The Reactions of Metal-ion Complexes with Hydrocarbons. Part 5.[1] Some Catalytic Reactions of Palladium Acetate and its Derivatives: the Oxidations of Cyclohexene, Cyclo-octene, 3,3-Dimethylbut-1-ene, and n-Hexenes and the Isomerisation of Linear Alkene Derivatives

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The oxidation of cyclohexene, (28), cyclo-octene, (32), 3,3-dimethylbut-1-ene, (1), hex-1-ene, (15), and *cis*-hex-2-ene, (16), by dioxygen catalysed by ' palladium acetate ' has been studied in acetic acid solution at 25 °C and *ca.* 1 atm pressure. Trimeric palladium acetate or a dissociation product is catalytically active but is converted by olefins into complexes of the type $[Pd_3(\eta^3\text{-allyl})_2(\mu\text{-}O_2CMe)_4]$ which are also catalytically active probably by virtue of the presence of one palladium atom not complexed by an allyl group. Compounds (1) and (15) are oxidised by addition of $Pd(O_2CMe)$ to the double bond and then by elimination of PdH to give 3,3-dimethylbut-1-en-2-yl acetate, (2), and hex-1-en-2-yl acetate, (19), respectively and very little of the corresponding primary esters. The palladium hydride generated by (15) leads to extensive isomerisation of the hexenyl ester products and to selective formation of *cis*- and *trans*-hex-2-ene. In the case of (1), a complication is the oxidative coupling of the olefin to di(t-butyl)butadienes and di(t-butyl)cyclobutene which remain complexed to the catalyst as addition compounds of η^3-allylic structure. Some 1,3,5-tri(t-butyl)benzene is also formed. Studies of the continuous catalytic rate with (1) and (28) and of the initial rate with (15) show that the reaction of olefins with the catalytic species (displacement) is usually rate determining, although under some circumstances decomposition of a complex or reaction with dioxygen (' regeneration ') can be rate determining. In the case of (15), the addition of sodium acetate to the acetic acid promoted the formation of isomerised ester products such as hex-4-en-2-yl actate. Perchloric acid promotes the rapid formation of stable η^3-allyl complexes that are catalytically inactive. Oxidation of (16) by the addition–elimination route is very slow and, in the presence of dioxygen, a free-radical process yielding allylic esters such as hex-1-en-3-yl acetate and unsaturated alcohols and ketones becomes dominant.

A NUMBER of papers describe reactions in acetic acid of complexes of palladium(II) derived from olefins.[2] Typically, palladium acetate reacts with stoicheiometric amounts of olefins to give oxidative coupling of the olefin[3] or vinylation of acetic acid.[4,5] Such reactions can be included in a ' catalytic cycle ' or chain sequence in which the reduced palladium species is said to be re-oxidised by the ultimate oxidant, *e.g.* dioxygen,[6] benzo-

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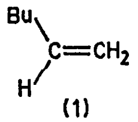
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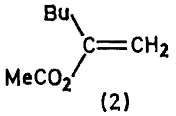
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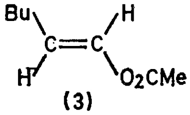
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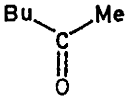
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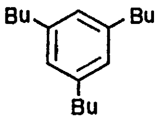
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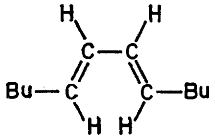
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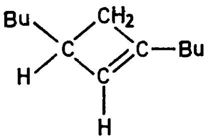
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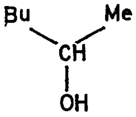
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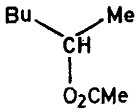
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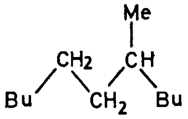
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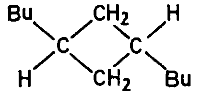
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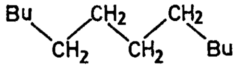
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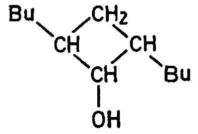
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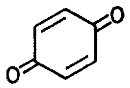
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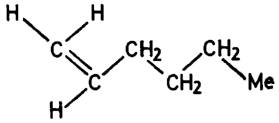
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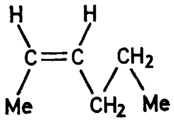
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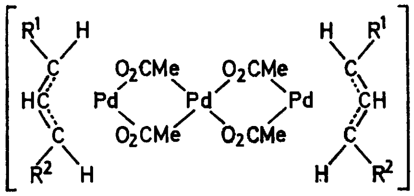
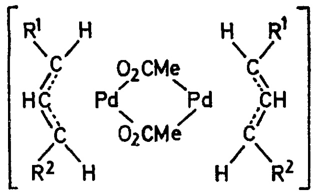
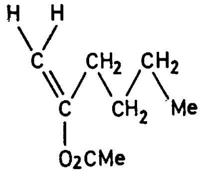


	R^1	R^2
(17a)	H	Pr
(17b)	Me	Et



	R^1	R^2
(18a)	H	Pr
(18b)	Me	Et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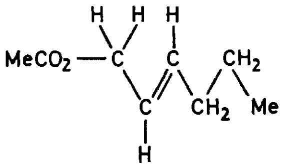
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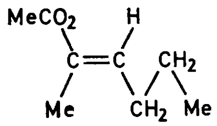
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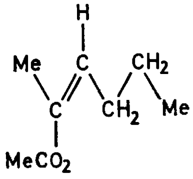
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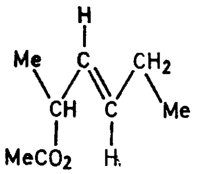
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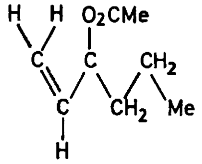
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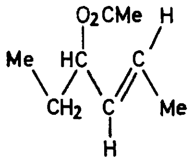
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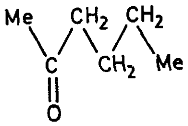
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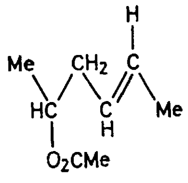
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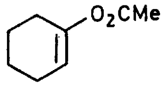
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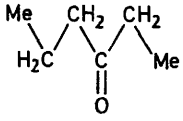
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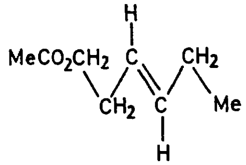
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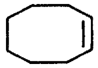
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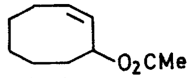
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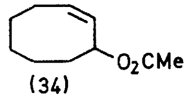
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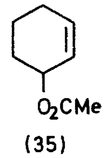
(35)

quinone,[7] or copper(II).[8] It is usually possible to account for the overall catalytic sequence in terms of relatively few types of reaction step. These are complex formation and displacement, oxypalladation, and reversible elimination of palladium hydride. Oxypalladation of mono-olefins has ample precedent in the chemistry of the acetates of mercury(II),[9] thallium(III),[10] and lead(IV).[10,11] The σ complexes of mercury are usually stable, but those of thallium and lead decompose *via* carbonium-ion mechanisms to organic acetates. σ Complexes of palladium also decompose with reduction of the metal but the carbon-skeleton rearrangements associated with carbonium-ion formation are absent. It is usually proposed that decomposition involves β-hydrogen abstraction with the formation of a palladium hydride complex. The existence of such hydrides has been inferred from the stereospecific shifts that occur in the oxidation of ethylene [12,13] or in the isomerisation of olefins by the addition–elimination sequence of Cramer and Lindsey,[14] and by the mode of 'activation' of the catalyst. Less is known of the redox steps in oxidations catalysed by palladium. The hydrides themselves are likely to be easily oxidised by dioxygen, which is consistent with the observed inhibition of isomerisation during catalytic oxidation. Alternatively the hydrido-complex could decompose to H^+ and either Pd^0 or Pd^I. Oxidative coupling of benzene does in fact proceed by reduction of palladium acetate to soluble Pd^I which is easily reoxidised to Pd^{II}.[15] With both Cu^{II} and benzoquinone, kinetic involvement has been demonstrated, and in these cases Pd^{II} may do no more than act as a bridge for electron transfer between the complexed organic ligand and the oxidant.

