Reactions of Palladium(II) with Organic Compounds. Part I. Oxidative Cyclisation of 3-Methyl-3-phenylbut-1-ene and 3,3,3-Triphenylpropene

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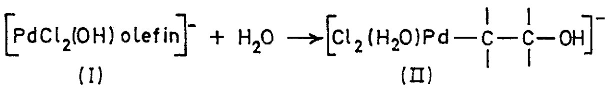
The olefins $PhR_2C{\cdot}CH{:}CH_2$ (R = Ph or Me) undergo oxidative cyclisation to give the corresponding 1,1-disubstituted indenes when treated with palladium(II) acetate in acetic acid at 80°. Evidence is adduced that reaction does not occur *via* the expected oxypalladation adducts and that little or no carbonium-ion character is generated in the olefinic carbon skeleton during reaction. The probable pathway involves a relatively slow intramolecular electrophilic aromatic substitution within a π-olefin complex.

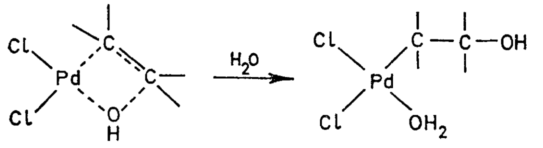
SINCE the development of the Wacker process, in which palladium(II) ions are used to catalyse the oxidation of ethylene to acetaldehyde with oxygen as the ultimate electron acceptor,[1] there has been intensive interest in the mechanisms of reaction of palladium(II) salts with olefins.[2] We have initiated studies in this field, and in the present work have focused attention on one facet of the problem, namely, the possible development of carbonium-ion character in the organic component during the addition of palladium(II) ion to an olefinic bond.

The rate-determining step in the oxypalladation of simple olefins with palladium(II) chloride in water is considered to be the reaction of the complex (I) with water to give the oxypalladation product (II). The rate varies little with the structure of the olefin, from which it has been concluded that there is little carbonium-ion character in the transition state; the results are consistent with the occurrence of a concerted, non-polar, four-centre addition reaction (2).[3]



$$[\mathrm{PdCl_2(OH)\,olefin}]^- + \mathrm{H_2O} \longrightarrow [\mathrm{Cl_2(H_2O)Pd{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}OH}]^- \quad (1)$$

(I) (II)



(2)

There is less detailed information about the mode of reaction of olefins with palladium(II) acetate in acetic acid. However, the distribution of the products (enol and allyl acetates) from simple monosubstituted ethylenes, which are thought to be formed by way of the oxypalladation adducts $RCH(OAc){\cdot}CH_2{\cdot}Pd(OAc)$ and $RCH(PdOAc){\cdot}CH_2{\cdot}OAc$,[4] shows that there is a marked discrimination by the reagent between the two olefinic carbon atoms, as would be expected if the addition of the reagent were to give a carbonium ion.

The method which we used to seek further information bearing on this problem was based on the principle that the development of a carbonium ion of the type (IV) by reaction of an olefin with palladium(II) acetate should be followed by, or attended with, rearrangement to give the carbonium ion (V). We chose the olefins (III; R = Ph) and (III; R = Me) for this purpose, the choice of the former being based on two considerations. First, we wished to compare the behaviour of palladium(II) with that of lead(IV) as an oxidant for olefins; both metal ions can effect two-electron oxidations, and it has already been shown that a 1,2-phenyl shift occurs when the olefin (III; R = Ph) is oxidised with lead tetraacetate [reaction (3); R = Ph, $Pb(OAc)_3$ for $Pd(OAc)$].[5] Secondly, whereas 3,3-dimethylbut-1-ene reacts with hydrogen chloride to give 60% of the adduct $Me_2CCl{\cdot}CHMe_2$ *via* the carbonium-ion rearrangement[6] $Me_3C{\cdot}\overset{+}{C}HMe \longrightarrow Me_2\overset{+}{C}{\cdot}CHMe_2$, no rearranged product has been detected from reaction of this olefin with bromine,[7] probably because the cation (VI) is stabilised, as shown, by the neighbouring bromine substituent[8] so that its tendency towards rearrangement is less than for the cation $Me_3C{\cdot}\overset{+}{C}HMe$. In contrast, reaction of the olefin (III; R = Ph) with bromine gives rearranged products [*e.g.*, $Ph_2C(OMe){\cdot}CHPh{\cdot}CH_2Br$ in methanol[9]], reflecting the greater migratory aptitude of a phenyl as compared with a methyl group within the system $R_3C{\cdot}\overset{+}{C}HR'$ (R = Ph or Me). Thus, the olefin (III; R = Ph) provides a more sensitive probe than, *e.g.*, 3,3-dimethylbut-1-ene for the development of carbonium-ion character during electrophilic addition; in particular, we should expect to observe a 1,2-phenyl shift in the cation (IV) providing

