectrum identical with that of authentic tetraphenylfuran.

Elution with benzene–light petroleum (85 : 15; 1 l.) gave an oil (0·21 g.) that deposited yellow crystals, m. p. 238—240° (from benzene–light petroleum) [Found: C, 94·2; H, 5·8%; *M* (Rast), 830. $C_{56}H_{40}$ requires C, 94·3; H, 5·7%; *M*, 712].

(*b*) *In the absence of oxygen.* The complex (VIII) (1 g.) in dry benzene (100 ml.) containing triphenylphosphine (2 g.) was heated at 50° under nitrogen for 2 hr. The initially red solution rapidly assumed a green colour which persisted for 12 hr. but rapidly disappeared on admission of air. The mixture was filtered, and the precipitate boiled with chloroform. The insoluble portion (0·34 g.), purified by Soxhlet extraction, gave white needles of the tetraphenylcyclobutadiene dimer, m. p. >360°, i.r. spectrum not identical with that of hexaphenylbenzene, $\lambda_{max.}$ 266 mμ (ε 44,600). The yellow bistriphenylphosphine complex (0·44 g.) was deposited on concentration of the chloroform solution.

Reaction of Complex (VIII) *with Triphenylphosphine in the Presence of Cyclopentadiene.*—The complex (1 g.) in dry benzene (125 ml.) was mixed with triphenylphosphine (2 g.) and freshly prepared cyclopentadiene (20 ml.) was added. The mixture was stirred and heated at 50° under nitrogen for 2 hr. Solution of the yellow complex (1·2 g.) in chloroform showed the absence of any tetraphenylcyclobutadiene dimer. The evaporated solution gave an oil that was taken up in light petroleum and chromatographed on alumina. Elution with light petroleum (5 × 250 ml.) gave an oil (1·26 g.) that crystallised from ethanol as prisms of triphenylphosphine. Further elution (5 × 250 ml.) gave an oil (0·156 g). After being taken up in ethanol the oil deposited a nodular solid (62 mg.), which gave 3a,7a-*dihydro*-4,5,6,7-*tetraphenylindene* (XXa), m. p. 184—187° (from ethanol) [Found: C, 93·6; H, 6·2%; *M* (Rast), 400. $C_{33}H_{26}$ requires C, 93·8; H, 6·2%; *M*, 422), $\lambda_{max.}$ (EtOH) 312 mμ (ε 9450)]. Hydrogenation of the adduct over PtO_2,H_2O in ethyl acetate at room temperature and pressure led to uptake of 1 mol. of hydrogen. The product, $\lambda_{max.}$ 320 mμ (ε 13,100), had m. p. 179—180°, undepressed on admixture with the compound (XXIIa) obtained by reduction and decarbonylation of the adduct of tetraphenylcyclopentadienone with cyclopentadiene.[24]

[24] Grummit, Klopper, and Blenkhorn, *J. Amer. Chem. Soc.*, 1942, **64**, 604.

Reaction of the Dihydro-adduct (XXIIa) *with* N-*Bromosuccinimide.*—(*a*) *In refluxing carbon tetrachloride.* The dihydro-adduct (0·5 g.) in dry carbon tetrachloride (35 ml.) was refluxed with *N*-bromosuccinimide (0·215 g.) for 15 min. Filtration of the succinimide, followed by evaporation of the solvent, gave an oil which yielded 4,5,6,7-tetraphenylindane (XXVI), m. p. 225—227° (from chloroform–ethanol).

(*b*) *At room temperature.* The dihydro-adduct (0·1 g.) in dry carbon tetrachloride (25 ml.) was shaken with *N*-bromosuccinimide (1 mol.) for 2 hr. The filtered solution, on evaporation at room temperature under reduced pressure, afforded an oil which had an i.r. spectrum identical with that of compound (XXVI) obtained in (*a*) above, and which gave prisms, m. p. 223—225° (from chloroform–ethanol).

Decarbonylation of the Adduct (XXIa).—The adduct (1 g.) in *p*-cymene (10 ml.) was boiled under reflux for 20 hr. The product was diluted with light petroleum and chromatographed on alumina in light petroleum. Elution with the same solvent (2 × 250 ml.) gave *p*-cymene. Further elution (5 × 250 ml.) gave an oily solid, that crystallised from chloroform–ethanol as prisms (0·146 g.), m. p. 208—210° (from light petroleum). The ultraviolet spectrum of this solid indicated that it was 4,5,6,7-tetraphenylindene. The concentrated mother-liquor afforded a white solid (10 mg.) which had an infrared spectrum identical with that of the tetraphenyl-cyclobutadiene–cyclopentadiene adduct (XXa).