Our own interest is in the use of palladium acetate as catalyst for the oxidation of olefins to unsaturated esters in acetic acid solution. Unfortunately, these reactions are complicated by competing processes such as oxidative coupling, isomerisation, and the formation of stable organopalladium complexes. The formation of allylic complexes by reaction of palladium acetate with olefins has already been described,[1] and this paper is concerned with catalytic oxidation and isomerisation.

RESULTS

General.—Palladium acetate is a catalyst for the oxidation of a variety of mono-olefins in acetic acid solution. The reactions were usually carried out at 24.75 ± 0.02 °C and *ca*. 1 atm dioxygen.* The rate of uptake of dioxygen was reproducible only when the materials were purified carefully, and after consistent results had been obtained the rates were used to screen new batches of material. Palladium acetate prepared by nitric acid oxidation of the metal often contains trace amounts of oxo-anions of nitrogen and these are already known to alter the course of the oxidation of cyclohexene.[16,17] In order to remove these anions and also cyanide which is another possible contaminant,[18] palladium acetate was digested with H_2SO_4 and the resulting palladium sulphate was treated with aqueous acetic acid to regenerate the purified material.

Stoicheiometric reactions of palladium acetate were carried out in sealed evacuated tubes.

Reaction of 3,3-*Dimethylbut*-1-*ene*.—Solutions of (1) (0.079 1—0.316 mol dm^{-3}) and palladium acetate {introduced as $[Pd_3(O_2CMe)_6(OH_2)]$,[19] but recorded as the concentration of monomer in the range 0.003 18—0.147 mol dm^{-3}} were stirred with dioxygen (P_{O_2} 787—1 122 mmHg). After an induction period of 1—2 h the rate of absorption of dioxygen attained a steady value and rates were then checked through 5—10 catalyst turnovers. The data given in Table 1 refer to early parts of runs when conversion of the olefin did not exceed 6%. The concentration of olefin was therefore taken to be constant and reaction orders were obtained as gradients of plots of log(rate) against $\log[Pd(O_2CMe)_2]$ and log[olefin]. The rate was independent of dioxygen pressure and can therefore be expressed as in (i)

$$-dN/dt = k[Pd(O_2CMe)_2]^{0.51}[Olefin]^{1.32} \qquad (i)$$

where dN/dt is the molar rate of consumption of dioxygen. The Arrhenius plot was linear and gave an activation energy of 75 ± 5 kJ mol^{-1}.

The main oxidation product was 3,3-dimethylbut-1-en-2-yl acetate, (2), with a little 3,3-dimethylbut-1-enyl acetate, (3), and the yield was invariably *ca*. 50% of that expected if (2) were the only oxidation product of the dioxygen consumed. Numerous determinations of this yield were made by the following methods: (*i*) isotope dilution using the ester (2) labelled with $[^2H_3]$acetate; (*ii*) removal of the catalyst and then direct injection of the reaction solution into the chromatograph; (*iii*) complete recovery of the ester by the wet separation followed by g.l.c. analysis; (*iv*) n.m.r. analysis of the extent of conversion of (1) into (2) by comparison of the peak areas of the sharp singlets at τ 9.01 and 8.92 due to the t-butyl groups. These intensities could be measured most accurately using CD_3CO_2D as solvent. The other important product was apparently 3,3-dimethylbutan-2-one, (4), which probably arises by catalysed decomposition of (2).[20] A small amount of 1,3,5-tri(t-butyl)benzene, (5), was also formed. It was readily detected in solution by its characteristic n.m.r. spectrum (τ 2.69 and 8.81) and was formed in quite substantial amounts when certain impure samples of catalyst were used. Acidic products less volatile than acetic acid should be readily detected and, although

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* Throughout this paper: 1 atm = 101 325 Pa; 1 mmHg ≈ 13.6 × 9.8 Pa.

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glycolic acid was not found, sublimation of the acetic acid after warming samples of reaction solution with acetic anhydride yielded, from a few runs, a little polyglycolide (detected by its i.r. spectrum).* It is apparent that the material balance is seriously deficient since the yield of (2) + (4) was usually 50—55% and never more than 65%. A careful but fruitless search was made for other possible oxidation products such as CO_2, CH_4, or C_2H_6 from the acetic acid, 2,3-dimethylbuta-1,3-diene from (1), or t-butylbutyrolactone from (1) and acetic acid.[21] In general, any product containing a Bu^t group should have been readily detected as a singlet in the n.m.r. spectrum. The potassium iodide test for hydrogen peroxide was negative.

TABLE 1

Rates of oxidation of olefins [a]

$10^3[Pd(O_2CMe)_2]$ / mol dm^{-3}	10^2[Olefin] / mol dm^{-3}	P_{O_2} / mmHg	10^5 Rate / mol O_2 dm^{-3} h^{-1}
(*i*) Cyclohexene			
1.64	9.90	788 [b]	7.91 [c]
1.64	9.90	1 070 [b]	7.69
1.64	9.90	390 [b]	7.05
2.96	9.90	780 [b]	10.4
4.35	9.90	788 [b]	14.2
6.04	9.90	788 [b]	16.2
1.64	19.80	792 [b]	12.2
1.64	39.6	790 [b]	24.2
1.64	29.7	785 [b]	15.5
1.64	9.90	746 [d]	121.0 [e]
1.64	9.90	800 [f]	7.17
(*ii*) Cyclo-octene			
1.63	7.29	785	4.72
3.10	7.29	796	7.79
4.25	7.29	796	12.2
1.63	29.1	789	6.56
1.63	7.29	1 083	4.79
(*iii*) Hex-1-ene [h]			
1.64	3.96	793	(32.0) 23.9
1.64	3.96	1 078	33.1
1.64	3.96	973	29.0
1.64	15.8	802	(121.0) 41.6
1.64	7.91	805	(70.0) 24.2
1.64	2.37	800	24.0
1.64	10.3	811	(83.5) 30.7
2.75	3.95	798	(66.3) 43.8
1.05	3.96	804	(26.3) 12.9
3.82	3.96	802	(69.1) 59.1
1.65	23.7	798	(1.79) 55.8
1.62	31.6	802	(225.0) 74.7
1.63	1.58	807	21.4
1.64	15.8	1 071	(136.0) 57.6
1.63	15.8	477	(115.0) 33.2
1.64	15.8	973	(145.0) 53.0
1.05	15.8	801	(86.5) 29.8
2.75	15.8	807	(194.0) 57.1
3.81	15.8	799	(236.0) 78.2
1.62	3.96	810 [j]	21.6
1.63	3.96	796 [k]	34.1
1.63	15.8	827 [l]	35.4
(*iv*) *cis*-Hex-2-ene [g]			
1.60	3.16	798	62.1
2.70	3.16	803	69.2
0.817	3.16	802	51.7
1.62	3.16	500	45.5
1.61	3.16	1 071	66.5
1.62	4.75	781	80.6
1.63	3.96	780	70.7
1.63	5.54	778	84.8
3.55	3.16	795	75.2
1.31	3.16	782	57.0
1.62	3.16	924	67.0
1.64	3.32	801	53.8 [m]
(*v*) *trans*-Hex-3-ene [g]			
1.63	3.16	822	79.6
(*vi*) 3,3-Dimethylbut-1-ene [i]			
1.06	16.7	811	18.8
1.64	16.7	808	25.6
1.64	16.7	804	24.7
2.12	16.7	805	30.2
2.76	16.7	706	31.7
38.3	16.7	790	35.4
4.93	16.7	796	44.8
1.64	16.7	974	26.8 [n]
1.63	16.7	1 122	24.1
1.64	8.36	787	10.6
1.63	25.0	800	45.9
1.63	33.4	792	65.5
1.63	16.7	775	21.6 [o]
1.65	16.7	796	41.0 [p]
1.63	16.7	800	48.7 [q]
1.63	16.7	767	73.6 [r]

