Reactions of Palladium(II) with Organic Compounds. Part 5.[1] Effect of Reaction Conditions upon Products of Oxidation of α-Methylstyrene

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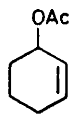
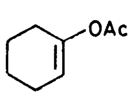
The effects upon product distribution of varying the temperature, time of reaction, and reagent concentrations have been investigated in the oxidation of α-methylstyrene by palladium(II) acetate. Two reaction pathways have been identified. A π-allylic organopalladium compound decomposes slowly in a process catalysed by excess of the alkene to give 2-phenylprop-2-enyl acetate. The second reaction leads to competitive formation of enolic acetates and oxidative dimers but the organopalladium species involved has not been unambiguously identified. The addition of sodium acetate to the reaction, contrary to earlier reports, has only a marginal effect upon the distribution of products.

DESPITE the considerable volume of work directed at elucidating the mode of action of palladium(II) salts with alkenes, a detailed understanding of the factors governing the formation of oxidation products still eludes us. This oxidant, more than most, seems to be critically affected by reaction conditions, the ligands about the metal, and the nature of the alkene. Unfortunately, many apparently complementary studies have used conditions which differed slightly from one another, so reducing the value of comparisons.



(I)



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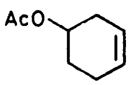


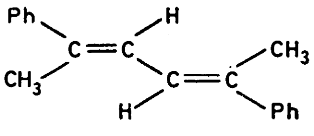
(III)

Two examples will serve to illustrate the problem. In the first report of the oxidation of cyclohexene, Anderson and Winstein claimed that palladium(II) acetate, in acetic acid as solvent, gives exclusively cyclohex-2-enyl acetate (I).[2] Brown and Davidson confirmed this to be the case provided that additives, fortuitous or otherwise, are present to reoxidise palladium(0).[3] In this context oxygen can be employed but it also results in products from free-radical oxygenation at the allylic position. In the absence of a re-oxidant the palladium(0) brings about rapid dehydrogenation of cyclohexene to benzene. The presence of small amounts of strong acid results in the enolic acetate (II) and the homoallylic acetate (III) being formed. Other reports,[4,5] in which the ligands on the metal have been varied, claim that (I) and (III) are produced but not (II). The inclusion of copper(II) salts in such systems results in products of addition across the double bond.[6]

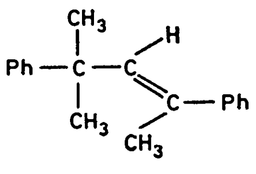
An example of the extreme sensitivity of alkene structure on product distribution comes from the work of Kikukawa *et al.*[7] Three methylenecycloalkanes, from which similar products might have been expected, were oxidised by palladium(II) acetate in acetic acid. Oxidative dimers predominated with methylenecyclohexane, allylic acetates were formed exclusively with a seven-membered ring, whilst methylenecyclopentane produced a large amount of intractable solid material containing palladium.

A detailed investigation was therefore warranted into the effect of reaction parameters on product distribution in oxidations of alkenes. α-Methylstyrene (2-phenylpropene) was chosen as a suitable substrate on several grounds. (i) The expected products are sufficiently volatile that they may be analysed by gas chromatography yet not so low boiling that loss by evaporation poses problems. (ii) Migration of the double bond in the alkene has no effect on the course of reaction. We have found this to be a problem with other systems.[8] (iii) Stereochemical complications in the products are minimal. (iv) Three earlier investigations[9-11] have shown that allylic substitution and oxidative dimerisation are competitive processes with similar rates. The relative effect of changes in conditions can thus easily be studied.

In the first of the previous investigations, Hüttel *et al.* found that, in 50% acetic acid, α-methylstyrene and palladium(II) chloride gave two isolable organopalladium compounds but that, at 105 °C in the presence of sodium acetate, acetophenone and the oxidative dimer (IV) are formed.[9] Volger reported that, with palladium(II) acetate in glacial acetic acid at 85 °C in the presence of sodium acetate, (IV) is obtained in 91%[†] yield together



(IV)



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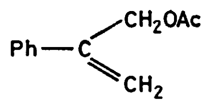
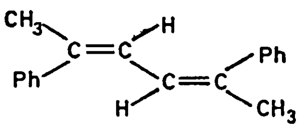


(VI)



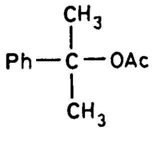
(VII)

[†] The yield claimed may be high by a factor of 2. 1.28 mmol of (IV) was obtained when 2.83 mmol of palladium(II) acetate was required for its production.

