OXIDATION OF ISOBUTENE AND METHYLENECYCLOALKANES BY PALLADIUM(II) ACETATE

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Summary

Reactions of isobutene, methylenecyclopentane, methylenecyclohexane and methylenecycloheptane with palladium acetate were studied in acetic acid at 30 to 80°. Two types of oxidation were identified: acetoxylation to allylic acetates (methylenecycloheptane) and oxidative coupling to dimers (isobutene and methylenecyclohexane). A mechanistic study indicated that the former was produced by thermal decomposition of the initially formed π-allylic complex. The latter process was presumed to proceed via an insertion of the olefin into the carbon—palladium bond in the acetoxypalladate adduct, $-CH_2 \diagdown C-CH_2-Pd(OAc)$, $-CH_2 \diagup \overset{|}{OAc}$

followed by the elimination of the elements of acetic acid and palladium hydride.

Introduction

In an ordinary oxidation of olefins by palladium salts, it is generally accepted [1] that the Markovnikov-type addition of divalent palladium species is followed by either a 1,2-hydride shift to form a saturated carbonyl compound (palladium chloride in aqueous media) or by 1,2-palladium hydride elimination to afford enol and allylic acetates (palladium acetate). This concept implies that in the absence of a β-hydrogen to palladium in the adduct, the formation of normal products cannot be expected. Thus, in the oxidation by palladium chloride in aqueous media, isobutene predominantly produced methacrolein via a π-allylic intermediate [2], and the reaction with Pd(OAc)$_2$—NaOAc in acetic acid yielded oxidatively coupled dimers, 2,4-dimethyl-2,4-hexadiene and 2,5-dimethyl-1,5-hexadiene [3]. A similar oxidative coupling is reported in the reaction of α-methylstyrene with Pd(OAc)$_2$—NaOAc [4] or PdCl$_2$—NaOAc [5]. It should be noted, however, that the olefins carrying an electron-withdrawing group, such as vinyl acetate [6] or ethyl crotonate [7], strongly tend to produce similar coupling

products in the reaction with Pd(OAc)$_2$, although these olefins possess a hydrogen that could be eliminated.

We have now extended the reaction to some of the alicyclic homologues of 1,1-disubstituted ethylene, (CH$_2$)$_n$C=CH$_2$ (n = 4, 5, 6). Isobutene also has been studied under our conditions for comparison.

Experimental

The preparation of Pd(OAc)$_2$ has been described [7]. Isobutene was prepared by the dehydration of t-butyl alcohol. Methylenecyclopentane and methyl enecyclohexane were obtained by the method of Vilkas et al. [8] with a small modification. The modification is concerned with the hydrolysis of the intermediate, ethyl 1-hydroxycycloalkylacetate, to the corresponding acid. While the literature claimed only 19 and 78% yield for the cyclopentyl and the cyclohexyl derivatives, respectively, using methanolic potassium hydroxide, increased yields, 92 and 89%, respectively, were attained by stirring with excess 10% aq. sodium hydroxide at room temperature (1 h). Methylenecyclopentane b.p. 75 ~ 76.5°; methylenecyclohexane b.p. 102 ~ 104°. Methylenecycloheptane was prepared from cycloheptanone and triphenylphosphine methylide in a 40% yield, b.p. 131 ~ 133°.

Reaction of olefins with palladium acetate

The olefin* (6 ~ 8 g) was added to a solution of Pd(OAc)$_2$ (2 g) in acetic acid (40 g) in a 100 ml flask equipped with a reflux condenser and a magnetic stirrer. The mixture was stirred in an oil bath under a nitrogen atmosphere until palladium metal deposited (metal precipitation was not complete for methylenecyclopentane, refer to Table 3). The reaction time and temperature generally ranged from 10 to 400 h and 30 to 80°, respectively. After filtration, the reaction mixture was combined with 100 ml of ether, washed successively with water (twice), 10% aq. sodium bicarbonate solution and saturated sodium chloride solution, and dried. The product mixture obtained by distillation was resolved by GLC Each component was identified by means of its IR and NMR spectra. Spectral date of the products are summarized in Table 1. 1,2-Dicyclohexylethane and 1-phenyl-2-cyclohexylethane were also identified by comparing their IR, NMR spectra and the retention times on GLC with those of authentic samples prepared by standard methods. The reaction of methylenecyclopentane yielded an intractable solid material containing palladium (1.85 g, Anal: C, 57.42; H, 5.24%) from which a small amount of di-μ-chlorobis(π-methylenecyclopentyl)dipalladium was isolated

