(14 mm.), was obtained. The infrared spectrum of this product, while containing absorptions attributable to those of phenylbicycloheptane, was definitely different from that of the hydrocarbon isolated from the addition of triphenyl-chromium to bicycloheptadiene. Several attempts to separate the main fraction into components by vapor phase chromatography were unsuccessful.

The product was then dissolved with an equal amount of phenyl azide in ethyl acetate. After 3 days standing and frequent scratching, a crop of white crystals, m.p. 110–130°, was deposited. Recrystallization of this mixture from ethyl acetate gave as first fraction a small amount of adduct, m.p. 143–145°, melting undepressed with and showing a superimposable infrared spectrum with that of 5-phenylbicyclo-[2,2,1] heptene-2 obtained above from addition of triphenyl-chromium to the bicycloheptadiene.

A second fraction was obtainable from the 110–130° product by chromatography with ether on a basic alumina column. The first eluted fractions melted between 133–135° corresponding with the phenyl azide derivative prepared by Alder and Rickert from *endo*-5-phenylbicyclo [2,2,1]hep-tene-2, m.p. 134–135°. The eutectic temperature for the 145°- and 135°-melting azides was found to be 110°. A semiquantitative study of infrared spectra revealed that the 110–130° azide mixture contained the 145°- and 135°-azides in a ratio of about 1:1. According to the infrared spectrum of the parent hydrocarbon mixture, a large excess of the 135° azide would have been expected in the 110–130° azide mixture had it not been for its greater solubility in ethyl acetate and methanol.

Addition of Triphenylchromium to Maleic Anhydride.—To a solution of 0.029 mole of triphenylchromium in tetrahydro-furan was added 5.7 g. (0.059 mole) of maleic anhydride. A spontaneous reaction ensued, the whole mixture reaching a temperature of 40°. After standing for 48 hours the solvent was removed, the residue treated with ice-water and then filtered. A green solid was collected on the filter from which only biphenyl could be extracted with benzene. The infrared spectrum of the remainder indicated it to be a metal salt of a carboxylic acid. Treatment of this green powder with strong hydrochloric acid and extraction with ether overnight yielded a dark brown solution from which organic acids could be removed with aqueous sodium bicarbonate. The alkaline solution was acidified and extracted with ether again overnight. Removal of the ether left 2.25 g. of crude product in the form of a brown, sticky mass which was now esterified by dissolution in 25 ml. of methanol, addition of 3 ml. of concentrated sulfuric acid and refluxing on the steam-bath for 3 hours. This reaction mixture was diluted with water, extracted with ether, and the unesterified acid fraction removed from the ether layer with bicarbonate. The ester fraction was distilled in a ball tube at a bath temperature of 180–250° (0.5 mm.), yielding a yellow oil which crystallized after scratching. Recrystallization from ethanol gave white crystals of methyl α-phenyl-β-benzoylpropionate, m.p. 100–102°.[9]

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01; CH_3O, 11.5. Found: C, 76.41; H, 6.06; CH_3O, 11.9.

(9) Rupe, *et al.*, *Ber.*, **28**, 963 (1895), reported m.p. 104°.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y.]

Reactions of Palladium Compounds with Acetylenes. I.
Tetraphenylcyclobutadienepalladium(II) Chloride

BY A. T. BLOMQUIST AND P. M. MAITLIS

In non-hydroxylic solvents, bis-(benzonitrile)-palladium chloride (I) catalyzes the trimerization of tolan to hexaphenyl-benzene. In ethanol–chloroform (3:1), tolan reacts with compound I to give an orange-red complex (A), $(C_{30}H_{25}OPdCl)_x$, which on treatment with hydrogen chloride affords a deep red crystalline complex (B), $(C_{28}H_{20}PdCl_2)_x$. Spectroscopic and degradation studies of complex B show that it is tetraphenylcyclobutadienepalladium(II) chloride. Complex B, which can also be obtained directly by reaction of tolan with palladium chloride, fails to react with tolan, 2-butyne and dimethyl acetylenedicarboxylate. Treatment of B with ethanol converts it to a yellow complex (C), isomeric with complex A. Complex A reacts with bromine to give tetraphenylfuran and it decomposes thermally to 2,3,8-triphenylbenzofulvene and 8-ethoxy-2,3,8-triphenylbenzofulvene. Structures are postulated for complexes A and C, and a mechanism is proposed for the reactions leading to their formation.

Considerable effort has been expended by a large number of workers over the last fifty years in attempts to prepare derivatives of cyclobuta-diene.[1] Apart from the preparation of diphenylene and its derivatives[2] this quest has hitherto been fruitless, with the exception of a number of cyclo-butadiene–metal complexes which have recently been reported.[3–6] It would seem that one of the most practical and hopeful routes to cyclobuta-dienes would be by decomposition of suitably stabilized cyclobutadiene–metal complexes. However, the routes used to obtain these metal complexes do not, for the most part, appear to be broadly useful for the preparation of complexes other than the specific ones described.

As yet very little work has been carried out on reactions of acetylenes with palladium compounds; one brief note by Malatesta and co-workers[7] has appeared which describes, *with complete absence of detail*, the preparation of a cyclobutadiene–palladium complex in two steps from tolan (di-phenylacetylene) and palladium chloride. Since this is certainly the simplest route yet discovered to cyclobutadiene complexes and one which should be capable of great extension, its reinvestigation was undertaken, preparatory to a more complete study of the route as a general method.