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[1] J. Smidt, W. Hafner, R. Jira, R. Sieber, J. Sedlmeier, and A. Sabel, *Angew. Chem. Internat. Edn.*, 1962, **1**, 80.

[2] E. W. Stern, *Catalysis Reviews*, 1967, **1**, 73.

[3] P. M. Henry, *J. Amer. Chem. Soc.*, 1966, **88**, 1595.

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[5] R. O. C. Norman and C. B. Thomas, *J. Chem. Soc.* (*B*), 1967, 604.

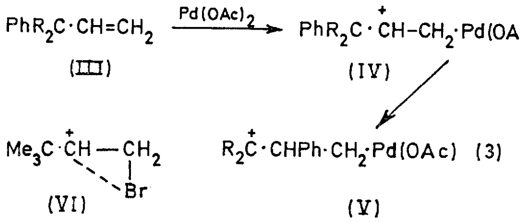
[6] G. G. Ecke, N. C. Cook, and F. C. Whitmore, *J. Amer. Chem. Soc.*, 1950, **72**, 1511.

[7] W. H. Puterbaugh and M. S. Newman, *J. Amer. Chem. Soc.*, 1957, **79**, 3469.

[8] P. B. D. de la Mare and J. G. Pritchard, *J. Chem. Soc.*, 1954, 3990; P. B. D. de la Mare, P. G. Naylor, and D. L. H. Williams, *ibid.*, 1962, 443; P. B. D. de la Mare and S. Galandauer, *ibid.*, 1958, 36.

[9] R. O. C. Norman and C. B. Thomas, *J. Chem. Soc.* (*B*), 1967, 598.

that stabilisation by the neighbouring palladium substituent was no greater than by neighbouring bromine.



RESULTS AND DISCUSSION

Oxidation of the olefin (III; R = Ph) with palladium(II) acetate at 80° in acetic acid gave 1,1-diphenylindene (IX; R = Ph) as the major product. 1,2-Diphenylindene, 2-acetoxy-1,1-diphenylindane, and 2,3,3-triphenylallyl acetate could not be detected, and although ^{1}H n.m.r. and i.r. spectrometry of the crude product showed the presence of small quantities of other materials including acetates, none were eluted by g.l.c. at 230° and they were probably polymeric. In some reactions up to 1% of 1,1-diphenylindane was detected, but its yield was irreproducible; in some reactions which were monitored periodically it was observed only in some samples, its proportion generally increasing with time. It was probably formed from the indene at the surface of the precipitated palladium, the state of coagulation (and hence the surface activity) of which would probably vary from one sample to another; it is notable that 1-methylindene gives a small yield of 1-methylindane on palladium–charcoal at 100°.[10]

In initial experiments, samples from the oxidation mixture were removed periodically and added to carbon tetrachloride; after this solution had been washed, dried, and evaporated to small volume, it was analysed by g.l.c. As the results in Table 1 show, the material balance, particularly after the first 4 min of the reaction, was very low; the data suggested that much of the olefin was rapidly removed to form a complex which generated the indene slowly and which regenerated a variable proportion of the olefin during work-up (see later). In an attempt to release the olefin from such a complex, bis(methylenediphenylphosphine) was included in the carbon tetrachloride solution for work-up; this substantially increased the proportion of the reactant which was accounted for by g.l.c. analysis, as shown in Table 2. Deaeration of the reactant solutions failed to improve the yield of either recovered olefin or indene.