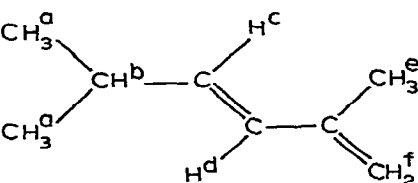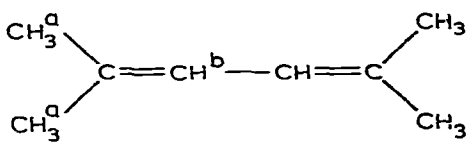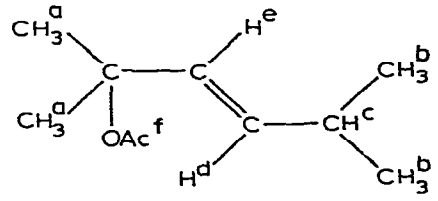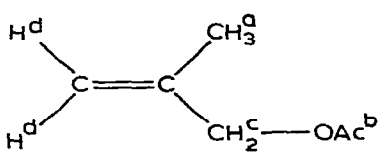### Reaction of olefins with palladium acetate in the presence of carbon monoxide

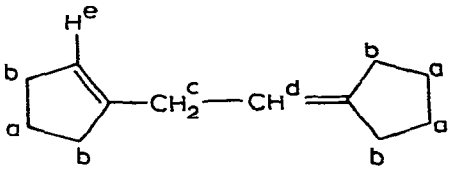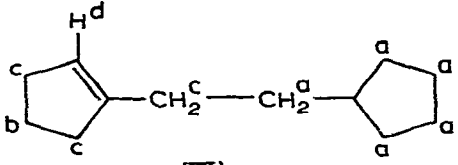Two procedures were utilized. In procedure A, to the acetic acid (50 ml) containing Pd(OAc)$_2$ (2 g)** olefin (6 ~ 8 g) was added slowly to form an upper layer in a glass autoclave. Methanol (4 ml) and then carbon monoxide (10 atm) were introduced, and the mixture was stirred vigorously at room temperature. In

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* Isobutane (10 ml) was condensed in a 200 ml glass autoclave containing the Pd(OAc)$_2$ solution and allowed to react in a sealed system.

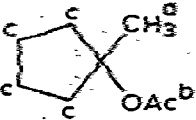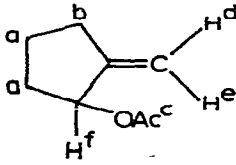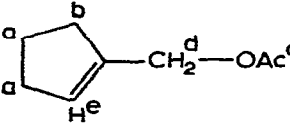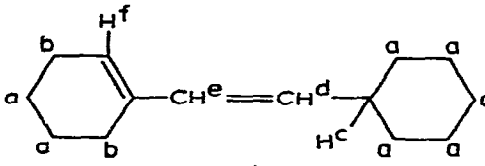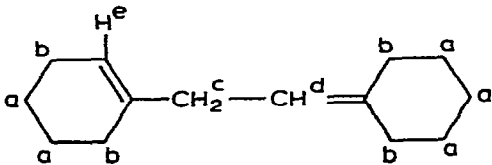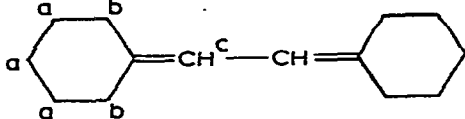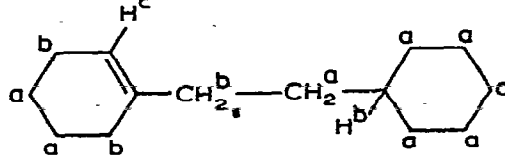** Pd(OAc)$_2$ did not dissolve completely in acetic acid under these conditions, but the addition of olefin to the suspension gave a homogeneous solution immediately.