Results

Bis-(benzonitrile)-palladium chloride (I), $(C_6H_5CN)_2PdCl_2$,[8] was chosen as the source of palladium in the present study. This palladium

(1) W. Baker and J. F. W. McOmie, "Non-benzenoid Aromatic Compounds," Ed. D. Ginsburg, Interscience Publishers, Inc., New York, N. Y., 1959, p. 43.

(2) W. Baker and J. F. McOmie, *Chem. Soc. Special Publ. No. 12*, 49 (1958).

(3) M. Avram, E. Marica and C. D. Nenitzescu, *Chem. Ber.*, **92**, 1088 (1959); *Tetrahedron Letters*, 21 (1961).

(4) R. Criegee and G. Schroeder, *Ann.*, **623**, 1 (1959).

(5) W. Hübel and E. H. Braye, *J. Inorg. Nucl. Chem.*, **9**, 250 (1959); *cf.* W. Hübel, *et al.*, *ibid.*, **9**, 204 (1959), and R. P. Dodge and V. Schomaker, *Nature*, **186**, 798 (1960).
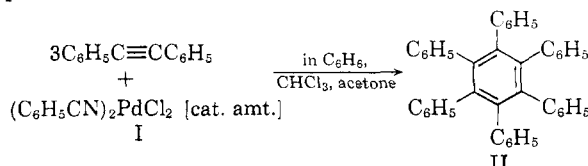
(6) H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2194, 2195 (1961).

(7) L. Malatesta, G. Santarella, L. Vallarino and F. Zingales, *Angew. Chem.*, **72**, 34 (1960); *Atti. accad. naz. Lincei, Rend. Classe sci. fis. mat. a nat.*, **27**, 230 (1959).

(8) M. S. Kharasch, R. C. Seyler and F. R. Mayo, *J. Am. Chem. Soc.*, **60**, 882 (1938).

compound was attractive because of its ready solubility in organic solvents such as benzene, chloroform and acetone. Further, the benzonitrile ligands in I are easily replaced by other groups.

The compound I, in catalytic amounts in non-hydroxylic solvents such as benzene, chloroform and acetone, effects a smooth trimerization (80–85%) of tolan to hexaphenylbenzene (II); this is probably the easiest route to the hydrocarbon II. Other catalysts reported for this trimerization reaction[9–11] are more difficult to handle than compound I.

$$3C_6H_5C{\equiv}CC_6H_5 + (C_6H_5CN)_2PdCl_2 \text{ [cat. amt.]} \xrightarrow[\text{CHCl}_3,\ \text{acetone}]{\text{in } C_6H_6,}$$

I

II

In ethanol–chloroform (3:1) the palladium compound I combines with two molecules of tolan to give easily a complex A (83%) which has the empirical formula $(C_{30}H_{25}OPdCl)_x$. Since complex A is also obtained, in poor yield, by reaction of tolan with palladium chloride in ethanol it must be the compound for which Malatesta, et al.,[7] proposed the structure III.
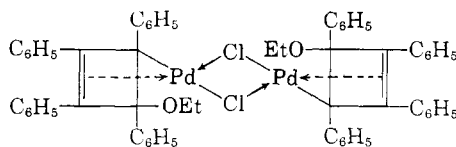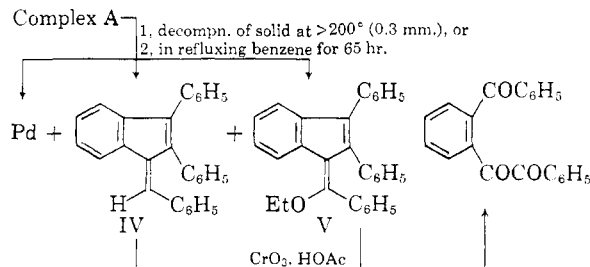
III, complex A as per Malatesta

Consistent with the formulation III for the complex A, the n.m.r. spectrum of A in methylene chloride shows only the presence of aromatic hydrogens and a C–ethoxy group; the infrared spectrum is also consistent with this formulation. This spectroscopic evidence does not, however, rule out the possibility that A may have a different structural formula, as indeed it is believed (infra vide).

The complex A is an orange-red crystalline solid which is stable to air indefinitely and, as a solid, does not decompose below 190° (0.3 mm.). The complex A in solution decomposes slowly on moderate heating and decomposition is complete in 65 hr. in refluxing benzene. The products of thermal decomposition in both cases are palladium, deposited as a bright metallic mirror, and two organic compounds. One is a bright yellow hydrocarbon, $C_{28}H_{20}$, and the other a pale yellow enol-ether, $C_{30}H_{24}O$ (indicated by its ready conversion to a ketone by acid hydrolysis and by its infrared spectrum). The hydrocarbon was shown to be 2,3,8-triphenylbenzofulvene (IV) by comparison with an authentic sample. Both IV and the enol-ether undergo oxidation with chromic anhydride under the same conditions to give comparable yields of o-benzoylbenzil. The similarity of the ultraviolet spectra of the two compounds (Fig. 2) also points to the presence of the same ring system in both compounds; thus the enol-ether must be

8-ethoxy-2,3,8-triphenylbenzofulvene (V), since the 8-position is the only one which the ethoxy group can occupy if it affords a ketone by acid hydrolysis.