Oxidation of the olefin (III; R = Me) under similar conditions gave 1,1-dimethylindene (IX; R = Me) as the major product; 1,2-diacetoxy-3-methyl-3-phenylbutane and 1,3-diacetoxy-3-methyl-2-phenylbutane could not be detected. The results obtained by periodic sampling of the reaction mixture, with the inclusion of bis(methylenediphenylphosphine) in the work-up procedure, are in Table 3. Both the indenes (IX; R = Ph or Me) were shown to be susceptible to oxidation under the reaction conditions, and this doubtless underlies the eventual reduction in the yield of each recorded in Tables 1—3.

TABLE 1

Products from the oxidation of 3,3,3-triphenylpropene with palladium(II) acetate in acetic acid at 80°

Time/min	Unchanged olefin (%)	1,1-Diphenylindene (%)
4	19	10
9	27	25
13	28	38
20	3	51
65	2	65
115	0·8	65
250	0·1	63
500	0	44

TABLE 2

Products from the oxidation of 3,3,3-triphenylpropene with palladium(II) acetate in acetic acid at 80° with inclusion of the phosphine in work-up

Time/min	Unchanged olefin (%)	1,1-Diphenylindene (%)
4	77	6·3
8	56	20
12	46	26
21	26	35
40	14	52
120	1·0	62
250	0·3	52
500	0	37

TABLE 3

Products from the oxidation of 3-methyl-3-phenylbut-1-ene with palladium(II) acetate in acetic acid at 80° with inclusion of the phosphine in work-up

Time/min	Unchanged olefin (%)	1,1-Dimethylindene (%)
5	76	4
10	59	11
20	39	16
35	22	23
150	12	41
250	2·4	48
600	0·9	54
870	0	45

The course of oxidation of the olefin (III; R = Ph) with palladium(II) acetate is markedly different from that with lead(IV) acetate, the former reaction giving cyclised product and none of the rearranged products such as 2,3,3-triphenylallyl acetate which characterise the latter reaction. Comparison of the results with those for reaction of this olefin with bromine shows also that less carbonium-ion character is developed at C-2 of the olefin in the oxidation than in the bromination.

Two mechanisms are consistent with this observation. The first involves a four-centre reaction to give the oxypalladation adduct (VII); the formation of the indene (IX; R = Ph) from this adduct could in principle occur according to reaction (4). However, when the

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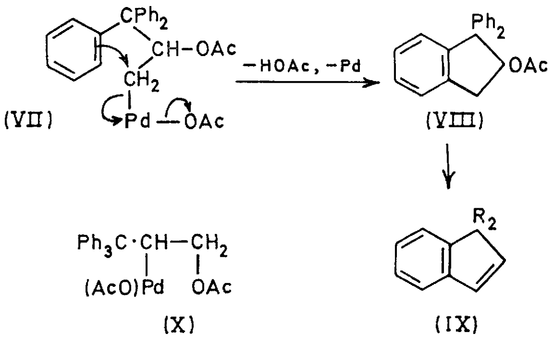
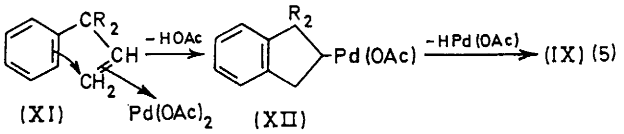
[10] H. Christol, F. Plenat, and C. F. Huebner, *Bull. Soc. chim. France*, 1964, 2640.

proposed intermediate acetoxy-compound (VIII) was submitted to the oxidation procedure it was recovered unchanged, so that the indene itself is not formed in this way. Moreover, neither the acetoxy-compound (VIII) nor other products to be expected from the oxypalladation adduct (VII) or its isomer (X) (*i.e.*, enol and allyl acetates [4]) could be detected, from which we infer that oxypalladation does not occur under our conditions.