TABLE 1

NMR AND IR SPECTRAL DATA OF THE PRODUCTS

Compound	NMR (ppm)[a]	IR, (cm^{-1})[b]
(I)	1.03d(a), 1.80s(e), 2.35m(b), 4.82s(f), 5.52q(c), 6.07d(d) J_{ab} 6.5, J_{bc} 6.5, J_{cd} 16.0 cps	1609, conj. diene, 1385, 1370, iso-Pr, 970, trans-CH=CH, 885, —C=CH$_2$)
(II)	1.69s, 1.76s(a), 5.87s(b)	1622 diene, 1378.δ(CH$_3$)
(III)	0.90d-d(b), 1.72s(a), ~1.9m(c), 1.95s(f), 4.98q(d), 5.20d(e) J_{cd} 6.5, J_{de} 15.5 cps	1736 ν(C=O), 1370 δ(CH$_3$), 1240 ν(C—O), 973 trans-CH=CH
(IV)	1.73s(a), 2.02s(b), 4.42s(c), 4.90bs(d)	1747 ν(C=O), 1660 ν(C=C), 1235 ν(C—O), 908 (C=CH$_2$)
(V)	1.5~1.8m(a), 1.8~2.4m(b), 2.67d(c), 5.28m(d, e)	
(VI)	1.52s, 1.67s(a), 1.75 2.05m(b), 2.23m(c), 5.35bs(b)	
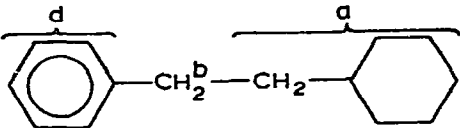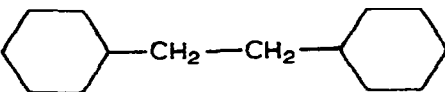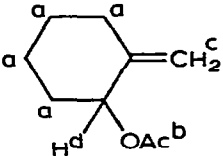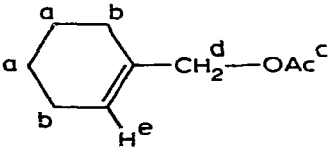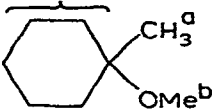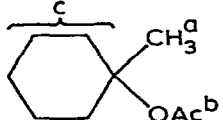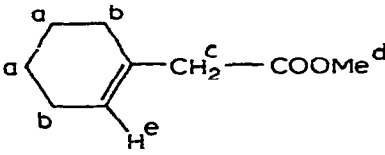
TABLE 1 (continued)

Compound	NMR (ppm)[a]	IR (cm^{-1})[b]
(VII)	1.50s(a), 1.90s(b), 1.6bs(c)	1740 ν(C=O) 1370 δ(CH$_3$)
(VIII)	1.8m(a), 2.2~2.5(b), 2.00s(c), 5.05bs(d), 5.15bs(e), 5.42bs(f)	1738 ν(C=O), 1663 ν(C=C), 900 (C=CH$_2$)
(IX)	1.9(a), 2.2~2.4(b), 2.00s(c), 4.75s(d), 5.63bs(e)	1747 ν(C=O), 1662 ν(C=C)
(X)	1.1~1.3(ax.-H in a), 1.4~1.8 (eq.-H in a, & a') 2.1(b,c) 5.35q(d), 5.92d(e), 5.53bs(f) J_{cd} 6.5, J_{de} 15.5 cps	962 (trans-CH=CH-)
(XI)	1.54bs(a), 1.8~2.2(b), 2.55d(c), 5.05t(d), 5.38bs(e) J_{cd} 7.5	
(XII)	1.55s(a), 2.20m(b), 5.87s(c)	
(XIII)	0.9~1.7(a), 1.7 2(b), 5.31bs(c)	
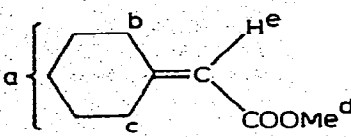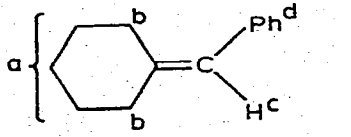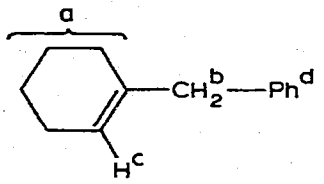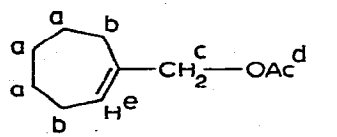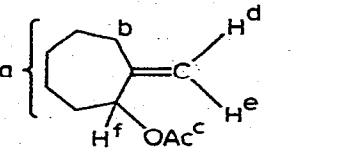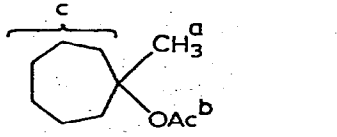
TABLE 1 (continued)