Elution of the column with benzene gave tetraphenylcyclopentadienone (0·3 g.).

Reaction of Complex (VIII) *with* 1,2-*Bisdiphenylphosphinoethane.*—The complex (1 g.) and the diphosphine (2 g.) were dissolved in dry benzene and heated at gentle reflux under dry nitrogen for 5 hr. The precipitated solid was boiled with chloroform (500 ml.) and filtered hot. The precipitate (82 mg.) had infrared absorption identical with that of the tetraphenylcyclo-butadiene dimer. The chloroform solution deposited the complex (X), identical with a sample prepared from palladium dichloride, benzonitrile, and the diphosphine in chloroform solution.

When the above reaction was carried out in the presence of cyclopentadiene (30 ml.) at room temperature and the filtered solution evaporated and worked up by alumina chromatography, elution with light petroleum (5 × 250 ml.) gave an oil that deposited *ca.* 15 mg. of a solid on trituration with ethanol. The infrared spectrum of this solid was identical with that of the adduct (XXa) obtained previously.

Reaction of Complex (VIII) *with Triphenylphosphine in the Presence of Methyl Phenylpropiolate* (XV).—The complex (1 g.) in benzene (75 ml.) was treated with triphenylphosphine (2 g.) under nitrogen at 60° for 5 hr. in the presence of the acetylene ester (XV) (17 g.). The yield of dimer was 250 mg., and of bistriphenylphosphinepalladium dichloride 1·15 g. The evaporated mother-liquor was applied to an alumina column in benzene, and eluted with benzene (500 ml.) to remove palladium complexes. The eluate was evaporated and applied to an alumina column in light petroleum. Elution with light petroleum (1·5 l.) gave triphenylphosphine and tetraphenylfuran (20 mg.), together with the acetylene ester (15 ml.). Elution with light petroleum–benzene, (95 : 5) then (9 : 1), gave oils that crystallised from chloroform–ethanol as yellow crystals (40 mg.), m. p. 234—236° (the compound encountered earlier). Light petroleum–benzene (80 : 20; 2 l.) eluted a yellow band that gave a yellow oil (273 mg.) which could not be crystallised, and light petroleum–benzene (3 : 2; 4 l.) gave a reddish band that yielded a white solid (95 mg.) contaminated with some red material. Recrystallisation from chloroform–ethanol gave white crystals (45 mg.), identical (i.r. spectrum) with methyl pentaphenylbenzoate (XVI).[16]

No adduct could be isolated from an analogous trapping experiment employing but-2-yne.

Irradiation of the Hydrocarbon (XXIIa).—The diene (XXIIa) (2 g.) in dry benzene (250 ml.) was irradiated in a Pyrex flask over an 80w lamp under nitrogen for 20 hr. Evaporation of the solvent gave a pale yellow oil that was taken up in light petroleum and chromatographed on alumina. Elution with the same solvent (4 × 250 ml.) gave a colourless oil (1·9 g.) that solidified on trituration with ethanol. The filtered solid crystallised from ethanol as rods, m. p. 124—125° [Found: C, 93·4; H, 6·7%; *M* (Rast), 389. Calc. for $C_{33}H_{26}$: C, 93·8; H, 6·2%; *M*, 422], $\lambda_{max.}$ 278 mμ (ε 12,700). 1-Ethyl-2,3,4,5-tetraphenylcyclopentadiene [19] and 2,3,4,5-tetraphenylcyclopentadiene [25] underwent no change on prolonged irradiation under the above conditions or through silica in ethyl acetate solution.