[a] At 297.9 K except where stated otherwise. [b] The solutions contained 4.4 × 10^{-5} mol dm^{-3} quinol. [c] Reaction of 10.3 cm^3 of O_2 (reduced to s.t.p.) yielded 4.20 × 10^{-4} mol of (35). [d] No quinol. [e] 21.7 cm^3 of O_2 (reduced to s.t.p.) yielded 3.97 × 10^{-4} mol of (35). [f] The solution contained 2.4 × 10^{-4} mol dm^{-3} quinol. [g] Solutions contained no quinol. [h] Solutions contained 4.4 × 10^{-5} mol dm^{-3} quinol. [i] Initial rates are given in parentheses. [j] Contained 2 × 10^{-3} mol dm^{-3} mixed hexenyl acetates. [k] Contained 0.053 mol dm^{-3} sodium acetate. [l] Catalyst introduced as (17a). [m] Contained 0.490 mol dm^{-3} sodium acetate. [n] Reaction of 15.5 cm^{-3} of O_2 (reduced s.t.p.) yielded 7.67 × 10^{-4} mol of (2). [o] At 298.21 K. [p] At 301.22 K. [q] At 304.01 K. [r] At 307.91 K.

In some runs, after a few catalyst cycles, almost pure palladium acetate could be recovered but the i.r. spectrum always showed the presence of variable amounts of other species. Better yields of these palladium complexes could be obtained by reaction of (1) with palladium acetate *in vacuo*. After an induction period of 1—2 h, palladium metal began to precipitate. Reaction was complete after precipitation of *ca.* 80% of the palladium and the remainder was present as a straw-coloured complex. The i.r. spectrum of this material was very similar to that of complexes derived from di(t-butyl)butadienes, but the n.m.r. spectrum

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* Although we were not able to find glycolic acid reproducibly in these systems, its formation by oxidation of acetic acid by Pd^{II} seems very reasonable in view of the generation of $HOCOCH_2$ radicals from $Mn(O_2CMe)_3$ under similar conditions.[21] A precursor might be a palladium analogue of the known carboxymethylenemercury(II) polymer which is formed by decomposition of phenylmercury(II) acetate.[22]

$$[HgPh(O_2CMe)] \longrightarrow PhH + (Hg\text{–}CH_2\text{–}CO\text{–}O)_n$$

[21] E. I. Heiba, R. M. Dessau, and P. G. Rodewald, *J. Amer. Chem. Soc.*, 1974, **96**, 7977.

[22] P. R. Wells and W. Kitching, *Austral. J. Chem.*, 1963, **16**, 508.

in CD_3CO_2D showed it to be a very complex mixture. Degradation by treatment with aqueous K[CN] in the presence of diethyl ether yielded 2,2,7,7-tetramethylocta-3,5-diene, (6), and possibly a 2,4-di(t-butyl)cyclobut-1-ene, (7), or another isomer of (6), and hydrogenation of the whole reaction mixture yielded a very complex mixture of at least 16 volatile organic compounds from which the following were isolated by preparative g.l.c.: 3,3-dimethylbutan-2-ol, (8); 3,3-dimethylbut-2-yl acetate, (9); 2,2,3,6,6-pentamethylheptane, (10); 1,3-di(t-butyl)cyclobutane, (11); 2,2,7,7-tetramethyloctane, (12); 2,4-di(t-butyl)cyclobutanol, (13); together with a C_{12} acetate and a C_{12} ketone which were analysed only by mass spectroscopy. Compound (13) was only formed in the presence of dioxygen. Apart from (9), the most abundant of these products were (10) and (13) which even then amounted to only a few mol percent of the palladium catalyst.

The activity of some other complexes for the catalytic oxidation of (1) was tested. The η^3-allyl complexes derived from 1,3-di(t-butyl)buta-1,3-diene and hexa-2,4-diene were very inactive, while tetra-μ-acetato-di(2—4-η-hex-3-en-2-yl)tripalladium, (17b), gave a very similar rate to palladium acetate itself. The addition of palladium black at the beginning of a run did not influence the catalytic rate due to $Pd(O_2CMe)_2$, nor did the prior addition of (2).

In many oxidation reactions catalyzed by palladium complexes benzoquinone, (14), may be used as the ultimate oxidant. The kinetics of oxidation of (1) to (2) could be studied by using ^1H n.m.r. spectroscopy of the acetic acid solutions to determine the conversion of olefin into ester or benzoquinone to quinol by integration of the peaks. Runs were carried out using carefully degassed solutions in sealed n.m.r. tubes. Unfortunately the rates were not reproducible and only broad trends were discernible. Thus the rate of consumption of benzoquinone was similar to that of dioxygen and showed no strong dependence on its own concentration. The yield of (2) was *ca.* 50% of the theoretical based on the benzoquinone consumption.

Isomerisation and Non-catalytic Oxidation of n-Hexenes.—Palladium acetate was converted into η^3-hexenyl complexes by hex-1-ene, (15), and *cis*-hex-2-ene, (16), in neutral acetic acid *in vacuo*. Formation of $[Pd_3(1\text{—}3\text{-}\eta\text{-}C_6H_{11})_2(\mu\text{-}O_2CMe)_4]$, (17a), from hex-1-ene was complete after 6 h during which time 20% of the palladium acetate was reduced. Subsequently, oxidation of (15) was very slow and conversion of Pd^{II} reached only 22% after 144 h by which time it was present as $[Pd_2(1\text{—}3\text{-}\eta\text{-}C_6H_{11})_2(\mu\text{-}O_2CMe)_2]$, (18a). Based on palladium acetate consumed, a 65% yield of hexenyl acetates was obtained after 6 h comprising hex-1-en-2-yl acetate, (19) (mol fraction 0.58), hex-2-enyl acetate, (20) (mol fraction 0.13), and smaller amounts of *cis*-hex-2-en-2-yl acetate, (21), *trans*-hex-2-en-2-yl acetate, (22), hex-3-en-2-yl acetate, (23), hex-1-en-3-yl acetate, (24), hex-4-en-3-yl acetate, (25), and hexan-2-one, (26) (Table 2, run 1). The fractions of the various products changed as reaction proceeded, *e.g.* hex-1-en-2-yl acetate was slowly converted [20] into hexan-2-one. During oxidation, hex-1-ene underwent isomerisation to *cis*- and *trans*-hex-2-ene preferentially, the selectivity remaining constant in the slow and fast stages with a *trans* : *cis* ratio of 5.3—6.8 : 1. In the reactions of (16) the 2—4-η^3-hexenyl complexes, (17b) and (18b), were formed consecutively but oxidation was very slow and only 4% of the palladium acetate was reduced after 144 h (Table 2, run 2). The oxidation products were the same as those obtained by catalytic oxidation (see below). *cis*-Hex-2-ene did not undergo isomerisation.

The co-catalytic effect of perchloric acid when Pd^{II} is used as an isomerisation catalyst has been noted before.[14] Perchloric acid also promotes stoicheiometric oxidation and the formation of complexes.[1] Using $Pd(O_2CMe)_2$ in 0.5 mol dm^{-3} $HClO_4$ in acetic acid, both (15) and (16) were converted into the equilibrium mixture of olefins very rapidly [mol fractions: (15), 0.01; (16), 0.17; *trans*-hex-2-ene, 0.59; *cis*-hex-3-ene, 0.01; and *trans*-hex-3-ene 0.22]. Incorporation of deuterium from CH_3CO_2D was only slightly greater than in neutral solution, and i.r. analysis of a gaseous sample showed that the intensities of stretching vibrations were in the ratio 5 : 1 for the aliphatic (2 166 cm^{-1}) and olefinic (2 210 cm^{-1}) bands. A control experiment showed that *ca.* 11% of the isomerisation took place through acid catalysis. In the presence of 0.05 mol dm^{-3} $HClO_4$, $Pd(O_2CMe)_2$ oxidised the equilibrium mixture of hexenes to the thermodynamically preferred hex-4-en-2-yl acetate, (27) (76% yield based on the weight of precipitated palladium), (22), and trace amounts of other esters and ketones. Higher concentrations of $HClO_4$ caused extensive decomposition of the hexenyl esters into (26) and hexan-3-one (30).