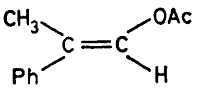
with ' minor amounts of allyl or enol acetates '.[10] In the absence of sodium acetate the non-oxidative dimer (V) was found. Deuterium labelling demonstrated that oxidative dimerisation involved the loss of a vinylic rather than an allylic hydrogen. Uemura *et al.*,[11] under what appear to be essentially similar conditions to those of Volger, obtained 41% (IV), some (V), and 18% of the allylic acetate (VI). The presence of sodium acetate increased the yield of (VI) but otherwise had little effect. The use of palladium(II) chloride led to much lower yields whilst palladium(II) nitrate reversed the ratio of (IV) : (VI) and resulted in a 51% conversion to acetophenone.

RESULTS AND DISCUSSION

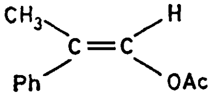
Reaction of α-methylstyrene with palladium(II) acetate in acetic acid at 80 °C gave three major products and several minor ones. Compound (VI) was the predominant monomeric product whilst *two* oxidative dimers were obtained in moderate yield. One of these had ^{1}H n.m.r. parameters in agreement with those reported for (IV).[10] The second is assigned the structure (VII) on the basis of a very similar mass spectrum to that of (IV) and its single ^{1}H n.m.r. signal for a vinylic hydrogen. The chemical shift of this nucleus (τ 3.55) is in reasonable agreement with that calculated by the method of Pascual[12] (τ 3.82). Five minor products were identified: acetophenone, 2-phenylprop-2-yl acetate (VIII), the two enolic acetates (IXa and b), and a third oxidative dimer (molecular ion at *m/e* 234 but the yield was too small for isolation by preparative g.l.c.). It was demonstrated that the first two of these were produced in comparable yields in the absence of palladium(II) and their modes of formation, presumably by autoxidation[13,14] and acid-catalysed addition, respectively, are not discussed further.



(VIII)



(IXa)



(IXb)

The yields from this reaction are in Table 1. Also shown there are the results of a number of experiments in which increasing quantities of sodium acetate were included in the reaction. It can be seen that, contrary to the earlier claims by Volger,[10] the additive has only a marginal effect. It does cause a small decrease in the ratio of (VI) to (IV), but this is the opposite effect to that observed by Uemura *et al.*[11] There is also a minor change in the ratio of (IV) to (VII). The yields of enolic acetates increase steadily but they never become major products.

The relative amounts of alkene and palladium(II) in the system have a much more marked effect on product distribution, as Table 2 shows. Allylic substitution is little affected by increasing the proportion of alkene, but the yield of dimers increases dramatically. On the other hand, enolic acetate formation is repressed, though the results show that this cannot solely be a case of a common intermediate being diverted to give dimers rather than (IX).

TABLE 1

Effect of sodium acetate on the yields of products (% based on Pd^{II}) from the oxidation of α-methylstyrene by palladium(II) acetate[a]

Mol ratio NaOAc : $Pd(OAc)_2$	Products (%)				
			Oxidative dimers		
	(VI)	(IX a and b)	(IV)	(VII)	Other
0	20.9	1.0	18.0	10.5	3.5
1	15.5	2.2	15.7	11.1	2.2
2	13.0	2.6	16.7	11.7	2.2
4	13.6	3.3	16.5	12.1	2.0
7	12.7	4.7	16.7	12.8	2.0
10	12.5	4.8	16.2	13.3	2.0

[a] Palladium acetate (1 mmol) and α-methylstyrene (10 mmol) heated at 80 °C for 20 h in glacial acetic acid (50 ml).

The effect of temperature upon the products is shown in Table 3; increasing temperature favours the allylic acetate at the expense of oxidative dimers. Table 4 sets out the product distribution as a function of reaction time. It is seen that formation of dimers * and enolic products is effectively complete within an hour, indicating that all free oxidant has been consumed at this stage. However, allylic acetate continues to form over a much longer period of time.