(4)

The second mechanism involves formation of the π-olefin complex (XI), analogous to the species which have been invoked as intermediates in the oxidation of olefins by mercury(II) acetate [11] and thallium(III) acetate.[12] We envisage formation of the indene (IX; $R = Ph$ or Me) as in reaction (5) (in which other palladium ligands are not specified), and this pathway * is consistent with all the experimental data, as the following comments show.



First, little cationic character should be associated with the olefinic part of the complex (XI) since donation of electrons from the bonding π-orbital of the olefin should be largely offset by the acceptance of electrons into the antibonding π-orbital from a palladium *d*-orbital. Secondly, the lack of formation of enol and allyl acetates would follow given only the reasonable proviso that intramolecular nucleophilic attack by the aromatic ring as in reaction (5), which is stereochemically favourable, occurs in preference to external attack by acetate ion to give oxypalladation adducts. Thirdly, the formation of the indene (IX) from the suggested intermediate (XII) has precedent in the generation of enol and allyl acetates from oxypalladation adducts by the loss, formally, of HPd(OAc).[4] Finally, the effect of addition of the bidentate phosphine ligand in the work-up described shows that the olefin and palladium(II) form a complex from which the olefin is readily displaced. The complex is unlikely to be an oxypalladation adduct or a related species such as (XII) since tertiary phosphine ligands, including the one we used, do not cleave σ-C–Pd bonds; [15] however, they are effective at displacing ligands such as chloride and amino from palladium.[15]

We sought further information about the nature of the complex by following the changes with time of the electronic absorption spectrum when a solution of palladium(II) acetate and the olefin (III; $R = Me$ or Ph) in acetic acid was kept at 40°. With each olefin, the peak due to palladium(II) acetate at 398 nm decreased slowly during 4 h; with olefin (III; $R = Me$) it was replaced by new maxima at 286—292 and 345 nm, with an isosbestic point at 378 nm, and with olefin (III; $R = Ph$) it was replaced by new maxima at 291, 298·5, and 347 nm, with an isosbestic point at 377 nm. The new maxima are not those of the indenes, and are evidently due to the complex. A product study of reaction of the olefin (III; $R = Ph$) at the same temperature, with inclusion of the bidentate phosphine ligand in the work-up procedure, showed that no indene had been formed after 30 min and 89% of the olefin was recovered. However, when the phosphine ligand was omitted, only 51% of the olefin was recovered, palladium precipitated when the carbon tetrachloride solution of the crude product was heated, and 18% of the indene (IX; $R = Ph$) was obtained. We infer that formation of the complex at 40° occurs much more rapidly than its conversion into the indene and that the complex, which is soluble in carbon tetrachloride, can yield the indene readily at a higher temperature.

EXPERIMENTAL

^{1}H N.m.r. spectra of solutions were measured with a Perkin-Elmer R10 60 MHz spectrometer; i.r. spectra with a Unicam SP 200G spectrometer, with polystyrene calibration; u.v. spectra with a Unicam SP 800 spectrometer; mass spectra with an A.E.I. MS 12 spectrometer. G.l.c. analyses were carried out with a Pye instrument (Series 104,

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* For the formation of styrenes from olefins and benzenoid compounds under the influence of palladium(II), it has been suggested that an initial π-arene–π-olefin complex collapses successively to a σ-arene-π-olefin and a σ-arene–σ-olefin complex before extruding palladium(0).[13] An intramolecular variant of this process is unlikely to apply to reaction of the compounds (III), for steric reasons. Thus, the only authenticated examples of dienes which complex with palladium(II) through both unsaturated sites are those in which the two olefinic bonds can lie parallel (*e.g.*, 4-vinylcyclohexene and norbornadiene); [14] this cannot be so for the aromatic ring and the bond in the compounds (III) without introduction of severe compressional forces, in particular between an *ortho*-hydrogen atom and a hydrogen atom at C-1.