Compound	NMR (ppm)[a]	IR (cm^{-1})[b]
(XIV)	0.8~1.9(a), 2.6m(b) 7.12s(d)	1605, 1495, 704, 749 (mono substd. benzene)
(XV)	1.2(axial proton), 1.7(equatorial proton)	
(XVI)	1.65m(a), 1.98s(b), 4.75bs(c), 5.15bs(d)	
(XVII)	1.65(a), 2.0(b), 2.02s(c), 4.35s(d), 5.67bs(e)	
(XVIII)	1.05s(a), 3.10s(b), 1.25~1.7(c)	1375 δ(CH$_3$) 1085 δ(C—O)
(XIX)	1.43s(a), 1.93s(b), 1.5~2.0(c)	1734 ν(C=O), 1235 ν(C—O),
(XX)	1.63m(a), 2.00bs(b), 2.85s(c), 3.61s(d), 5.51bs(e)	1740 ν(C=O),

TABLE 1 (continued)

Compound	NMR (ppm)[a]	IR (cm^{-1})[b]
(XXI)	1.62s(a), 2.2bs(b), 2.82bs(c) 3.62s(d), 5.53s(e)	1713 ν(C=O), 1652 ν(C=C), 1380 δ(CH$_3$)
(XXII)	1.60m(a), 2.30m(b), 6.20s(c), 7.15s(d)	
(XXIII)	1.4~2.2m(a), 3.20s(b) 5.40bs(c), 7.15s(d)	
(XXIV)	1.64m(a), 2.15m(b), 2.00s(d), 4.37s(c), 5.87t(e)	1745 ν(C=O),
(XXV)	1.53m(a), 2.25m(b), 1.99s(c), 4.87s(d), 4.97s(e), 5.29t(f)	1743 ν(C=O), 1653 δ(C=C), 903 (C=CH$_2$)
(XXVI)	1.45s(a), 1.88s(b), 1.5~2.3m(c)	

[a] These were examined as 5—10 vol % solution in carbon tetrachloride and the chemical shifts were measured from tetramethylsilane internal reference. s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs, broad signal. [b] These were measured as neat.

procedure B, while the same amounts of materials were employed, Pd(OAc)$_2$ was dissolved completely in the acetic acid—olefin mixture and the solution was allowed to stand for an hour at room temperature before the introduction of methanol and carbon monoxide. After they had been stirred for the periods shown in Table 4 at room temperature, the reaction mixtures were treated similarly as described above. The introduction of carbon monoxide and methanol generally resulted in a rapid (sometimes immediate) precipitation of palladium metal, and the reaction seemed complete in a few hours.

NMR spectra of reaction intermediate

To a suspension of Pd(OAc)$_2$ (100 mg) in acetic acid (2 ml), 0.5 ml of olefin was added to give a homogeneous solution. After the mixture was stirred at room temperature for a desired period (1 or 10 h), the solvent and the excess olefin were evaporated to dryness under vacuum at room temperature. The residual solid was dissolved in CDCl$_3$ and the NMR spectrum was measured at room temperature (Varian A-60).

TABLE 2

NMR SPECTRAL DATA FOR π-ALLYLIC PALLADIUM COMPLEXES OF THREE METHYLENE-CYCLOALKANES
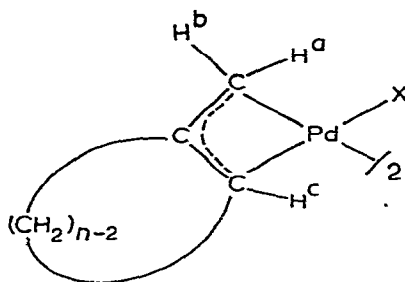
n	X	H^a	H^b	H^c
5	Cl	3.02 s	3.87 s	4.12 s [b]
5	OAc	2.81 s	3.75 s	3.96 s [b]
6	Cl	2.60 s	3.60 s	4.18 s [b]
6	OAc	2.37 s	3.48 s	3.98 s [b]
7	Cl	2.70 s	3.68 s	3.88 m
7	OAc	2.60 s	3.60 s	3.75 m

[a] Measured from TMS in CDCl$_3$ at room temperature. s = singlet, m = multiplet. [b] These signals are relatively broad as compared with those of H^a and H^b.