Reaction of the complex A with one equivalent of bromine in chloroform, in the cold, gives tetraphenylfuran (VI) (80%). Complex A cannot be hydrogenated at atmospheric pressure and room temperature over palladized charcoal. The complex A is inert toward methanol, which indicates

Complex A → 1, decompn. of solid at >200° (0.3 mm.), or
2, in refluxing benzene for 65 hr.

Pd + (IV) + (V) (COC₆H₅/COCOC₆H₅)

CrO₃, HOAc

that the ethoxy group is not easily displaced and hence not bonded directly to the palladium.

No reacn. ←(H₂, Pd-C / 1 atm., 25°)— Complex A —(Br₂, CHCl₃)→ VI

No reacn. ←(CH₃OH)—
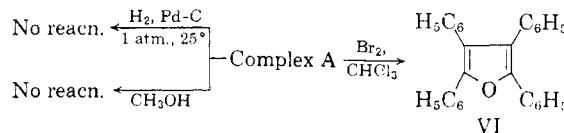
Passage of dry hydrogen chloride for one hour through a solution of complex A in chloroform gives a new palladium complex (B) which separates (76%) as deep red prisms and has the empirical formula $(C_{28}H_{20}PdCl_2)_x$. Complex B is extremely stable toward many reagents. It is unaffected by air, unreactive with bromine or aqueous sodium nitrite, and dissolves in sulfuric acid.[12] It is quite insoluble in water and all organic solvents except chloroform saturated with hydrogen chloride[13] (solubility 1.5 g./100 ml.), and dimethylformamide; it appears to react with the latter.[14] The n.m.r. spectrum of complex B in CHCl₃–HCl shows the presence of only aromatic hydrogens; the infrared spectrum (Fig. 1) is quite simple and essentially identical with that of a sample of tetraphenylcyclobutadiene nickel (II) bromide,[6] kindly furnished by Dr. H. H. Freedman.

From the above it is concluded that complex B must be formulated as a cyclobutadiene complex, since the infrared spectra of all cyclobutadiene complexes, in the region measured, will be similar as only the organic moiety absorbs here. The small differences between the spectra of palladium chloride and nickel bromide complexes of tetraphenylcyclobutadiene are probably due to differing strengths of the metal–ring bonds and are reflected in the relative intensities of some of the

(9) W. Hübel and C. Hoogzand, Chem. Ber., 93, 103 (1960).

(10) M. Tsutsui and H. Zeiss, J. Am. Chem. Soc., 82, 6255 (1960).

(11) G. N. Schrauzer, Chem. Ber., 94, 1403 (1961).

(12) Dilution of the sulfuric acid solution precipitates the sulfate analog of the chloroform-soluble chloride of complex B (infra vide). Treatment of this sulfate with hydrogen chloride reforms the original complex B chloride, which is soluble in chloroform.

(13) This is the only solvent from which complex B can be recovered unchanged. The complex dissolves, with decomposition, in many complexing solvents.

(14) Reaction of complex B with dimethylformamide (DMF) occurs rapidly in the cold to give a product which has not been characterized. The same product is obtained by reaction of complex B with sodium nitrite in aqueous DMF.
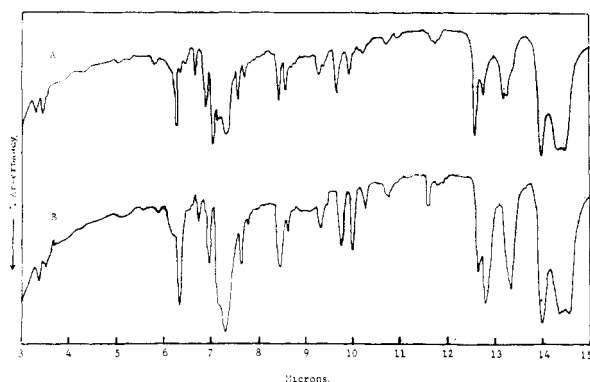
Fig. 1.—Infrared spectra of 1,2,3,4-tetraphenylcyclobutadienepalladium(II) chloride (A) and of 1,2,3,4-tetraphenylcyclobutadienenickel(II) bromide (B) in potassium bromide disks.

absorption bonds which differ in the two complexes.

Thermal decomposition confirms the formulation of B as tetraphenylcyclobutadiene palladium(II) chloride. Complex B, which is not appreciably decomposed below 330°, can be pyrolyzed *in vacuo* over a free flame to give solely 1,4-dichloro-1,2,3,4-tetraphenyl-1,3-butadiene (VII). The latter, VII, was characterized by its conversion to the furan VI with boiling 50% sulfuric acid.