[11] H. J. Lucas, F. R. Hepner, and S. Winstein, *J. Amer. Chem. Soc.*, 1939, **61**, 3102.

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model 24), with 5 ft × 0·25 in columns and a flow rate of 100 ml min^{-1} of nitrogen carrier-gas; results were reproducible to within ±2%. In some experiments the eluant was fed from the chromatograph *via* a heated stainless-steel capillary into the mass spectrometer.

Materials.—Palladium(II) acetate was Johnson-Matthey reagent. Acetic acid (SLR grade) had m.p. 16·48°, which corresponds[16] to a water content of 0·06% by weight. Light petroleum had b.p. 40—60°. 3,3,3-Triphenylpropene,[17] 1,2-diphenylindene,[5] and 2,3,3-triphenylallyl acetate[5] were available from previous work.

3-Methyl-3-phenylbut-1-ene was prepared by addition of allylbenzene and then bromomethane to a solution of sodamide in liquid ammonia.[18] Fractional distillation of the organic products gave the required olefin, b.p. 81° at 15 mmHg; *m/e* 146 (*M*); τ (CCl_4) 2·8 (5H, m), 4·0 (1H, m), 5·0 (2H, m), and 6·82 (6H, s). G.l.c. (10% diethylene glycol adipate, 125°) showed the product to be 98% pure, the impurities being 3-phenylbut-1-ene and 1-phenylbut-1-ene.

1,1-Dimethylindene was prepared from mesityl oxide in six steps. The oxide was converted into 4-methyl-4-phenylpentan-2-one,[19] τ (neat liquid) 2·6—2·9 (5H, m), 7·40 (2H, s), 8·37 (3H, s), and 8·65 (6H, s). This ketone was subjected to the haloform reaction to give 3-methyl-3-phenylbutanoic acid,[19] b.p. 130° at 0·14 mmHg (lit.,[19] 155° at 10 mmHg), τ (CCl_4) −1·86 (1H, s), 2·6—3·0 (5H, m), 7·45 (2H, s), and 8·59 (6H, s). Treatment of this acid with phosphorus pentachloride and then aluminium trichloride in dry benzene[19] gave 3,3-dimethylindan-1-one, b.p. 83° at 0·3 mmHg (lit.,[19] 110° at 8 mmHg), τ (neat liquid) 2·2—2·9 (4H, m), 7·52 (2H, s), and 8·70 (6H, s); no impurities were detected by g.l.c. (5% Carbowax, 130°). Reduction of the ketone (21·5 g) in ethanol (80 ml) with sodium borohydride (2·8 g) in water (35 ml) at pH 8·5, during 45 min at 0° and then 90 min at 20°, yielded 3,3-dimethylindan-1-ol (19·9 g, 91%), b.p. 72° at 0·1 mmHg (lit.[20] 107° at 4·2 mmHg), τ (CCl_4) 2·7—3·0 (4H, m), 4·9—5·1 (1H, apparent t), 6·73 (1H, s, exchanged in D_2O), 7·7—8·5 (2H, 8-line m), 8·72 (3H, s), and 8·88 (3H, s); the multiplets centred at τ 5·0 and 8·1 were analysed as an ABX system[21] with τ_A 8·35, τ_B 7·83, τ_X 4·99, J_{AX} 7·0, J_{BX} 6·5, and J_{AB} 12·8 Hz. The indanol (6 g) was heated under reflux in 30% sulphuric acid (50 ml) for 4 h. The cooled solution was diluted to 150 ml and then extracted with ether (2 × 50 ml) to give 1,1-dimethylindene (4·5 g, 84%), b.p. 185° (corrected); *m/e* 144 (*M*); τ (CCl_4) 2·85 (4H, s), 3·44 (1H, d, *J* 5·5 Hz), 3·74 (1H, d, *J* 5·5 Hz), and 8·72 (6H, s), matching the spectrum illustrated in ref. 20. The indene (1·0 g) was hydrogenated in ethanol (30 ml) over 10% palladium on charcoal (0·1 g) during 2 h at 60 lb in^{-2} and 20°. Evaporation of the filtered solution gave 1,1-dimethylindane (1·0 g, 99%), b.p. 186° (lit.,[22] 187—188°), in which no impurities could be detected by g.l.c. (2·5% polyethylene glycol adipate, 120°); *m/e* 146 (*M*); ^1H n.m.r. spectrum as previously reported.[22]