Oxidation of Hex-1-ene by O_2 catalysed by Palladium Acetate.—Runs were carried out using hex-1-ene (0.158—0.316 mol dm^{-3}), palladium acetate (0.001 05—0.003 82 mol dm^{-3}), and dioxygen (474—1 234 mmHg) and samples were taken for analysis at various times. In the rate studies, quinol was used as a free-radical inhibitor. Material balances were difficult to establish but, approximately (Table 2, run 3), for each mol of dioxygen consumed 2 mol of (15) were oxidised and 2 mol were isomerised to a mixture of *cis*- and *trans*-hex-2-ene. The yield of volatile oxidised products was generally 50—80% of the theoretical, which at least partly reflects the importance of non-volatile products of oxidative-coupling reactions and polymerisation, *etc.* and also the losses in the wet separation.

Although the stoicheiometry and selectivity were constant throughout the runs, there was a change in rate marking the conversion of $[Pd_3(O_2CMe)_6]$ into $[Pd(1\text{—}3\text{-}\eta\text{-}C_6H_{11})_2(\mu\text{-}O_2CMe)_4]$. The rate was constant for the first 1—3 h and this was taken as the initial rate which was independent of dioxygen pressure and showed a nearly first-order (0.9) dependence on olefin concentration and a complex dependence on palladium(II) concentration. After *ca.* 4 h, transition to a slower rate was complete with simultaneous conversion of the Pd^{II} into $[Pd_3(1\text{—}3\text{-}\eta\text{-}C_6H_{11})_2(\mu\text{-}O_2CMe)_4]$ and the same rate could be obtained, without the initial fast stage, by direct introduction of this complex. The rate behaviour was different from the early fast stage, being independent of olefin concentration for fairly low concentrations of (15) (0.015 8—0.079 1 mol dm^{-3}) [equation (ii)]. Above *ca.* 0.1 mol dm^{-3} hex-1-ene, a strong

$$-\mathrm{d}N/\mathrm{d}t = k_{\text{obs.}}[Pd_3(1\text{—}3\text{-}\eta\text{-}C_6H_{11})_2(\mu\text{-}O_2CMe)_4]^{1.08}(P_{O_2})^{1.04} \quad \text{(ii)}$$

dependence on olefin concentration was increasingly apparent. Infrared analysis of the mixed complexes obtained from reaction samples showed that very little of the inactive dimer $[Pd_2(1\text{—}3\text{-}\eta\text{-}C_6H_{11})_2(\mu\text{-}O_2CMe)_2]$, (18a), was formed under conditions of catalytic oxidation. When quinol was not added to the reaction solution, after *ca.* 8—10 h there was a second transition to a faster reaction,

TABLE 2

Run	1	2	3	4	4	4	5	6	7	8	9	9	9	10	11
Volume of $MeCO_2H/cm^3$	30	30	60	60	60	60	30	30	30	30	30	30	30	30	30
Amount of palladium acetate/g	0.41	0.41	0.053	0.502	0.502	0.502	0.15	0.15	0.15	0.15	0.25	0.25	0.25	0.41	0 41
Amount of olefin/g	0.69 [a]	0.69 [b]	1.34 [a]	1.34 [a]	1.34 [a]	1.34 [a]	0.34 [a]	0.34 [a]	0.34 [a]	0.34 [a]	0.67 [a]	0.67 [a]	0.67 [a]	0.69 [b]	0.69 [b]
Reaction time/h	6	144	94	1	19	98	150	150	150	150	3	25	94	144	144
Volume of O_2 consumed/cm^{-3}			26	10	32	92					9	22	62	50	*c*
Palladium acetate weight (g)			*c*												
(17) in	0.48														
(18) residue		0.41													
Weight of palladium precipitate/g	0.040	0.050													
Weight of oxidised products/g	0.035	0.010	0.37	0.095	0.26	0.66	0.132	*c*	0.134	0.130	0.065	0.24	0.33	0.92	0.111
Mol fraction of oxidised products															
(19)	0.58		0.62	0.62	0.52	0.34	0.50	0.40	0.21	0.03	0.32	0.31	0.18		
(20)	0.13		0.07	0.08	0.11	0.07	0.10	0.21	0.44	0.58	0.33	0.40	0.33	0.05	0.02
(21)	0.08		0.06	0.10	0.09	0.07	0.11	0.10	0.05	0.06	0.05	0.05	0.05		
(22), (23), (25), (27)	0.05	0.50 [d]	0.06	0.03	0.04	0.04	0.07	0.06	0.05	0.06	0.02 [e]	0.04 [e]	0.05 [a]	0.30 [f]	0.53[f]
(24)	0.03	0.50	0.09	0.02	0.06	0.05	0.10	0.08	0.05	0.06	0.04	0.05	0.08	0.24	0.31
(26)	0.12		0.06	0.09	0.11	0.32	0.08	0.14	0.11	0.16	0.01	0.03	0.18	0.04	0.01
(30)						0.03	0.03		0.05	0.02			0.02	0.01	0.01
(31)					0.01	0.01	0.01	0.01	0.04	0.02	0.05	0.09	0.08	0.02	0.01
Unsaturated ester and ketone			0.04	0.06	0.06	0.07					0.18	0.03	0.03	0.34	0.11
Amount of recovered olefin/g	0.67	0.50	0.90	1.2	0.95	0.40					0.55	0.40	0.20	0.35	*c*
Mol fraction of recovered olefins															
(15)	0.15	0.97	0.77	0.92	0.77	0.60	0.67		0.32		0.84	0.69	0.43		
cis-Hex-2-ene	0.13	0.03	0.03	0.01	0.03	0.05	0.06		0.15		0.02	0.04	0.06	0.97	0.95
trans-Hex-2-ene	0.65		0.19	0.05	0.16	0.29	0.21		0.43		0.11	0.23	0.40	0.03	0.05
cis-Hex-3-ene	0.03		0.01	0.01	0.02	0.03	0.02		0.05		0.01	0.02	0.05		
trans-Hex-3-ene	0.03			0.01	0.02	0.03	0.04		0.05		0.02	0.02	0.06		
Weight of sodium acetate/g								0.24	0.61	2.40					0.61

[a] (15). [b] *cis*-Hex-2-ene. [c] Not determined. [d] (22) was absent. [e] (27) was also formed. [f] Including some (27); (22) was absent.

presumably a free-radical process. The rate behaviour was not sensitive to the concentration of the ester products.

Product distributions are given in Table 2. *cis–trans*-Isomers were separated and analysed only for hex-2-en-2-yl acetate and the n-hexenes themselves. At low conversion the major oxidation product was (19). However, the mol fraction, which was initially 0.62 (Table 2, run 4), decreased from 0.52 at 19% conversion to 0.34 at 74% conversion. There was a corresponding increase in the mol fraction of (26) (initially 0.09) from 0.12 to 0.32. The mol fraction of (22) was usually 0.07—0.10 and it also decreased slowly during runs. The *trans* isomer (21) was formed in similar amounts. In general, a high ratio of hex-1-ene to palladium acetate seems to increase the selectivity for the terminal vinyl ester, (19), relative to the internal esters, (21) and (22) (compare Table 2, runs 3—5). A control experiment showed that (26) is formed mainly by catalytic decomposition of the ester (19), and this observation suggests that the mol fractions of (19) and (26) should be considered together. Indeed the sum of the fractions accounts for an essentially constant proportion of the product mixture (runs 3 and 4). Among other esters, (24) and hex-3-en-1-yl acetate, (31), appeared mainly at long reaction times presumably by isomerisation processes (compare Table 2, runs 3—5). Thus the mol fraction of (24) increased to 0.06—0.10 at long reaction times, having been negligible in the fast stage.