TABLE 2

Effect of alkene : oxidant ratio on product distribution from the reaction of α-methylstyrene with palladium(II) acetate[a]

Mol ratio alkene : $Pd(OAc)_2$	Products (% based on Pd^{II})					
			Oxidative dimers			
	(VI)	(IX)	(IV)	(VII)	Other	Total
1	17.7	4.2	0.6	0.2	1.2	2.0
2	24.9	3.7	3.4	5.9	0.9	10.2
4	22.7	2.3	10.9	6.4	1.0	18.3
6	23.1	2.2	14.8	8.5	2.0	25.3
8	21.7	2.1	17.8	9.8	2.3	29.9
10	20.9	1.0	18.0	10.5	3.5	32.0
20	18.3	1.4	20.8	10.9	4.0	35.7

[a] Conditions as in Table 1; no sodium acetate present.

The experiments described above rule out the possibility that the formation of allylic acetate and oxidative dimers is the result of competition between acetate and alkene for an intermediate which is common to both types of product. If this were so, a high concentration of

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* It appears, from the yields of the three oxidative dimers, that some isomerisation of the third, unidentified, one to (IV) occurs with prolonged reaction time. Since the three isomers are presumably formed by a common pathway this problem can be ignored.

acetate ion would favour ester formation and a large excess of alkene would be detrimental. We would also anticipate that the yield of each type of product would increase in a similar manner, whereas the production of dimers is complete before a third of the total allylic acetate has been formed. On the other hand, the small amount of enolic acetate is likely to be formed in competition with oxidative dimer.

TABLE 3

Effect of temperature on product distribution from the reaction of α-methylstyrene with palladium(II) acetate [a]

		Products (% based on Pd^{II})					
				Oxidative dimers			
Temp. (°C)	Reaction time (h)	(VI)	(IX)	(IV)	(VII)	Other	Total
20	336	4.3	1.2	19.6	16.4	11.8	47.8
40	139	8.8	1.3	19.5	15.0	13.0	47.5
60	72	10.2	1.5	16.4	11.0	5.4	32.8
80	20	20.9	1.0	18.0	10.5	3.5	32.0
98.5	15	20.2	1.8	12.9	9.9	1.4	24.2
116.5	12	32.0	3.6	15.5	9.7	1.1	26.3

[a] Reagent concentrations as in Table 1; no sodium acetate present.

The major problem is to identify the organopalladium intermediates involved in the reaction. Wolfe and Campbell[5] have demonstrated that allylic oxidation of cyclohexene by palladium(II) acetate in acetic acid proceeds *via* a symmetrical π-allyl complex but they have also claimed,[15] on the basis of the products of decomposition, that this cannot be the dimeric complex (X). We synthesised the analogous complex from α-methylstyrene and subjected it to the reaction conditions. It proved remarkably resistant to solvolysis. After 24 h at 80 °C only a small amount of palladium had deposited, most of the complex was recovered, and analysis of the organic material in solution revealed only a small amount (*ca.* 3%) of (VI) together with a trace of α-methylstyrene.

However, in the presence of added α-methylstyrene this π-allylic complex yielded (VI) as the sole product (35 and 59% after 4 and 6.5 h, respectively). No dimeric products were detected. It was shown that the π-allylic complex was not promoting the oxidation of the *added* alkene by using *trans*-β-methylstyrene [(*E*)-1-phenylpropene] as the additive in an otherwise similar experiment: 36% (VI) was obtained in 4 h and no products from β-methylstyrene were found. The rate of formation of (VI) from the complex is in line with its rate of production in the direct oxidation. The experiments of Wolfe and Campbell on the decomposition of (X) were carried out in the absence of cyclohexene.[15] We believe that they were wrong in ruling out species such as (X) as intermediates in allylic oxidation and conclude that the decomposition of such compounds is catalysed by excess of the alkene. The earlier workers speculated that the olefin-complexed monomeric structure (XI) 'is an intriguing possibility' as an intermediate. Our results are in accord with formation of (X) from which, with more alkene, the more labile (XI), and thence allylic product, is derived.