1,1-Diphenylindene was prepared from triphenylmethanol. Reaction of this alcohol with malonic acid at 160° gave[23] 3,3,3-triphenylpropionic acid, m.p. 179—181° (lit.,[24] 177°; lit.,[25] 179—180°), τ ($CDCl_3$) −0·30 (1H, s), 2·79 (15H, s), and 6·32 (2H, s). Treatment of the acid in dry benzene with phosphorus pentachloride and then aluminium trichloride[19] afforded 3,3-dimethylindan-1-one, m.p. 130—132° (lit.,[19] 131°), τ ($CDCl_3$) 2·0—2·9 (14H, m) and 6·50 (2H, s); $\nu_{\text{max.}}$ ($CHCl_3$) 1705 cm^{-1}. Reduction of this ketone with lithium aluminium hydride in dry ether[26] yielded 3,3-diphenylindan-1-ol as colourless rods, m.p. 136·0—136·5° (from ethanol) (lit.,[26] 131—132°), τ ($CDCl_3$) 2·5—3·0 (14H, m), 4·7—5·0 (1H, m), 6·6—7·5 (2H, m), and 7·85 (1H, d, exchangeable); the spectrum was simplified by D_2O exchange and was then analysed as an ABX system with τ_A 6·72, τ_B 7·32, τ_X 4·87, J_{AB} 13, J_{AX} 6·2, and J_{BX} 7·5 Hz. The alcohol was heated with toluene-*p*-sulphonic acid in acetic acid under reflux to give 1,1-diphenylindene[26] as colourless prisms, m.p. 90·5—91·5° (from ethanol) (lit.,[26] 91—92°); *m/e* 268 (*M*); τ 2·85 (14H, s) and 3·29 (2H, s).

The hydrogenation of 1,1-diphenylindene in dry methanol over 10% palladium on charcoal during 3 h at 60 lb in^{-2} and 20° yielded 1,1-diphenylindane (67%) as colourless flakes, m.p. 67—68° (from ethanol) (lit.,[27] 67° or lit.,[28] 70°); *m/e* 270 (*M*); τ ($CDCl_3$) 2·90 (14H, s) and 7·16 (4H, s). G.l.c. (2% Carbowax: 240°) showed that the indane was not contaminated by the indene.