The main effect of sodium acetate on the catalytic oxidation of (15) was to promote the formation of allylic esters and to increase the rate (Table 2, runs 6—8). The major product was (20) (up to a mol fraction of 0.58 in run 8) and (31) was also promoted. The nature of the palladium-containing species under these conditions is not known.[1]

Oxidation of cis-*Hex-2-ene by* O_2 *catalysed by Palladium Acetate*.—The sequential reactions whereby palladium acetate reacts with *cis*-hex-2-ene to give the trinuclear complex (17b) and then the dimer (18b) have already been described.[1] The oxidation of (16) by palladium acetate *in vacuo* was very sluggish. The catalysed oxidation by dioxygen proceeded at a steady rate after an induction period of 2—4 h. Sodium acetate had no effect on the rate, while quinol acted as a total inhibitor of oxidation. *cis*-Hex-2-ene did not undergo isomerisation concurrently with oxidation.

In neutral acetic acid the major products were the allylic esters (24) (mol fraction 0.32) and (23) as 60% of a mixture with (25) which in all amounted to a mol fraction of 0.52. Small amounts of the primary esters (20) and (31) were present and were presumably isomerisation products of (24). Almost half the olefin consumed was oxidised to unsaturated alcohols and ketones and there was a small amount of an oily non-volatile product which was not characterised (Table 2, run 10). Sodium acetate promoted the formation of (27) (Table 2, run 11).

Oxidation of n-Hexenes by Benzoquinone.—The oxidation of hex-1-ene by benzoquinone was catalysed by $Pd(O_2CMe)_2$. The reaction solution darkened rapidly and a copious precipitate of quinhydrone was present after a few hours. After 17 h the product distribution among the esters was very similar to that due to O_2 oxidation but unsaturated alcohols and ketones were absent. The corresponding oxidation of *cis*-hex-2-ene was very slow.

Oxidation of Cyclo-octene by O_2 *catalysed by Palladium Acetate*.—In the presence of dioxygen and acetic acid, cyclo-octene, (32), converted palladium acetate into a yellow complex which catalysed the oxidation of the olefin to cyclo-oct-2-enyl acetate, (33), and cyclo-oct-3-enyl acetate, (34). Using 0.001 64—0.003 81 mol dm^{-3} palladium acetate, the rate of oxidation became steady after a short induction period and it was less than that of all the other olefins studied. Quinol had little effect on the rate and suppressed a minor reaction product that was not identified. The rate data show (Table 1) that the reaction is approximately first order, being dependent on the catalyst concentration and independent of oxygen pressure.

The ^1H n.m.r. spectrum of (32) in CD_3CO_2D scarcely changed during formation of the yellow complex with Pd^{II}. Removal of the solvent and other volatile substances from the reaction solution left a yellow complex which was unstable and which decomposed *in vacuo* to palladium metal, the esters (33) and (34), acetic acid, and a little (32). A solution of this complex was prepared for n.m.r. studies by dissolving the solid in $CDCl_3$ at −65 °C in an evacuated tube. At low temperature it gave four singlets near τ 8.0 due to acetates together with other broad resonances. On warming the spectrum collapsed irreversibly to one with a single strong peak due to organic acetate (τ 0.08) and very similar to that of the cyclo-octenyl esters at ambient temperature. The clear solution was stable long enough to allow a test for metal hydride resonances (negative) and it deposited palladium metal on standing.

Oxidation of Cyclohexene by O_2 catalysed by Palladium Acetate.—This reaction, which yields principally cyclohex-2-en-1-yl acetate, (35), when quinol is used as an inhibitor, has been described previously [23] as has the isolation of a η^3-cyclohex-2-en-1-ylpalladium complex.[1] We report only rate data obtained with $Pd(O_2CMe)_2$ (0.001 64—0.004 37 mol dm^{-3}) and cyclohexene (0.0988—0.395 mol dm^{-3}) at dioxygen pressures in the range 390—1 106 mmHg. Quinol (4.4×10^{-5} mol dm^{-3}) reduced the rate markedly but the fast uninhibited reaction gave a low yield of (35) (20.5% based on consumption of dioxygen) and more autoxidation products. Attempts to establish a material balance were no more successful than with (1) as the yield of (35) determined by isotope dilution using $C_6H_9O_2CCD_3$ was only 45.5%. Very little benzene was formed, and there were no substantial amounts of C_{12} products. The rate of oxidation of cyclohexene was more sensitive to the state of purity of the reagents than was the case for any other olefin. One sample of palladium acetate from nitric acid oxidation and after one recrystallisation gave a rate 20 times that of the purified catalyst. Many duplicate runs were carried out and, for example, seven runs using 0.001 64 mol dm^{-3} $Pd(O_2CMe)_2$ and 0.098 8 mol dm^{-3} cyclohexene at 780—800 mmHg dioxygen gave a mean rate of consumption of 0.000 079 mol O_2 dm^{-3} h^{-1} with a standard deviation of 0.000 001. The rate of reaction was independent of the pressure of dioxygen and log–log plots gave the rate law (iii).

$$-\mathrm{d}N/\mathrm{d}t = k[\mathrm{Pd(O_2CMe)_2}]^{0.58}[\mathrm{cyclohexene}]^{0.82} \quad \text{(iii)}$$

DISCUSSION

We have studied the rates and selectivity of a number of reactions of different types of olefin that lead to oxidation, isomerisation, and the formation of complexes. Results of both types are undermined by the inexplicably poor material balances even in the cases of 3,3-dimethylbut-1-ene and cyclohexene when complete analysis of yields of products should have been possible. Despite this the differences in behaviour of the rates of reaction from one olefin to another are so gross as to be worthy of interpretation.

In Scheme 1 a path to the various products is set out such that it is possible to account for the selectivity in terms of the reaction steps described in the introduction. Geometric isomerism is ignored and for the present it is assumed that monomeric palladium acetate is the catalyst. This part of the discussion would not be altered for certain other possible catalytic species to which we shall return later. The following points are implicit in the assumption of Scheme 1. (*i*) Hex-1-ene reacts with palladium acetate to form a η^2 complex [reaction (1)] which rearranges to a σ complex (oxypalladation) and then eliminates hydridopalladium(II) which presumably remains complexed to the ester (26) [reactions (2) and (3)]. Because of Markovnikoff control, reaction (2) is favoured over (4) which leads ultimately to (19) as an oxidation product. (*ii*) Apparently complex (36) is the key intermediate in the reactions of hex-1-ene. It undergoes ready addition and re-elimination of hydridopalladium thus allowing successive isomerisation [reactions (5)—(10)]. Reduction of Pd^{II} to the metal [*e.g.* reaction (11)] may intervene at any stage *in vacuo* liberating the esters (19), (21), (22), (23), and (27). (*iii*) Oxygen suppresses isomerisation reactions of hex-1-ene and of the products and prevents the reduction of Pd^{II}. This is consistent with the first step in 'regeneration' being the oxidation of hydridopalladium(II) [reaction (12) or (13), *etc.*]. (*iv*) The crucial complex (36) may undergo displacement of the ester (19) by hex-1-ene to give a η^3-hex-1-ene complex of hydridopalladium(II), (37) [reaction (14)], which is the key intermediate in isomerisation of hex-1-ene. Therefore both a high hexene to catalyst ratio and a high O_2 pressure should enhance the selectivity for the unrearranged ester (19) which may amount to as much as 80% of the ester products. (*v*) Addition and re-elimination of hydridopalladium [reactions (15) and (16)] proceeds under kinetic control and leads to the hex-2-ene complex (38) with a high *trans* to *cis* ratio of 5.3—6.8 : 1. Displacement of the internal olefin by hex-1-ene (which may be a dissociative reaction) [reaction (17)] must be fast compared with readdition of hydridopalladium(II) since very little hex-3-ene is formed [reaction (18)]. (*vi*) Allylic isomerisation is an important process which is catalysed by palladium acetate itself [24] [reactions (22) and (23)]. The mol fractions of the pairs of esters (20) and (24) and (23) and (25) show that interconversion takes place slowly although other products in the system do not undergo isomerisation. (*vii*) Sodium acetate promotes oxypalladation in the anti-Markovnikoff direction. It also promotes migration of the double bond in the oxidation products and, in particular, enhances conversion into non-conjugated esters (27) and (31).