Complex B

VII
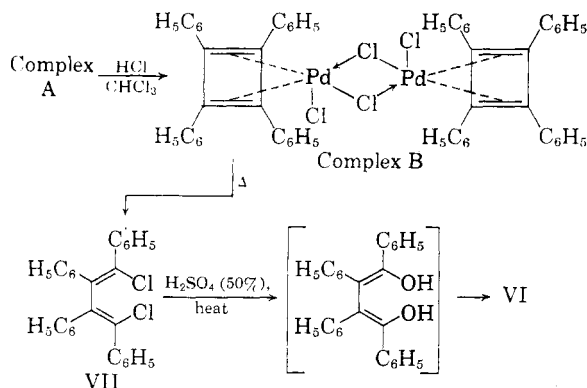
A number of attempts to effect a Diels–Alder condensation of the cyclobutadiene complex B with various acetylenic dienophiles to give benzene derivatives were unsuccessful. In particular, B fails to react with tolan even in large excess, to give any hexaphenylbenzene.

Reversal of the reaction which formed the cyclobutadiene complex B, *i.e.*, the transformation of B to the original complex A with ethanolic alkali, reported by Maltesta, *et al.*,[7] by analogy with reactions of platinum and palladium diolefin complexes,[15] did not work in our hands. However, complex B when stirred with ethanol either in the presence or absence of alkali gives a yellow insoluble complex C, $(C_{30}H_{25}OPdCl)_x$, different from complex A, but which on treatment with HCl/CHCl₃ regenerates the cyclobutadiene complex B.

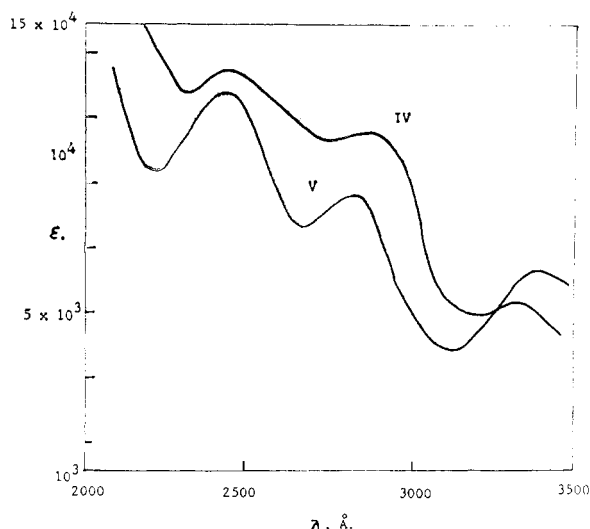The complex B is also formed directly from tolan and palladium chloride in alcoholic hydrochloric

(15) J. Chatt, L. M. Vallarino and L. M. Venanzi, *J. Chem. Soc.*, 2496, 3413 (1957).

Fig. 2.—Ultraviolet spectra of 2,3,8-triphenylbenzofulvene (IV) and 8-ethoxy-2,3,8-triphenylbenzofulvene (V) in isooctane.

acid, and together with hexaphenylbenzene, from tolan and palladium chloride in chloroform saturated with hydrogen chloride. The use of ethanol–chloroform mixtures containing more chloroform than described above give mixtures of A and B, both contaminated with other materials.

Discussion

The exact nature of the reactions leading to complex A and B, and hexaphenylbenzene (II) is not yet clear and it is only possible at the present time to speculate concerning them. Since the cyclobutadiene complex B does not react with tolan to form the hydrocarbon II, B cannot be an intermediate in the trimerization of tolan to II. (The suggestion of Tsutsui and Zeiss[16] that a tetraphenylcyclobutadiene-nickel complex is an intermediate in an analogous trimerization has not, as yet, been substantiated.) The reactive intermediate in the case of the palladium complexes must be a precursor of complexes B and A, and the hydrocarbon II. Furthermore, it now seems unlikely that A has the cylic structure III since it cannot be regenerated from the cyclobutadiene. Assignment of a definite structure for the intermediate is not possible but we should like to suggest VIII for it.[17]
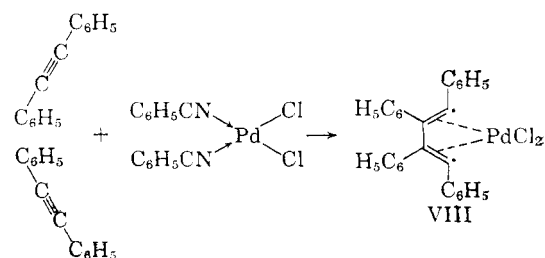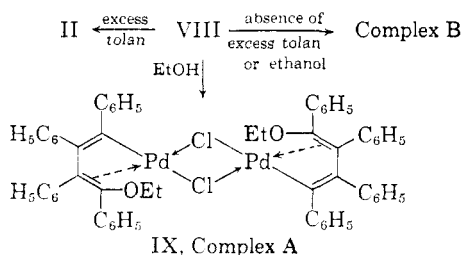

VIII

The reactions are considered to proceed by the following paths. Two tolan molecules first dis-

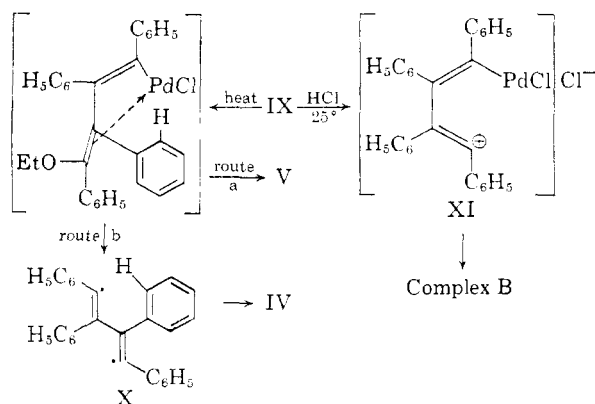(16) M. Tsutsui and H. Zeiss, Abstracts, A.C.S. Meeting, September, 1958, 59-P.