Preparation of π-allylic palladium complexes

Di-μ-chlorobis(π-methylenecyclopentyl)dipalladium. To a solution of Li$_2$-PdCl$_4$ (345 mg) in methanol (20 ml), methylenecyclopentane (0.3 ml) was added; the solution was stirred at room temperature until the brown color changed to yellow (2 ~ 4 days). The resulting solution was poured into 30 ml of water, extracted with three 30 ml portions of chloroform and dried over CaCl$_2$. The solvent was evaporated and the residue purified by column chromatography on silica gel (Wako-Gel C-200, 14 mm × 30 cm, chloroform), yield 130 mg (47%), m.p. 151

$\sim 152.5°$. Anal. found, C, 31.83; H, 3.97. $C_{12}H_{18}Pd_2Cl_2$ calcd.: C, 32.32; H, 4.07%.

The same procedure was employed for the other chloride bridged π-allylic complexes.

Di-μ-chlorobis(π-methylenecyclohexyl)dipalladium, yield 21%, m.p. 146 $\sim$ 150° (dec.). Anal. found: C, 35.01; H, 4.63. $C_{14}H_{22}Pd_2Cl_2$ calcd.: C, 35.47; H, 4.68%.

Di-μ-chlorobis(π-methylenecycloheptyl)dipalladium, yield 39%, m.p. 188 $\sim$ 190° (partially dec.). Anal. found: C, 38.46; H, 5.35. $C_{16}H_{26}Pd_2Cl_2$ calcd.: C, 38.28, H, 5.22%.

The corresponding π-allylic palladium acetate complexes were prepared by the reaction of the chloride complexes with AgOAc in acetone according to the method of B.L. Shaw [10].

NMR spectral data of these complexes are tabulated in Table 2.

Results

Reaction of isobutene and methylenecycloalkanes with palladium acetate

The products obtained under some of the typical reaction conditions are summarized in Table 3. The variation in reaction conditions (see experimental section) did not change the products except for methylenecyclohexane. When reacted with palladium acetate at 80°C for 6 h, this olefin gave 1-(1-cyclohexenyl)-2-cyclohexylethane (XIII), 1-cyclohexyl-2-phenylethane (XIV), and 1,2-dicyclohexylethane (XV) in 38, 30 and 15% yields, respectively, in place of the three oxidatively coupled dimers in Table 3. However, control experiments indicated that the former products were derived from the latter by a palladium-catalyzed hydrogenation-dehydrogenation process effected at higher reaction temperatures. The transformation was also found to be effected by a prolonged reaction time at a moderate temperature. The formation of non-oxidative coupling product VI from methylenecyclopentane could be explained by a similar secondary reaction of some of the primary diene products, since the oxidative coupling product V was isolated when the reaction was quenched at the early stages by the introduction of carbon monoxide (Table 4).

Table 3 reveals the marked difference in the products obtained from the olefins. The oxidative coupling products were predominantly formed from isobutene

TABLE 3

REACTION OF METHYLENECYCLOALKANES AND ISOBUTENE WITH Pd(OAc)$_2$

Olefin	Conditions		Products and yields (%, based on Pd(OAc)$_2$)
	temp. (°C)	time (h)	
Isobutene	55	20	I (40), II (26), III (15) and IV (13)
Methylenecyclopentane	50	432	VI (7)
Methylenecyclohexane [a]	30	168	X (41), XI (18), XII (15) and a small amount of oligomers
Methylenecycloheptane [b]	80	15	XXIV (51) and XXV (16)

[a] A non-oxidative product, 1-methylcyclopentyl acetate (VII) (40% on molar basis for palladium) and a considerable amount of dark brown solid (1.85 g) were obtained. [b] Other product, 1-methylcycloheptyl acetate (XXVI) (10%).