It is noteworthy that under conditions of catalytic oxidation, just over 1 mol of hex-2-ene is produced for each mol of hexenyl ester or ketone. The ratio (1.4 : 1) is the same in the fast and slow stages and is not even altered by the addition of $Na(O_2CMe)$. This suggests that a palladium hydride complex of hex-2-ene dissociates prior to further isomerisation to hex-3-ene and is then oxidised to the original catalytic species, thus re-

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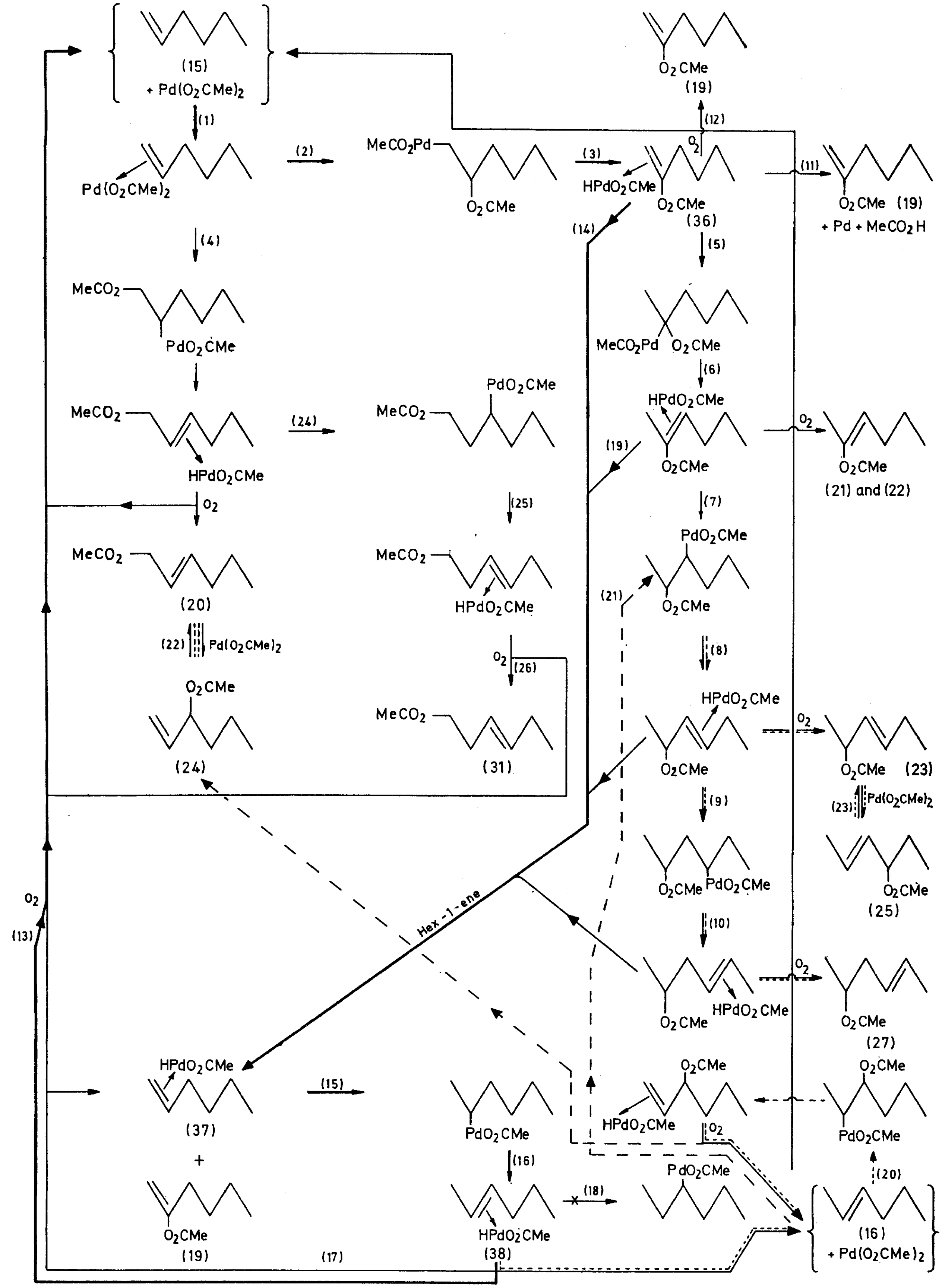
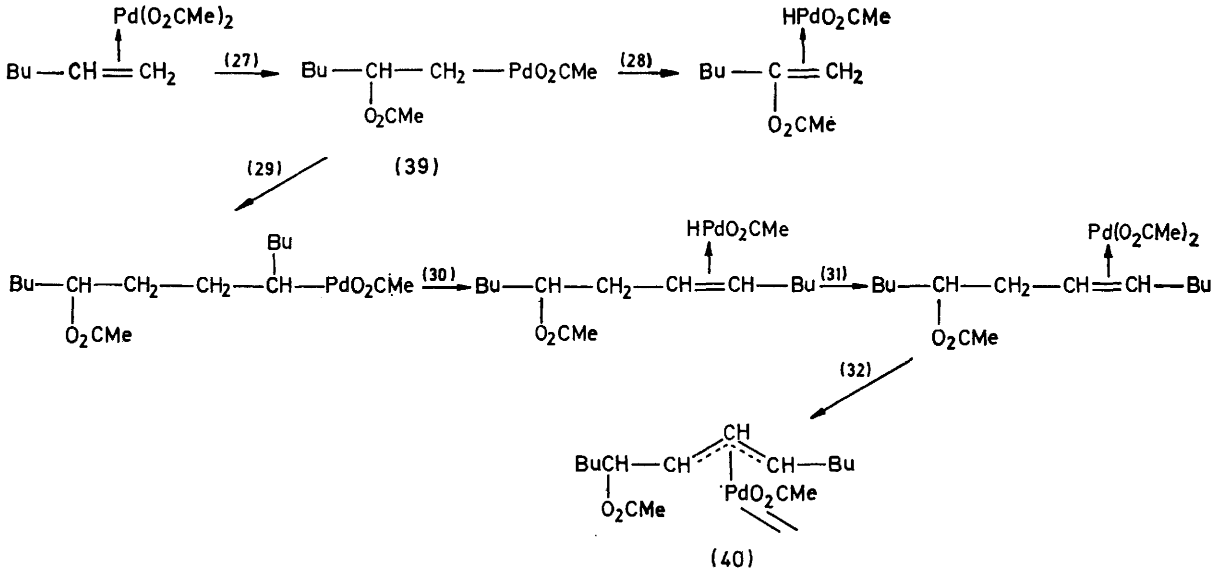
[23] R. G. Brown and J. M. Davidson, *J. Chem. Soc.* (*A*), 1971, 1321.

[24] P. M. Henry, *J. Amer. Chem. Soc.*, 1972, **94**, 1527.



SCHEME 1 (——) Reaction of hex-1-ene; (— — —), reactions of hex-2-ene



SCHEME 2

starting the cycle and preventing further isomerisation of hex-2-ene. The sequence [reactions (2), (3), (14), (15), (16), and (13)] leading to hex-2-ene and (19) as the major products is marked by bold arrows in Scheme 1.