(17) The formula as written for VIII is not meant to imply one particular state of electron localization.

place the benzonitrile, or other, groups from I and couple to give the very reactive intermediate VIII. The latter then behaves in one of three ways: (1) in the absence of other molecules with which it might react, such as excess tolan or ethanol, it collapses or rearranges to complex B; (2) in the presence of excess tolan it reacts further to give the hydrocarbon II and palladium chloride (the latter, now present in a molecular dispersion will react further with more tolan along the same path); (3) in the presence of ethanol VIII reacts by addition to give the complex A. The best structure for A is then an acyclic structure as IX;

$$\text{II} \xleftarrow[tolan]{excess} \text{VIII} \xrightarrow[\substack{excess\ tolan\\or\ ethanol}]{absence\ of} \text{Complex B}$$

$$\text{EtOH} \downarrow$$

IX, Complex A

this could also account for the easy formation of the benzofulvenes from A by thermal decomposition, by analogy with the dehydrobromination of di-bromotetraphenylbutenes to 2,3,8-triphenylbenzo-fulvene.[18-20] Both in this case and in the high temperature pyrolysis of the cyclobutadiene complex B, the ready decomposition of palladium halides to palladium metal and the halogen must play an important part. In A the chlorine is probably not far removed from the *ortho*-hydrogen of the phenyl group in the 3-position, and on heating, both the palladium–carbon and the palladium–chlorine bonds break, the chlorine detaches the phenyl hydrogen, forming hydrogen chloride and palladium, while the organic moiety, in a transoid configuration, cyclizes to give the benzofulvene V (route a). Alternatively, route b, the palladium–carbon bond and the ethoxy–carbon bond are broken, perhaps in the latter case with assistance from the palladium, to leave the diradical X which then rearranges to the fulvene IV. Reaction of A with hydrogen chloride must cause cleavage of

(18) A. Orechoff, *Ber.*, **47**, 89 (1914).

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

(20) J. M. Morton, E. A. Flood and N. F. H. Bright, *Can. J. Chem.*, **5**, 1097 (1957).

the C–ethoxy group to give ethanol plus a carbon-ium ion XI, in a cisoid configuration, which rear-ranges to the cyclobutadiene complex B.

In view of the ease of formation of complex C from the cyclobutadiene complex B with ethanol, and the regeneration of B by treatment with hy-drogen chloride, it is very probable that this is another case of the palladium–diolefin reactions discovered by Chatt,[15] and hence C most probably has either structure III or structure XII.[21]
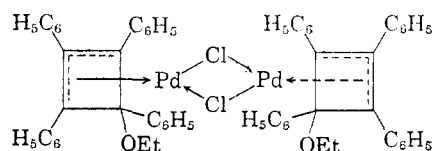
XII, complex C; see also III.

Due to the insolubilities of the complexes A, B and C, molecular weight determinations were not possible. It is very probable that none of these compounds are monomeric and that structures involving chlorine bridges, such as III (XII) and IX are formed. The cyclobutadiene B in particu-lar will have a structure similar to Criegee and Schroeder's tetramethylcyclobutadiene nickel(II) chloride; the solubility of B in chloroform satu-rated with hydrogen chloride must be due to breakdown of the dimer and the formation of ions such as H^+ (tetraphenylcyclobutadiene-$PdCl_3$)$^-$, in which the palladium reaches the inert gas configuration, or $2H^+$ (tetraphenylcyclobutadiene $PdCl_4$)$^{--}$, by analogy with H_2PdCl_4. These solu-tions readily lose hydrogen chloride on standing and deposit the crystalline cyclobutadiene com-plex again.

Thermal decomposition of the cyclobutadiene complex B involves scission of the metal–ring and metal–halogen bonds, to give the very un-stable cyclobutadiene and chlorine atoms which combine together to give 3,4-dichloro-1,2,3,4-tetraphenylcyclobutene which, like many cyclo-butenes[22] at elevated temperatures, readily under-goes ring opening to the dichlorotetraphenylbuta-diene actually isolated.

VII
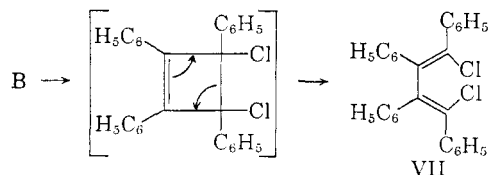
Acknowledgments.—This investigation was sup-ported by a grant from the National Science Foundation (G 5923). The authors express their thanks to Drs. F. G. A. Stone, W. Hübel, R. Plow-man and H. H. Freedman for helpful discussions.