2′,3′-*Dihydro*-4,4′′-*dimethoxy*-2′,5′,6′-*triphenyl*-p-*terphenyl* (XXIV; R = OMe).—2,5-Di-*p*-methoxyphenyl-3,4-diphenylcyclopentadienone [26] (3·5 g.) in decalin (10 ml.) was mixed with

[25] Ziegler and Schnell, *Annalen*, 1925, **445**, 266.
[26] Coan, Trucker, and Becker, *J. Amer. Chem. Soc.*, 1955, **77**, 60.

styrene (3 ml.) and the mixture refluxed for 60 hr. The product was chromatographed on alumina in light petroleum. Light petroleum (250 ml.) eluted decalin (9 ml.) and benzene–light petroleum (containing, successively, 5, 10, and 15% benzene) eluted only traces of oil. Elution with benzene–light petroleum (1 : 4; 6 × 250 ml.) gave a pale yellow oil (1·5 g.) which gave the *terphenyl* as prisms, m. p. 142—143° (from chloroform–ethanol) [Found: C, 87·7; H, 6·6; OMe, 11·75%; *M* (Rast), 497. $C_{38}H_{32}O_2$ requires C, 87·7; H, 6·2; OMe, 11·9%; *M*, 520], $\lambda_{max.}$ 335·6 mμ (ε 17,800).

2,3,3a,7a-*Tetrahydro*-4,7-*di*-p-*methoxyphenyl*-5,6-*diphenylindene* (XXV).—2,5-Di-*p*-methoxyphenyl-3,4-diphenylcyclopentadienone (2·3 g.) in benzene (7 ml.) was refluxed with cyclopentadiene (3 ml.) for 5 hr. Dilution with light petroleum (20 ml.) gave a pink solid (1·5 g.) that crystallised from chloroform–ethanol as prisms, m. p. 205° (decomp.). This material was not further purified, as crystallisation caused some decomposition. The adduct (1 g.) in ethyl acetate (100 ml.) was shaken with hydrogen at room temperature and atmospheric pressure over Adams catalyst (50 mg.). Uptake of 1 mol. of hydrogen was complete in 15 min. Work-up in the usual way gave 2,3,3a,4,7,7a-*hexahydro*-4,7-*di*-p-*methoxyphenyl*-8-*oxo*-5,6-*diphenyl*-4,7-*methanoindene* as prisms (0·86 g.), m. p. 210° (decomp.) (from chloroform–ethanol) (Found: C, 84·5; H, 6·5. $C_{36}H_{32}O_3$ requires C, 84·3; H, 6·3%). The foregoing compound (0·4 g.) was slowly heated in a tube until all effervescence ceased. The *tetrahydroindene* crystallised from chloroform–ethanol as needles, m. p. 169—170° [Found: C, 87·0; H, 6·6; OMe, 12·6%; *M* (Rast), 433. $C_{35}H_{32}O_2$ requires C, 86·7; H, 6·7; OMe, 12·8%; *M*, 485], $\lambda_{max.}$ 333 mμ (ε, 13,900).

2,5-Di-*p*-methoxyphenyl-3,4-diphenylcyclopentadienone (0·5 g.) was refluxed in dicyclopentadiene (10 ml.) for 1 hr. Removal of the dicyclopentadiene under reduced pressure on a water-bath, followed by addition of ethanol, caused separation of a white solid (0·21 g.) which gave needles, m. p. 224—225° (from ethanol) [Found: C, 88·0; H, 6·65%; *M* (Rast), 548. Calc. for $C_{40}H_{36}O_2$: C, 87·6; H, 6·6%; *M*, 549], $\lambda_{max.}$ 319·5 mμ (ε, 10,100).

*Preparation of (Tetra-*p*-chlorophenylcyclobutadiene)palladium Dichloride.*—Di-*p*-chlorophenyl-acetylene [27] (0·3 g.), partly suspended in a mixture of chloroform (5 ml.) and dry ethanol (15 ml.), was shaken with bisbenzonitrilepalladium chloride (0·229 g., 2 mol.). After a short time a yellow complex started to separate. After magnetic stirring for 24 hr. the *ethoxychloropalladium complex* (0·42 g.) was filtered off and crystallised from chloroform–ethanol as yellow prismatic needles (Found: C, 51·25; H, 3·2; OEt, 6·0. $C_{30}H_{21}Cl_5OPd$ requires C, 52·8; H, 3·1; OEt, 6·6%). The foregoing complex (200 mg.) in AnalaR chloroform (25 ml.) was treated with a slow stream of dry hydrogen chloride for 1 hr. with stirring. The precipitated orange *complex* (0·147 g.) became deep red on drying (Found: C, 50·8; H, 2·9; OEt, 0. $C_{28}H_{16}Cl_6Pd$ requires C, 50·0; H, 2·4; OEt, 0%). Reaction of this complex with ethanol afforded an orange complex. the infrared spectrum of which showed ethoxyl absorption.