Although 3,3-dimethylbut-1-ene was chosen for study to minimise the number of reactions that compete with oxidation to the vinyl ester (2), a number of other products are formed in low yield by oxidative coupling, *etc.* The formation of 3,3-dimethylbut-1-en-2-yl acetate is readily understood in terms of an addition-elimination sequence[25] [Scheme 2, reactions (27) and (28)], the high selectivity for the Markovnikoff product being partly due to the steric effect of the Bu^t group. Oxidative coupling of olefins has been discussed for non-catalytic reactions by Kikukawa *et al.*[3] In our system it would involve the insertion of (1) into the σ complex (39) prior to elimination of $PdH(O_2CMe)$ [reactions (29) and (30)]. Oxidation of the hydride and loss of acetic acid would then yield the observed acetoxyalkylallyl complex (40) [reactions (31) and (32)]. The cyclisation reactions to cyclobutane derivatives and (5) are novel. They would necessarily involve even longer sequences of similar steps.

Hitherto a number of oxidation reactions have been discussed in terms of complexes of monomeric palladium acetate.[2] In our studies we have observed that different types of complex are present in solution during the oxidation of various olefins and these give rise to different reaction kinetics. Only hex-1-ene was oxidised immediately on mixing with the palladium acetate catalyst without an induction period and the rate law in the early stages was first order in [olefin] and low order (*ca.* 0.4) in $[Pd^{II}]$. This is consistent with rate-determining formation of a monomeric olefin complex from one of the species $[Pd_3(O_2CMe)_6]$, $[Pd_2(O_2CMe)_4]$, or $Pd(O_2CMe)_2$. 3,3-Dimethylbut-1-ene showed similar kinetics which were again first order in [olefin] and half order in $[Pd^{II}]$, and commencing only after an induction period. Thus the initially present species that react rapidly with hex-1-ene are unreactive towards (1). The rate law could be explained by either the formation of a monomeric complex of (1) from a dimeric palladium species [reaction (33) and (34)] or its decomposition [reactions (35) and (36)]. Dimeric complexes of the

$$[Pd_2(O_2CMe)_4L_2] \rightleftharpoons 2[Pd(O_2CMe)_2L] \quad (33)$$

$$[Pd(O_2CMe)_2L] + \text{olefin} \longrightarrow \text{complex} \quad (34)$$

$$[Pd_2(O_2CMe)_4L_2] + 2\text{olefin} \rightleftharpoons 2[Pd(\text{olefin})(O_2CMe)_2L] \quad (35)$$

$$[Pd(\text{olefin})(O_2CMe)_2L] \longrightarrow \text{products} \quad (36)$$

type $[Pd_2(O_2CMe)_4L_2]$ are known[26,27] and in this case L might be acetic acid or (1).

Cyclo-octene was the only olefin studied that yielded an isolable complex that may actually have been of the η^2 type, albeit a labile one. Its decomposition reactions are consistent with its having the stoicheiometry $[Pd(\text{cyclo-octene})(O_2CMe)_2]$ and the rate of consumption of dioxygen during catalytic oxidation is simply first order as would be expected from rate-determining decomposition of the complex.

Several of the olefins studied react with palladium acetate to form allylic complexes which are themselves catalytically active although the η^3-alkenyl group is stable and is not the immediate source of oxidised organic products. In the case of hex-1-ene, after oxidation has proceeded for a few hours, the catalyst is present mainly as (17a). However, the distinctive selectivity pattern is the same in both the fast and slow

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[25] W. Kitching, A. Rappoport, S. Winstein, and W. G. Young, *J. Amer. Chem. Soc.*, 1966, **88**, 2054.

[26] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1967, **29**, 2122.

[27] J. Powell and T. Jack, *Inorg. Chem.*, 1972, **11**, 1039.

stages suggesting kinetic control by the same species and indeed, 'palladium acetate' could be generated according to reaction (37) which was used in the reverse direction as a preparative reaction for the trinuclear species.[1]

$$[\mathrm{Pd_3(1\text{—}3\text{-}\eta\text{-}C_6H_{11})_2(\mu\text{-}O_2CMe)_4}] \rightleftharpoons [\mathrm{Pd_2(C_6H_{11})_2(O_2CMe)_2}] + \tfrac{1}{3}[\mathrm{Pd_3(O_2CMe)_6}] \quad (37)$$

The central palladium atom in (17a) does seem to have a crucial role in the catalytic reactions since (18a) is inactive. Although (18a) could be formed from (17a) and hex-1-ene by elimination of acetic acid [reaction (2), ref. 1], the stoicheiometry observed for the reaction *in vacuo* is consistent with reduction of $\mathrm{Pd^{II}}$ [reaction (38)]. In the presence of dioxygen the concentration of

$$[\mathrm{Pd_3(1\text{—}3\text{-}\eta\text{-}C_6H_{11})_2(\mu\text{-}O_2CMe)_4}] + \mathrm{C_6H_{12}} \longrightarrow \mathrm{Pd^0} + \mathrm{C_6H_{11}O_2CMe} + \mathrm{MeCO_2H} + [\mathrm{Pd_2(1\text{—}3\text{-}\eta\text{-}C_6H_{11})_2(\mu\text{-}O_2CMe)_2}] \quad (38)$$

(17a) would be sustained by 'regeneration' of $\mathrm{Pd^{II}}$ and the formation of (18a) would be inhibited. Undoubtedly the rate-determining step changes after the fast stage since it is only in the slow stage of the oxidation of hex-1-ene that the rate depends on the concentration of dioxygen. Apparently, the reduced complex that undergoes 'regeneration' after formation of the organic oxidation product is less reactive than usual. It could be a polynuclear hydride species or even a palladium(I) complex.

The internal olefins, cyclohexene and *cis*-hex-2-ene, are both less reactive than hex-1-ene, presumably for steric reasons. Cyclohexene converts palladium acetate into an allylic complex which then reacts with more olefin in the slow step. Wolfe and Cambell [16,17] reached similar conclusions for different reasons. Thus the rather unstable cyclohexenylpalladium group is not the source of (25) under these conditions. The oxidation of *cis*-hex-2-ene *via* the oxypalladation route is even slower and in the presence of dioxygen is masked by a faster free-radical reaction.

Finally, it is important to note the effect of acids on these oxidation reactions carried out in acetic acid solution. The internal olefins (16) and (28) yield alk-1-enyl acetates only in the presence of acids. Perchloric acid also promotes the isomerisation of hex-1-ene to all the four internal isomers and allows extensive double-bond shifts in the oxidation products giving hex-4-en-2-yl acetate. This ester was the main oxidation product using palladium chloride complexes.[28] In general the commonly used palladium chloride complexes will generate HCl on reduction which in turn promotes isomerisation. This is a particular advantage of palladium acetate which is buffered by solvent acetic acid.

EXPERIMENTAL

Palladium acetate [29] was purified as follows. Finely powdered $\mathrm{Pd(O_2CMe)_2}$ (3 g) was made into a paste with $\mathrm{H_2SO_4}$ (3 cm^3) and was then heated at 135 ± 5 °C for 40 min. The mixture was cooled, dissolved in water (50 cm^3), and filtered. At this point the solution should contain a little acetic acid and *ca.* 0.5 cm^3 may be introduced if necessary. Sodium carbonate was then added in small portions and after 4—5 g precipitation commenced. The first small crop of crystals was discarded (these were often a maroon basic acetate of $\mathrm{Pd^{II}}$ which gives palladium acetate on boiling with acetic acid) and the solution was treated with more $\mathrm{Na_2[CO_3]}$ (0.5 g) and then acetic acid (20 cm^3). Palladium acetate crystallised during 24 h and was collected and recrystallised from acetic acid.

Rates of Dioxygen Oxidation.—Reactions were carried out using 40 cm^3 of solution in the stirred reaction vessel described in Supplementary Publication No. SUP 21900 (5 pp.).* Dioxygen was metered from a constant-pressure gas burette in which the limbs were filled with acetic acid. Both reaction vessel and gas burette were totally immersed in the thermostat bath which was controlled to ±0.02 °C. The amount of dioxygen consumed during runs was in the range 5—20 cm^3 at s.t.p.