Experimental Part

Complex A.—A solution of 5.7 g. of bis-(benzonitrile)-palladium chloride (I)[3] in 50 ml. of chloroform was added

(21) Complex C is perhaps represented better by structure XII than by III since the latter would involve considerable strain. There is ample precedent for the existence of π-allylic palladium complexes: H. C. Dehm and J. C. W. Chien, *J. Am. Chem. Soc.*, **82**, 4429 (1960), *Chemistry & Industry*, 745 (1961); B. L. Shaw, *Proc. Chem. Soc.*, 247 (1960); E. O. Fischer and G. Burger, *Z. Naturforsch.*, **16b**, 702 (1961).

(22) E. Vogel, *Angew. Chem.*, **72**, 13 (1960).

to a solution of 5.0 g. of tolan in 150 ml. of ethanol. After 6 hr. at room temperature 5.85 g. of the orange-red crystalline complex A separated from the solution; an additional quantity of the complex, 0.5 g., separated after 1 week to give a total of 6.53 g. (83%) of complex A, which was recrystallized from methylene chloride.

Anal. Calcd. for $(C_{30}H_{23}OPdCl)_2$: C, 66.3; H, 4.5; Pd, 19.6. Found: C, 66.1; H, 4.8; Pd, 19.1.

Tetraphenylcyclobutadiene Palladium(II) Chloride, Complex B.—Dry hydrogen chloride was passed through a solution of 11.0 g. of complex A in 250 ml. of chloroform, with vigorous stirring. Deep red prisms of B crystallized slowly from the filtered reaction mixture as the hydrogen chloride evaporated. There was obtained 8.2 g. (76%) of the complex.

Anal. Calcd. for $(C_{28}H_{20}PdCl_2)_x$: C, 63.00; H, 3.8; Pd, 20.0; Cl, 13.3. Found: C, 62.7, 63.0; H, 4.1, 4.1; Pd, 19.8; Cl, 13.9.

Trimerization of Tolan. A.—A solution of 1.0 g. of the palladium complex I in 50 ml. of cold benzene was added to 0.85 g. of tolan dissolved in 20 ml. of benzene and the mixture warmed. The heavy brown precipitate which separated was recrystallized from a large volume of hot benzene to give 0.8 g. (90%) of small colorless prisms of hexaphenylbenzene (II), m.p. > 400°. The infrared spectrum of this hydrocarbon II was identical with that of an authentic specimen of the hydrocarbon prepared by the method of Dilthey and Hurtig.[23] Only the complex I, identified by its infrared spectrum, was isolated upon concentration of the original reaction mixture.

Anal. Calcd. for $C_{42}H_{30}$: C, 94.3; H, 5.7. Found: C, 94.3; H, 5.6.

B.—From a reaction mixture prepared by the addition of a solution of 1.0 g. (0.056 mole) of tolan in 20 ml. of acetone to 0.1 g. (0.0024 mole) of the palladium complex I dissolved in 10 ml. of acetone there was obtained, after the mixture had stood at room temp. for 2 days, 0.85 g. (85%) of hexaphenylbenzene. Similar results were obtained when either benzene or chloroform were used as solvents.

Pyrolysis of Complex A.—A solution of 5.85 g. of complex A in 150 ml. of benzene was refluxed for 65 hr. A metallic mirror formed slowly on the sides of the reaction flask. The mixture was cooled, filtered to remove a powdery gray-green deposit (1.8 g.) which was largely palladium, and the solvent removed. The 3.7 g. of yellow residual oil was taken up in ether, in which all but 0.1 g. of hexaphenylbenzene was soluble, and chromatographed on alumina with ether-petroleum ether (b.p. 30–60°). Elution of the yellow band gave a total of 1.55 g. of a yellow solid which had m.p. 160–180°. Careful crystallization from ether–light petroleum gave a mixture of red prisms and yellow needles. The latter dissolved readily in a small quantity of ether; the dark prisms were filtered and recrystallized from ethanol–benzene to give 25 mg. of fine yellow needles which had m.p. 183–184°. Admixture of this compound with an authentic sample of 2,3,8-triphenylbenzofulvene (IV),[18,19] m.p. 183–184°, did not depress the m.p. The infrared spectra of the two hydrocarbons were identical.

Anal. Calcd. for $C_{28}H_{20}$: C, 94.4; H, 5.6; mol. wt., 356. Found: C, 94.2; H, 5.7; mol. wt., 342.

The more soluble second component of the mixture, mainly present in the mother liquors, was obtained free from compound IV with great difficulty. However, after many recrystallizations from ethanol there was obtained 40 mg. of pale yellow needles, m.p. 166–167°, which gave a satisfactory analysis for 8-ethoxy-2,8,8-triphenylbenzofulvene (V). The structure assigned to compound V was based on its ultraviolet spectrum (Fig. 2) and its oxidation to *o*-benzoylbenzil (*infra vide*).

Anal. Calcd. for $C_{30}H_{24}O$: C, 89.5; H, 6.0; mol. wt., 400. Found: C, 89.5; H, 6.0; mol. wt., 421.

Although the two pure compounds IV and V could be isolated in only low yield, infrared analysis of the crude pyrolysate from complex A showed that it comprised almost entirely the ether V and the hydrocarbon IV in a 2:1 ratio. Thermal decomposition of A *in vacuo* at >200° and 0.3 mm. gave the same mixture but in lower yield.