2-*Acetoxy*-1,1-*diphenylindane*. Triphenylacetic acid was converted into its acid chloride[29] and thence into the diazo-ketone.[30] The diazo-ketone with boron trifluoride–ether complex[31] gave 1,1-diphenylindan-2-one as pale yellow rhombs, m.p. 125·5—126° (from light petroleum) (lit.,[31] 120·5—121·5° and 129—130·5°); τ ($CDCl_3$) 2·6—3·1 (14H, m) and 6·34 (2H, s); $\nu_{\text{max.}}$ ($CHCl_3$) 1745 cm^{-1} (C=O); $\lambda_{\text{max.}}$ as reported.[31] Reduction of the ketone with lithium aluminium hydride in dry ether yielded the alcohol as a low-melting solid which could not be crystallised [τ (CCl_4) 2·2—3·4 (14H, aromatic m), 4·8—5·1 (1H, 4-line m), 6·7—7·6 (2H, 8-line m), and 8·59 (1H, exchangeable in D_2O); the non-aromatic multiplets were analysed as an ABX system with τ_A 6·91, τ_B 7·4 3,τ_X 4·96, J_{AB} 14·7, J_{AX} 6·0, and J_{BX} 6·8 Hz; $\nu_{\text{max.}}$ ($CHCl_3$) 3610 cm^{-1} (O–H) and no C=O absorption; *m/e* 286 (*M*, 100%), 269 (*M* − OH, 32), and 268 (*M* − H_2O, 87)]. This was heated with acetic anhydride on a steam-bath for 1 h to give 2-*acetoxy*-1,1-*diphenylindane* as an oily solid which was recrystallised, with difficulty, from light petroleum or carbon tetrachloride to yield colourless prisms, m.p. 118—122° (slow decomp.); τ (CCl_4) 2·4—2·9 (14H, m), ABX system (3H) (with τ_A

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6·68, τ_B 7·21, τ_X 3·77, J_{AB} 16·0, J_{AX} 5·0, and J_{BX} 4·5 Hz), and 8·33 (3H, s); $\nu_{max.}$ 1735 and 1240 cm^{-1} (C=O); *m/e* 286 (*M* − keten, 54%), 268 (*M* − AcOH, 100), and 43 (CH_3CO^+, 81) (Found: C, 84·3; H, 6·2. $C_{23}H_{20}O_2$ requires C, 84·1; H, 6·1%).

Oxidations with Palladium(II) *Acetate*.—(i) *Product identification*. 3,3,3-Triphenylpropene (40·5 mg, 0·151 mmol) and palladium(II) acetate (33·4 mg, 0·156 mmol) were heated in acetic acid (10 ml) at 80°. Black palladium separated after 30 min. After 3 h the mixture was poured into carbon tetrachloride (40 ml) and extracted with ice–water (40 ml). The organic layer and the carbon tetrachloride extract of the aqueous layer were combined, washed with water (2 × 280 ml), and dried (K_2CO_3). The volume of the solution was reduced by distillation, the colloidal palladium which had coagulated was filtered off, and the remaining solvent was distilled to leave a gum (40·5 mg) whose ^{1}H n.m.r. and i.r. spectra were essentially the same as those of 1,1-diphenylindene. A weak ^{1}H n.m.r. signal at τ 8·77 and i.r. bands at 2940 and 2870 cm^{-1} suggested saturated hydrocarbon groupings, and very weak i.r. absorption between 1710 and 1790 cm^{-1} was consistent with trace amounts of acetates.

G.l.c. analysis on a 2% Carbowax (*M* = 20,000) column at 225° showed one major product (retention time 6·5 min), shown by mixed injection with an authentic sample and mass spectrometry (see later) to be 1,1-diphenylindene, and a minor product (retention time 11·7 min) whose peak area was <0·5% that of the indene peak. There were no peaks corresponding to 1,1-diphenylindane, 1,2-diphenylindene, 2-acetoxy-1,1-diphenylindane, or 2,3,3-triphenylallyl acetate, showing that these materials could not have been present in more than 0·1% yield (for 1,1-diphenylindane) or 0·3% yield (for the remainder). The g.l.c. identification of 1,1-diphenylindene was confirmed with a 5% silicone column (retention time 4·8 min at 220°), and elution of the material into the mass spectrometer gave a spectrum matching that of an authentic sample. The other products indicated by the ^{1}H n.m.r. and i.r. spectra were presumed to be polymeric since they were not eluted from the g.l.c. columns after 1 h at 230°.