Typically, $\mathrm{Pd(O_2CMe)_2}$ (0.056 8 g) was dissolved in acetic acid and 3,3-dimethylbut-1-ene (2.0 cm^3) was added. The solution was made up to 50 cm^3 at 20 °C and 40 cm^3 was transferred to the reactor. The run was carried out at 297.91 ± 0.02 K and 792 mmHg total pressure ($\mathrm{O_2}$ + acetic acid) and, after 28.75 h, 16.45 cm^3 of $\mathrm{O_2}$ at s.t.p. had been consumed. The rate of uptake of oxygen was obtained by a least-squares fit (root-mean-squares deviation = 0.000 020 mol dm^{-3} h^{-1}) to a straight line after the end of the induction period. Six separate runs carried out under these conditions [0.004 89 mol dm^{-3} $\mathrm{Pd(O_2CMe)_2}$, 0.158 mol dm^{-3} (1)] gave an average rate of 2.51×10^{-4} mol $\mathrm{O_2}$ dm^{-3} h^{-1} with a standard deviation of 0.07×10^{-4}.

At the end of the run the mixture was transferred to a vacuum line, frozen, and sublimed at 10^{-6} mmHg (20 °C) to leave a residue principally of palladium acetate (0.050 9 g, 112%). The volatile reactants and products were collected in a U trap at −196 °C. To the liquid solution (10 cm^3) was added $\mathrm{Me_3CC(O_2CCD_3){=}CH_2}$ (0.067 06 g) after which the usual chemical separation gave a concentrate from which the pure ester (2) was obtained by preparative g.l.c. using polypropylene glycol LB550-X on Chromosorb W at 100 °C. The relative abundances of the ions at *m/e* 46 and 43 in the mass spectrum (averaged from seven spectra) were used to calculate the yield of (2) (6.2×10^{-4} mol) by comparison with the abundances in the original deuterium-enriched specimen. Also the acetic acid solution (25 cm^3) was worked up by partition between diethyl ether and aqueous $\mathrm{Na[HCO_3]}$, and ultimately the amount of the recovered ester was estimated by comparison with a blank sample which had been similarly treated. The yield of (2) determined in this way was 6.9×10^{-4} mol. A comparison with a standard solution showed that 74% of the ester had been recovered in the wet separation. The recovered palladium acetate from the separation by sublimation often contained a small amount of (5) which crystallised in the cool part of the apparatus when the residue was warmed *in vacuo*. Samples of this residue were also treated with aqueous K[CN] and with $\mathrm{H_2}$ in

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, **1976**, Index issue (items less than 10 pp. are supplied as full-size copies).

[28] O. G. Levanda and I. I. Moiseev, *Zhur. obshchei Khim.*, 1968, **4**, 1533.

[29] T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, **1965**, 3632.

methanol (using platinum on charcoal as a catalyst) and the products were analysed by g.l.c. (see below).

The oxidation of other olefins was studied in the same way but in the cases of hex-1-ene and *cis*-hex-2-ene unchanged olefins were separated from the solvent acetic acid and oxidation products by fractional condensation of the latter at −45 °C. When reactions were carried out *in vacuo*, the separations were performed in the same way except that the precipitate of palladium metal was first removed by filtration.

Oxidation of Olefins by Benzoquinone.—Typically, palladium acetate (0.046 1 g), benzoquinone (0.502 g, freshly purified by steam distillation and crystallisation), acetic acid (40 cm^3), and (1) (0.80 cm^3) were sealed into an evacuated tube after degassing. The reaction was carried out at 25 °C for 88 h after which the mixture was frozen and then sublimed at 10^{-6} mmHg (20 °C). The residue weighed 0.232 5 g and thus contained 0.186 4 g of quinhydrone (0.000 855 mol). The sublimate contained acetic acid, (1), (2), and unchanged benzoquinone. The latter was removed quantitatively by reaction with quinol (0.404 g) which converted it into quinhydrone. The acetic acid, (1), and (2) were again removed by sublimation and the residue was dissolved in a mixture of water (18 cm^3), H_2SO_4 (2 cm^3), and acetic acid (20 cm^3) and was titrated with 0.1N $Na_2[S_2O_3]$ to a colourless end-point. The recovery of benzoquinone was thus 0.340 g, indicating consumption of 0.000 750 mol. 3,3-Dimethylbut-1-en-2-yl acetate was estimated by g.l.c. as described above (0.059 3 g, 0.000 418 mol).

Similar reactions with (1) were carried out on a smaller scale in sealed n.m.r. tubes. Benzoquinone, quinol, (1), and (2) were monitored by the resonances at τ 7.22, 7.34, 8.92, and 9.01.

Reaction of Hexenyl Esters with Acetic Acid.—A mixture of hex-1-en-2-yl acetate (24%), *trans*-hex-2-en-yl acetate (58%), and *cis*-hex-2-en-2-yl acetate (18%) (0.85 g) with palladium acetate (0.20 g) in acetic acid (50 cm^3) was shaken with O_2. After 72 h the esters were recovered in the ratio 1 : 40 : 9.

Synthesis of Unsaturated Acetate Esters.—Synthetic procedures and n.m.r. data for the authentic unsaturated esters are given in SUP 21900.

Degradation of the Complexes derived from Palladium Acetate and 3,3-*Dimethylbut*-1-*ene.*—Solutions from catalytic or stoicheiometric runs were filtered and volatile materials were removed *in vacuo* at 25 °C. A small amount of 1,3,5-tri(t-butyl)benzene sublimed from the yellow-brown residue on warming. A sample of the residue was treated with diethyl ether and aqueous K[CN], and on separation and evaporation the etherate afforded an oil from which two components were collected by g.l.c. One component was a solid, identical with 2,2,7,7-tetramethylbuta-3,5-diene, having a parent ion *m/e* 166 and a singlet in the n.m.r. at τ 8.93. The other substance also had a parent ion at *m/e* 166 but was not one of the other known[30-32] di(t-butyl)-butadienes. It had two singlets in the n.m.r. at τ 8.86 and 8.98 and was presumed to be one of the possible di(t-butyl)-cyclobutenes.

Hydrogenation of the recovered catalyst with H_2 (1 atm) in methanol in the presence of a little platinum (1% on charcoal) afforded a very complex mixture. The hydrogenation products corresponding to the above hydrocarbons obtained by reaction with K[CN] were 2,2,7,7-tetramethyloctane (parent ion *m/e* 170 and singlets at τ 8.82 and 9.15 in the n.m.r.) and a presumed di(t-butyl)cyclobutane with a parent ion at *m/e* 168 and having singlets in the n.m.r. at τ 8.97 and 9.03. 2,2,3,6,6-Pentamethylheptane was also obtained and identified by comparison with an authentic specimen from the hydrogenation of 5,5-dimethyl-2-(t-butyl)hexa-1,3-diene (which was not itself observed in the K[CN] degradation) and had parent ion *m/e* 170 and singlets in the n.m.r. at τ 9.14 and 9.17. Neither 2,3-di(t-butyl)buta-1,3-diene nor its hydrogenation product was found in these experiments. In general the mass spectra of these hydrocarbons were characterised by loss of Bu^t and Me groups. Another saturated product from the hydrogenation experiments was probably 2,4-di(t-butyl)-cyclobutanol. In the mass spectrum the parent ion had *m/e* 184 and accurate *m/e* values were measured as 184.181 644, 183.174 261, and 182.167 057 ($C_{12}H_{24}O$ requires 184.182 706, $C_{12}H_{23}O$ requires 183.174 261, and $C_{12}H_{22}O$ requires 182.167 056). The $P - 1$ peak was about twice as abundant as the parent ion, and otherwise the spectrum was characterised by loss of C_4H_9, CH_3, and H_2 to give *m/e* 184, 183, 169, 165, 151, 127, 126, and 109. The n.m.r. spectrum had a singlet at τ 9.15 and symmetrical complex multiplets at τ 6.7 and 8.3, the latter overlying another broad peak.

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