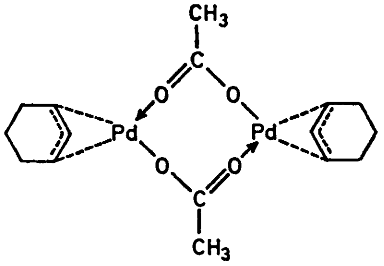
TABLE 4

Effect of reaction time on product distribution from the reaction of α-methylstyrene with palladium(II) acetate [a]

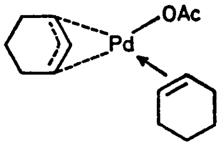
	Products (% based on Pd^{II})					
			Oxidative dimers			
Time (h)	(VI)	(IX)	(IV)	(VII)	Other	Total
1	6.3	1.3	20.6	18.2	9.2	48.0
2	7.7	1.5	18.7	19.2	6.9	44.8
4	9.8	1.2	18.3	20.0	6.0	44.3
6	15.3	1.4	26.1	15.9	5.7	47.7
8	18.0	1.4	23.9	18.2	5.0	47.1
12	21.0	1.3	25.2	15.7	4.2	45.1

[a] Conditions, other than reaction time, as in Table 1; no sodium acetate present.

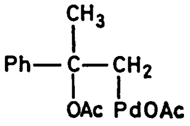
A second type of intermediate, and one frequently invoked in the formation of enolic esters from Pd^{II} catalysed oxidations of alkenes, is an oxypalladation adduct such as (XII). In our case, this cannot decompose to an enolic acetate nor can it lead directly to any of the other observed products. Adducts similar to (XII) are well established in the oxidation of α-methylstyrene by other metal oxidants but their decomposition involves the generation of carbonium-ion character on C-1,[14,16] a process for which no firm evidence has so far been presented in palladium chemistry. If (XII) is formed it presumably reverts to alkene and palladium(II) acetate.



(X)

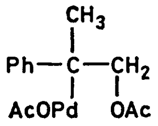


(XI)



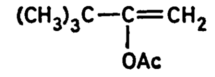
$\mathrm{Ph{-}C(CH_3)(OAc){-}CH_2(PdOAc)}$

(XII)



$\mathrm{Ph{-}C(CH_3)(PdOAc){-}CH_2(OAc)}$

(XIII)

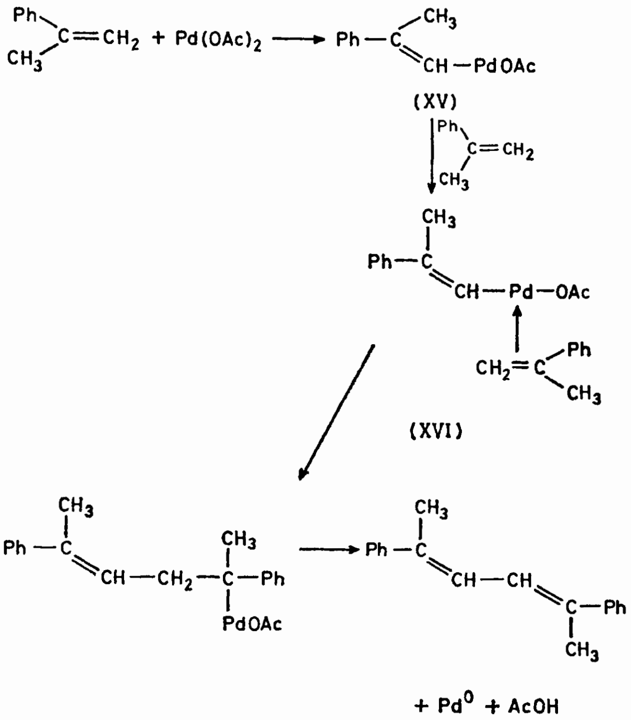


$\mathrm{(CH_3)_3C{-}C(OAc){=}CH_2}$

(XIV)

The alternative anti-Markownikov adduct (XIII) seems an unlikely intermediate on two counts. First, hindered alkenes do not give anti-Markownikov adducts [see the almost exclusive production of (XIV) from 3,3-dimethylbut-1-ene, a result attributed to steric inhibition of anti-Markownikov addition[17]]. Secondly, it is difficult to explain why (XIII) does not decompose to both (VI) and (IX), yet the formation of (IX) is complete long before that of (VI).