Acid hydrolysis of the vinyl ether V gave a colorless solid which could not be purified because of its tendency to polymerize, presumably by self-condensation. Impure samples of this hydrolysis product always showed a strong ketonic band at 6.05 μ in their infrared spectra

Oxidation of Compounds IV and V.—A mixture prepared by the addition of a solution of 2.0 g. of chromium trioxide in 30 ml. of glacial acetic acid to a suspension of 1.2 g. of the hydrocarbon IV in 30 ml. of acetic acid was heated to boiling briefly, whereupon all the solid dissolved and the solution became green in color. The reaction mixture was poured into 600 ml. of water, and the oily product which separated was filtered and dissolved in ether. From the dried ether solution there was obtained 1.0 g. of a yellow oil which was extracted with four 30-ml. portions of petroleum ether (b.p. 60–70°). Concentration of this extract gave 0.6 g. (57%) of yellow needles of *o*-benzoylbenzil, m.p. 91–92° (lit.[24] m.p. 94°).

A similar oxidation of 370 mg. of the vinyl ether V gave 150 mg. (52%) of *o*-benzoylbenzil, m.p. 90–92°, which after recrystallization from carbon tetrachloride had m.p. 91–92°. A mixture of the two samples of *o*-benzoylbenzil had m.p. 91–92°, and the infrared spectra of the two samples were identical.

Bromination of Complex A.—To 1.0 g. of complex A and 50 ml. of chloroform there was added 2.5 ml. of a solution of 0.4 ml. of bromine in 10.2 ml. of chloroform (approximately 1 mole of bromine per mole of A). After stirring this mixture for 1 hr. in the cold, the red solid which separated (either PdClBr or PdBr₂) was filtered and the chloroform removed *in vacuo* to give a black residue. Extraction of the residue with pentane gave 0.55 g. of a yellow oil which slowly solidified and was recrystallized twice from ethanol to yield colorless leaflets, m.p. 167.5–168.5°.

Anal. Calcd. for $C_{28}H_{20}O$: C, 90.3; H, 5.4; mol. wt., 372. Found: C, 90.5; H, 5.5; mol. wt., 383.

A comparison of infrared spectra and a mixed m.p. determination showed that this product was identical with an authentic specimen of tetraphenylfuran (VI), m.p. 169–170°, prepared by the method of Lutz, *et al.*[25]

Pyrolysis of Complex B.—A 3.4-g. sample of complex B, placed in a vacuum sublimation apparatus, was gently heated with a free flame at 0.1 mm. pressure until decomposition was complete. From the greenish-black sublimate there was obtained, after slow crystallization from benzene, 0.7 g. (26%) of large colorless prisms of 1,4-dichloro-1,2,3,4-tetraphenylbutadiene (VII), m.p. 183°. The ultraviolet spectrum of the diene showed two flat peaks: ca. 275 (ϵ, 3.9 × 10⁴) and ca. 230 mμ (ϵ, 8.7 × 10⁴).

Anal. Calcd. for $C_{28}H_{20}Cl_2$: C, 78.7; H, 4.7; Cl, 16.6; mol. wt., 427. Found: C, 78.5; H, 4.6; Cl, 16.5; mol. wt., 402.

Conversion of the Butadiene VII into the Furan VI.—A mixture of 193 mg. of the diene VII was refluxed with 20 ml. of 50% (v./v.) aqueous sulfuric acid for 24 hr. Ether extraction of the diluted reaction mixture afforded a crude brown crystalline product which was purified by chromatographing on alumina. There was thus obtained 100 mg. of the furan VI, m.p. 168–169°, which had m.p. 169–170° when mixed with an authentic sample of VI.[25] The infrared spectra of the two samples of VI were identical.

Attempted Diels-Alder Reactions with Complex B.—A solution of 1.0 g. of complex B in 100 ml. of chloroform, saturated with hydrogen chloride, containing 1.0 g. of dimethyl acetylenedicarboxylate was allowed to stand overnight. The 0.6 g. of a red crystalline solid which separated proved to be unchanged B. An additional 0.3 g. of B was obtained by evaporation of the chloroform filtrate and extraction with petroleum ether. From the petroleum ether extract there was obtained 1.0 g. of the unchanged acetylenic ester

Under identical conditions neither tolan nor 2-butyne reacted with complex B. Further, when 0.5 g. of B was heated for 24 hr. with 10.0 g. of tolan on the steam-bath, no reaction occurred.

Conversion of Complex B to Complex C.—Upon stirring 280 mg. of B with 30 ml. of ethanol for 18 hr. at room tem-

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(24) A. G. Banus, *Ann. Soc. espan.*, **26**, 387, 393 (1928); "Beilstein," Vol. II, part 7, II, p. 841.

(25) R. E. Lutz, C. R. Bauer, R. G. Lutz and J. S. Gillespie, *J. Org. Chem.*, **20**, 218 (1955).

perature there was obtained 262 mg. (88%) of a yellow insoluble complex (C) whose appearance, solubility properties and infrared spectrum were quite different from those of complex A. In particular, the infrared spectrum of C showed a very strong absorption band at 9.4 μ which is absent in that of A.

Anal. Calcd. for $(C_{30}H_{25}OPdCl)_x$: C, 66.3; H, 4.5; Pd, 19.6 EtO, 8.3. Found: C, 65.6; H, 4.7; Pd, 19.8; EtO, 8.3.