3-Methyl-3-phenylbut-1-ene was oxidised likewise during 8 h and the products were extracted as described previously. Most of the carbon tetrachloride was distilled off through a Vigreux column. The ^{1}H n.m.r. and i.r. spectra of the residue were essentially those of 1,1-dimethylindene, though weak i.r. absorption between 1730 and 1755 cm^{-1} suggested trace amounts of acetates. G.l.c. analysis on a 10% polyethylene glycol (*M* = 6000) column at 140°, a 2·5% polyethylene adipate (*M* = 20,000) column at 140°, or a 5% silicone column at 150° showed only one product; its retention time was the same as that of 1,1-dimethylindene, and its mass spectrum, obtained after elution from the second column into the spectrometer, was identical with that of 1,1-dimethylindene. The chromatograph from the third column showed that 1,2-diacetoxy-3-methyl-3-phenylbutane or 1,3-diacetoxy-3-methyl-2-phenylbutane could not have been present in greater than 0·3% yield.

(ii) *Quantitative analysis*. Separate solutions of the olefin (0·4 mmol) and palladium(II) acetate (0·4 mmol), each in acetic acid, were preheated in a thermostat-bath at 80° and then mixed to a total volume of 10 ml in a stoppered flask. At suitable intervals, 2 ml samples were removed and added to carbon tetrachloride (20 ml) containing a g.l.c. standard and (except for the experiments in Table 1) bis(methylenediphenylphosphine) (30 mg). The resulting mixture was washed with water (20 ml), and the organic solution and the carbon tetrachloride extract (10 ml) of the aqueous layer were combined. After further washing with water (2 × 20 ml), the organic solution was dried (K_2CO_3) to remove the last traces of acetic acid. Most of the carbon tetrachloride was then removed by distillation through a short Vigreux column, and the residue was submitted to g.l.c.

Products from 3-methyl-3-phenylbut-1-ene were analysed on 10% polyethylene glycol at 140° with nitrobenzene as internal standard; those from 3,3,3-triphenylpropene were analysed on 5% silicone oil at 220°, with benzil as internal standard.

(iii) *Evidence for formation of an olefin complex*. (*a*) 3,3,3-Triphenylpropene was oxidised in the usual way, but at 40°, during 30 min. The reaction mixture was then worked up, but without the phosphine ligand. No palladium had precipitated at this stage, but it did so during the distillation of the carbon tetrachloride extract to small volume. G.l.c. analysis revealed the formation of 1,1-diphenylindene (18%), and recovery of 51% of the olefin.

The experiment was repeated with inclusion of the phosphine ligand in the work-up procedure. No palladium was observed at any stage in the work-up, no 1,1-diphenylindene was detected, and 89% of the olefin was recovered. The recovery of the olefin increased to 100% when the reaction time was shortened to 2 min.

(*b*) For studies of the changes in the electronic spectrum a solution of palladium(II) acetate (3·9 × 10^{-4}M) and either 3-methyl-3-phenylbut-1-ene (7·0 × 10^{-3}M) or 3,3,3-triphenylpropene (2·6 × 10^{-3}M) in acetic acid was maintained at 40°.

(iv) *Oxidation of the indenes*. A solution of 1,1-diphenylindene (9·4 × 10^{-2} mmol) and palladium(II) acetate (21 × 10^{-2} mmol) was heated for 6·5 h at 80° in acetic acid. There was slow deposition of palladium, and g.l.c. showed that 5·3 × 10^{-2} mmol of the indene remained. In a similar experiment with 1,1-dimethylindene (17·5 × 10^{-2} mmol), 8·7 × 10^{-2} mmol remained.

(v) *Stability of* 2-*acetoxy*-1,1-*diphenylindane under the oxidation conditions*. Oxidation was carried out as in (ii) with 3,3,3-triphenylpropene (20·6 mg) in acetic acid (3 ml) at 80°. After 30 min, a 1 ml sample was added to 2-acetoxy-1,1-diphenylindane (8·9 mg) and then maintained at 80° during a further 30 min. G.l.c. analysis showed that 9·0 ± 0·2 mg of the acetoxy-compound was present.

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