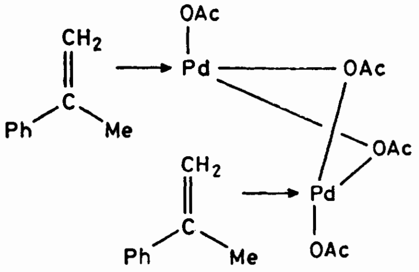
Maitlis[18] has suggested the mediation of a σ-vinylic palladium species (XV) to account for oxidative dimerisation (Scheme). It is probable that (XV) would couple with another molecule of alkene. In the years since such reactions were first noted,[19] many claims have been made that similar aryl- and alkyl-palladium acetates bring about vinylic substitution. However, as far as we are aware there is no unambiguous proof of the existence of these species; they are invariably said to be formed *in situ*. The Scheme would certainly explain the competitive formation of dimers and enolic acetates;



SCHEME

both acetate and alkene ligands on the palladium can serve to break the C–Pd bond. However, decomposition of a bimolecular π-alkene complex such as (XVII), originally suggested by Volger,[10] can equally well account for these products.

The problem with postulating an intermediate such as (XV) is in explaining how it is formed. Formally, it results from electrophilic substitution by the palladium(II), yet all the evidence suggests that this metal is not an electrophile in the sense of generating carbonium-ion character (note the lack of rearrangement with model alkenes [17,20]). It might conceivably be formed from



(XVII)

(XII) by loss of acetic acid, but such behaviour has not been noted with analogous organometallic compounds.

The lack of electrophilicity of palladium(II) towards alkenes is demonstrated by three other experiments that we carried out. First, *p*-methoxy-α-methylstyrene was found to be oxidised by palladium(II) acetate at a similar rate to, and to give a similar spectrum of products to, α-methylstyrene. After 1 h at 80 °C, allylic acetate was formed in 5.6% yield (6.3% for α-methylstyrene), enolic acetate in 2.4% yield (1.3%), and oxidative dimers in 36.0% yield (48.0%). In addition, a small amount (*ca.* 3%) of a non-oxidative dimer was formed, presumably by an acid-catalysed process.

Secondly, competitive oxidation of 4-phenylbut-1-ene and α-methylstyrene resulted in no products from the latter amongst those derived from the unconjugated alkene. Thirdly, conditions under which α-methylstyrene produces *ca.* 50% of oxidative dimers (3 h at 80 °C) resulted in only traces of products from both (*E*)- and (*Z*)-2-phenylbut-2-ene (α,β-dimethylstyrene). The order of reactivity to palladium(II) is thus (*E*)- and (*Z*)-α,β-dimethylstyrene < α-methylstyrene < 4-phenylbut-1-ene. The relative rates of bromination of the same four alkenes in methanol, a typical reaction involving electrophilic attack at the double bond, are *ca* 70 : 15 : 155 : 1.[*] Steric rather than electronic factors appear to be more important in dictating the rate of oxidation of alkenes by palladium(II). This is more consistent with π-bonding between the oxidant and alkene than with electrophilic attack by the one on the other.

In summary, there is evidence for two routes in the oxidation of α-methylstyrene. In one, π-allylic palladium complex decomposes slowly in a process catalysed by excess of the alkene to give an allylic acetate. Enolic acetates and oxidative dimers are produced competitively in a second reaction, though the nature of the organopalladium species involved has not been established: however, it is unlikely to be an oxypalladation adduct. We can offer no explanation for the discrepancies between our results and those in previous reports.[10,11] The variety of conditions we employed embrace those used earlier. It is possible that (V), reported in the previous studies but not found in ours, stems from an acid-catalysed dimerisation of the alkene which may not involve palladium(II). The pronounced effect of sodium acetate in Volger's system [10] could then be attributed to a buffering effect. If this suggestion is correct it would imply that the nature of the palladium acetate employed varies, since this would be the only source of acid.

EXPERIMENTAL

The analytical techniques employed in this study have been described previously.[14,16,20] Palladium(II) acetate (Johnson Matthey), acetic acid (May and Baker, AnalaR grade), and sodium acetate (Fisons, AnalaR grade) were used as supplied. α-Methylstyrene (B.D.H. laboratory reagent) and (*E*)-β-methylstyrene (Aldrich) were redistilled before use.