Treatment of complex C with hydrogen chloride in chloroform regenerated the cyclobutadiene complex B in virtually quantitative yield. When complex A was stirred with ethanol for 18 hr. it was recovered unchanged.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, STANFORD, CALIF.]

A Mechanism for the Cleavage of Unsaturated Acids with Molten Alkali
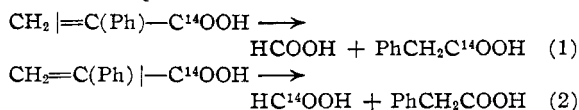
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A radiochemical and stoichiometric study of the scission of α,β-unsaturated acids with molten potassium hydroxide has been undertaken, using the cleavage of 2-phenylacrylic acid into formic and phenylacetic acids as a prototype. 2-Phenylacrylic-1-C^{14} acid yielded essentially non-radioactive formic acid, along with phenylacetic acid labeled exclusively at the carboxyl function. These results indicate that the formic acid product arose exclusively from the methylene carbon of 2-phenylacrylic acid and that no molecular rearrangements accompanied the fission, conclusions confirmed by similar experiments with 2-phenylacrylic-2-C^{14} acid. The alkali fusion of 2-phenylacrylic acid was accompanied by the liberation of over one mole of hydrogen and the production of no methanol, while the fusion of formaldehyde polymer with alkali yielded hydrogen, methanol and formic acid. A consistent mechanism for the alkali cleavage of α,β-unsaturated acids is proposed, involving β-hydroxylation followed by a retrograde aldol reaction.

Although the scission of an α,β-unsaturated acid into two acid fragments by action of molten alkali is a general reaction[2] recognized for over one-hundred years, no mechanistic study of this interesting process seems so far to have been undertaken. In the mid-nineteenth century Chiozza[3] and Kraut[4] noted the formation of benzoic and acetic acids along with hydrogen when cinnamic acid was added to molten potassium hydroxide. Later investigators made similar findings: acrylic acid yielded formic and acetic acids,[5] crotonic acid gave acetic acid,[6] and 2-phenylacrylic acid produced formic and phenylacetic acids[7] when fused with potassium hydroxide. Longer chain, non-conjugated fatty acids were observed to undergo a similar fission with molten alkali, with the interesting additional feature that the double bond usually migrated into the α,β-position prior to cleavage. Thus oleic acid yielded palmitic and acetic acids[8,9] and undecylenic acid gave nonanoic and acetic acids[10] under these conditions. That cleavage could occur prior to complete migration of the double bond into the conjugated position, however, was shown by Noorduyn[11] who isolated formic, acetic, propionic, butyric and valeric as well as C_{14}–C_{17} - acids when oleic acid was treated with potassium hydroxide at 260–280°. In view of the lack of fundamental information on such reactions, we have now undertaken their study from a mechanistic viewpoint. 2-Phenylacrylic acid was selected as the prototype for investigation in view of the ease of isolation of its reaction products and the smoothness (*e.g.*, lack of charring)

with which its fusion with potassium hydroxide was found to proceed.

The first question to be considered was the origin of the formic and phenylacetic acids produced when 2-phenylacrylic acid is cleaved with molten alkali. While the results described in the literature might argue that eq. 1 should summarize the cleavage path we felt in view of the very stringent reaction conditions that neither 2, a combination of 1 and 2, nor the possibility of accompanying molecular rearrangement could be excluded *a priori*. A distinction between 1 and 2

$$CH_2\!=\!C(Ph)\!-\!C^{14}OOH \longrightarrow$$
$$HCOOH + PhCH_2C^{14}OOH \quad (1)$$

$$CH_2\!=\!C(Ph)\!-\!C^{14}OOH \longrightarrow$$
$$HC^{14}OOH + PhCH_2COOH \quad (2)$$

should be possible using carboxyl-labeled 2-phenylacrylic acid, 1 affording carboxyl-labeled phenylacetic acid and 2 labeled formic acid.

The radiochemical consequences of the alkali fusion of 2-phenylacrylic-1-C^{14} acid are summarized in the first line of Table I, where it is seen that only

TABLE I

RELATIVE RADIOACTIVITIES ON FUSION OF LABELED 2-PHENYLACRYLIC ACIDS WITH POTASSIUM HYDROXIDE

2-Phenylacrylic acid labeled at	Formic acid	Phenylacetic acid	Benzoic acid
C1: 1.000	0.063	1.013	0.0027
C2: 1.000	0.015	1.021	1.012

6.3% of the original radioactivity was associated with the formic acid product. The bulk of the label was located in the carboxyl group of the phenylacetic acid product, as demonstrated by oxidation of the latter to benzoic acid bearing less than 0.3% of the base radioactivity. These results argue for the essentially total intervention of 1 as the cleavage pattern of 2-phenylacrylic acid, with significant contributions of 2, C2–C1 phenyl migration or C2–C3 phenyl migration being specifically excluded.

To confirm these conclusions we have also undertaken the alkaline cleavage of 2-phenylacrylic-

(1) The authors are grateful to the National Science Foundation (NSF-G9479) for its generous support of this investigation.

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(4) K. Kraut, *ibid.*, **147**, 113 (1868).

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