Reaction of Complex (A) *with Triphenylphosphine.*—The complex (1·5 g.) and triphenylphosphine (3 g.) in dry benzene (100 ml.) were heated in an oil-bath at 90° under dry nitrogen. The dark green colour remained after 18 hr. but disappeared immediately on admitting air. The cooled solution was filtered, giving bistriphenylphosphinepalladium dichloride (0·38 g.). The filtrate was passed down a short column of alumina constructed in benzene. Benzene (500 ml.) eluted a yellow band. The eluate was diluted with light petroleum until the precipitation of green plates ceased. The green crystals were filtered and dried *in vacuo* (1·2 g.) (Found: C, 65·2, 65·3; H, 4·95, 4·8%). This complex, $\nu_{max.}$ 890 cm.$^{-1}$, decomposed at 102° and was very unstable to oxygen in solution. The filtrate obtained after removal of the complex was evaporated and the oil dissolved in light petroleum and chromatographed on alumina. Light petroleum (5 × 250 ml.) eluted a blue band. Evaporation gave a blue oil (50 mg.) that crystallised from chloroform–ethanol as a mixture of white plates and blue prisms. The heavier prisms were removed by decantation and gave 1,2,3-triphenylazulene (XXXIII), m. p. 210—211° (from nitromethane), undepressed on mixture with an authentic sample.[28] The white plates (15 mg.) had m. p. 173° (from chloroform–ethanol); the infrared spectrum was identical with that of tetraphenylfuran. Gradient elution gave yellow oils (0·52 g.) that could not be crystallised from the usual solvents.

When the reaction was conducted in toluene or in the presence of cyclopentadiene the same result was obtained. When the reaction was conducted in the presence of air, 1-*ethoxy*-2,3,4-*tri-phenylnaphthalene* (XXXIV) (120 mg.), m. p. 142—143°, was eluted, after tetraphenylfuran,

[27] Kenner and Witham, *J.*, 1910, **97**, 1960.
[28] Assony and Kharasch, *J. Amer. Chem. Soc.*, 1958, **80**, 5978.

with benzene–light petroleum (5 : 95) [Found: C, 89·65; H, 6·0; O, 4·3; OEt, 8·7%; M (Rast), 501. $C_{30}H_{24}O$: C, 90·0; H, 6·0; O, 4·0; OEt, 11·25%; M, 400], identical with an authentic sample synthesised from 1-hydroxy-2,3,4-triphenylnaphthalene,[29] by reaction with diethyl sulphate in aqueous methanolic sodium hydroxide.

Reaction of Complex (A) *and Triphenylphosphine in Ethanol.*—The complex (1 g.) and triphenylphosphine (2 g.) in absolute ethanol (100 ml.), were heated at 90° (bath temperature) for $2\frac{1}{2}$ hr. whilst dry nitrogen was passed through the stirred solution. The yellow precipitate (1·59 g.) was filtered and dried *in vacuo*. The infrared spectrum of this material showed it to be a mixture of bistriphenylphosphinepalladium dichloride and the yellow complex termed (A₃) to be discussed later. (Solution in benzene gave the former and dilution of the filtrate with methanol gave the latter.) The solution obtained after removal of the complexes was evaporated, the resultant oil taken up in benzene–light petroleum (1 : 9), and chromatographed on alumina. Elution with the same solvent (4 × 250 ml.) gave triphenylphosphine (270 mg.), m. p. 80°. Further elution (2 × 250 ml.) gave an oil (22 mg.) that crystallised from methanol as prisms, m. p. 124°. Elution with light petroleum–benzene (4 : 1; 5 × 250 ml.) gave further quantities of this solid (235 mg.), which was identical (mixed m. p. and infrared spectrum) with 1,4-diethoxy-1,2,3,4-tetraphenylbutadiene (III; X = OEt) prepared above.

Benzene (2 × 250 ml.) eluted a yellow band which afforded an oil (0·367 g.) that could not be crystallised from the usual solvents.

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[29] Smith and Hoehn, *J. Amer. Chem. Soc.*, 1941, **63**, 1180.