2-(4-*Methoxyphenyl*)*propene*.—4-Bromoanisole (37.4 g) in dry ether (150 ml) was added dropwise to magnesium turnings (5.1 g) under dry ether (50 ml). After heating for 0.5 h and cooling, AnalaR acetone (14 g) in dry ether (50 ml) was

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[*] These figures are derived by comparison of kinetic data from different sources.[21]

added slowly. The mixture was heated for 0.5 h, cooled, and poured into concentrated hydrochloric acid (20 ml) and ice (300 g). The ether layer was separated, washed with sodium carbonate solution and water, and dried ($MgSO_4$). Evaporation of the solvent and distillation of the residue gave 2-(4-methoxyphenyl)propan-2-ol (17 g, 51%) as a liquid, b.p. 97—100 °C at 1.5 mmHg. The alcohol (15 g) was stirred vigorously with dilute sulphuric acid (150 ml) at 40 °C for 1 h. The product was extracted with ether and the extracts were washed with sodium carbonate solution and dried ($MgSO_4$). Removal of the solvent and distillation of the residual oil gave 2-(4-methoxyphenyl)propene (8 g, 72%) as a liquid, b.p. 53—56 °C at 0.3 mmHg (lit.,[22] 63—65 °C at 0.5 mmHg) which solidified on standing, τ 2.5—3.1 (4 H, AA'BB' system, ArH), 4.70 and 5.02 (2 H, narrow m, olefinic H), 6.21 (3 H, s, OCH_3), and 7.88 (3 H, s, CH_3).

2-*Phenylbut*-2-*ene* (α,β-*Dimethylstyrene*).—Bromoethane (55 g) in dry ether (200 ml) was added dropwise, with stirring, to magnesium turnings (12 g) in dry ether (50 ml). The mixture was refluxed for 0.5 h, cooled, and acetophenone (60 g) in dry ether (100 ml) was added slowly. The product was stood overnight and poured into 15% sulphuric acid (200 ml) and ice (250 g). The ether layer was separated, washed with sodium hydrogencarbonate solution, and dried ($MgSO_4$). Removal of solvent left 2-phenylbutan-2-ol as a pale yellow liquid contaminated with a small amount of acetophenone. The crude alcohol was stirred for 2 h at 60 °C with 30% sulphuric acid (150 ml) and the product worked up as above to give a liquid, b.p. 186—190 °C, which g.l.c.–m.s. showed to be a mixture of three isomeric alkenes contaminated with a small amount of acetophenone. The last was removed by passing the liquid down a short silica gel column with light petroleum (b.p. 40—60 °C) as eluant. Preparative gas chromatography of the eluate (45 g) gave (i) (*E*)-2-phenylbut-2-ene, τ 2.75 (5 H, s, ArH), 4.45 (1 H, q, =CH), 8.01 (3 H, narrow m, 1-CH_3), and 8.46 (3 H, dq, 4-CH_3); (ii) 2-phenylbut-1-ene, τ 2.6—2.9 (5 H, m, ArH), 4.75 and 4.97 (each 1 H, narrow m, =CH_2), 7.52 (2 H, q, CH_2), and 8.91 (3 H, t, CH_3); and (iii) (*Z*)-2-phenylbut-2-ene, τ 2.71 (5 H, s, ArH), 4.15 (1 H, q, =CH), 7.99 (3 H, narrow m, 1-CH_3), and 8.24 (3 H, dq, 4-CH_3). Stereochemical assignments are based on the data of Pascual.[23]

2-Phenylprop-2-enyl acetate (VI), prepared by the method of Hatch and Patton,[24] had b.p. 68—71 °C at 0.1 mmHg (lit.,[14] 78—81 °C at 0.7 mmHg).

2-*Phenylprop*-1-*enyl acetate* (IX).—A mixture of 2-phenylpropionaldehyde (13.4 g), 1-methylvinyl acetate (20.4 g), and 4-methylbenzenesulphonic acid (0.12 g), was refluxed for 48 h. After cooling, the mixture was poured into water, extracted with ether, and the extract dried (K_2CO_3). Removal of solvent and distillation of the residual oil gave a pale yellow liquid (10.4 g, 60%), b.p. 96.5—98.5 °C at 2.5 mmHg, containing a trace of unchanged aldehyde which was removed by passing the product down a short column of silica gel with benzene as eluant. The resultant liquid was a mixture of the geometric isomers (IXa and b), τ 2.7 (5 H, s, ArH), 2.48 and 2.81 (total 1 H, narrow ms, =CH), 7.85 and 8.02 (CH_3), and 7.93 and 7.96 (OAc) (6 H in all).

(*E,E*)-2,5-*Diphenylhexa*-2,4-*diene* (IV).—α-Methylstyrene (6 g) and iodine (12.7 g) were stirred at room temperature for 24 h in acetic acid (150 ml). Most of the acetic acid was removed by distillation under reduced pressure and the resultant mixture was allowed to stand for 3 days. The precipitate was filtered off, washed with cold light petroleum (b.p. 60—80 °C), and recrystallised from the same solvent to give (*E,E*)-2,5-diphenylhexa-2,4-diene (IV) (0.5 g, 8%) as needles, m.p. 137—139 °C (lit.,[25] 138—139 and[10] 133—135 °C), n.m.r. spectrum as previously described.[10] A sample of the same material was obtained by preparative g.l.c. of the product of palladium(II) oxidation.

Bis[μ-acetato-η^3-(2-phenylpropenyl)palladium(II)] was prepared by a similar method to that of Hüttel *et al.*[9] Palladium(II) chloride (3 g) and α-methylstyrene (7 g) were stirred in 50% aqueous acetic acid (135 ml) at 100 °C for 7 h and then cooled and filtered. The black solid obtained was placed in a Soxhlet extractor and extracted with dichloromethane. Removal of the solvent from the extract gave, on recrystallisation from benzene, bis[μ-chloro-η^3-(2-phenylpropenyl)palladium(II)] (2.2 g, 25%), decomposing at *ca.* 220 °C, τ 2.6 (10 H, s, ArH), 5.77 (2 H, s, *syn*-H), and 6.93 (2 H, s, *anti*-H).

This chloro-complex was shaken for 24 h with silver acetate (2.2 equiv.) in dichloromethane according to the procedure of Robinson and Shaw.[26] Filtration of the product and removal of the solvent gave *bis*[μ-*acetato*-η^3-(2-*phenylpropenyl*)-*palladium*(II)] (2.0 g, 90%) as yellow needles, m.p. 171—174 °C (decomp.), τ 2.3—2.7 (10 H, m, ArH), 5.92 (2 H, s, *syn*-H), 7.25 (2 H, s, *anti*-H), and 8.01 (3 H, s, OAc) (Found: C,46.75; H, 4.25. $C_{22}H_{24}O_4Pd_2$ requires C, 46.75; H, 4.3%).

Oxidations.—A typical procedure for the oxidation of α-methylstyrene with palladium(II) acetate was as follows. A flask containing palladium(II) acetate (0.224 g, 1 mmol) and acetic acid (48 ml) was fitted with a rubber seal and purged with nitrogen by means of needles inserted through the seal. Heating for *ca.* 10 min at 80 °C produced a homogeneous red solution to which the alkene (1.18 g, 10 mmol), dissolved in acetic acid (2 ml), was added through a syringe. Within 5 min deposition of palladium metal was observed and the solution became brown. The flask was shaken from time to time during the course of the reaction. After the appropriate time, the flask was cooled, the contents filtered, and the precipitate washed with trichloromethane. The filtrate and washings were added to water (*ca.* 200 ml) and shaken. The organic layer was separated, the aqueous layer extracted twice more with trichloromethane, and the combined extracts washed with water and dried ($MgSO_4$). The product was concentrated to *ca.* 10 ml and analysed by g.l.c. using a polyethylene glycol column at 150 °C to analyse for unsaturated esters and an SE 30 column at 240 °C for dimeric products. Other reactions were carried out under the conditions set out in the Tables.

Preparative g.l.c. of the combined products from several reactions yielded small amounts of two dimers of which one, a solid, m.p. 137—138 °C, was identical with (*E,E*)-2,5-diphenylhexa-2,4-diene prepared by an alternative route. The second was an oil, τ 2.4—2.8 (10 H, m, ArH), 3.52 (2 H, s, =CH), and 7.79 (6 H, s, CH_3), *m/e* 234 (100%, *M*) and 219 (75, $M - CH_3$). A third dimer was present in too small a quantity to be isolated; it too showed, on g.l.c.–m.s., a molecular ion at *m/e* 234 and an M—Me fragment.

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