TABLE 4

REACTION OF METHYLENECYCLOALKANES AND ISOBUTENE IN THE PRESENCE OF CARBON MONOXIDE AT ROOM TEMPERATURE

Olefin	Procedure [a]	Reaction time (h)	Products and yields (%, based on Pd(OAc)$_2$)
Isobutene	B	12	I (7)II (8) [b], III (15) and IV (14)
Methylenecyclopentane	B [c]	14	V (3), VIII (32) and IX (61)
	B [d]	21	V (3), VIII (24) and IX (54)
Methylenecyclohexane	A [e]	24	Dimers (trace), XVII (3), XX (21) and XXI (13)
	B [f]	24	X (11), XII (3), XVII (10), XX (31) and XXI (18)
Methylenecycloheptane	A [g]	4	XXIV (26) and XXV (trace)
	B	4	XXIV (72) and XXV (trace)

[a] See experimental section for procedures A and B. [b] This fraction contained structurally unknown hydrocarbon (oxidatively coupled dimer?). [c] A non-oxidative product, 1-methylcyclopentyl acetate (VII) (2% on molar bases for palladium), was also formed. [d] The reaction mixture was allowed to stand for 70 hours at room temperature before the introduction of carbon monoxide. [e] Other products: 1-methylcyclohexyl acetate (XIX) (102%), 1-methylcyclohexyl methyl ether (XVIII) (29%). [f] Other products: XIX (74%), XVIII (20%). [g] Other product: 1-methylcycloheptyl acetate (10%).

and methylenecyclohexane, while methylenecycloheptane produced allylic acetates (XXIV and XXV) and methylenecyclopentane produced a large amount of intractable solid material.

Examination of the reaction mixture

Two methods were employed to examine the nature of the reaction intermediates during the reaction. The first was the treatment of the reaction mixture with low pressure (10 atm) carbon monoxide and the second involved an NMR study.

It is known that π-allylic palladium acetate complexes decompose to allylic acetates and metallic palladium in the presence of low pressure carbon monoxide [11], while a species containing σ Pd—C bond undergoes insertion of carbon monoxide and subsequent decomposition under nucleophilic conditions to give carbonylated organic compounds [12]. Since these decompositions are very rapid processes as compared with the oxidation of the olefins in the current study, it would be expected that the introduction of carbon monoxide at the early stage of the reaction would yield information on the structure of the intermediates involved in the oxidation. The results shown in Table 4 suggest that π-allylic palladium acetate is the dominant intermediate in the reaction of methylenecycloheptane, while the presence of σ-bonded palladium species may be supposed in the reaction of methylenecyclohexane. Only a minor effect was observed in the similar reaction of isobutene. Apart from the oxidation, it can be seen in Table 4 that the introduction of carbon monoxide leads to the formation of a considerable amount of addition products from the methylenecycloalkanes and acetic acid or methanol. While the mechanism remains uncertain, this reaction no doubt is related to the presence of a palladium species which has not yet entered into full reaction with the olefin to form the intermediate π-allylic complex or the final oxidation product, since the formation of the adduct is favored by procedure A rather than by procedure B (Table 4, footnotes). The fact that methylenecyclohexane gave the highest yields of the adduct in both the procedures is in good accordance with the following NMR study which indicated that this olefin did not form any stable intermediate under the current reaction conditions.

In the NMR study, the reaction mixture obtained 10 h at ambient temperature
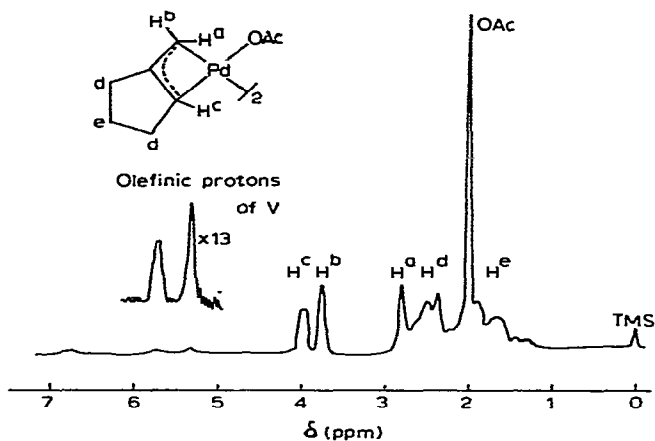
Fig. 1. NMR spectrum of reaction mixture of methylenecycloheptane with Pd(OAc)₂ concentrated under vacuum.

after the addition of olefin was concentrated under vacuum at room temperature and the NMR spectrum of the residue was measured in CDCl₃. The spectra illustrate in Figs. 1 and 2 for methylenecyclopentane and methylenecycloheptane respective show that the principal constituent of the reaction mixture is the π-allylic palladium acetate. A small amount of oxidatively coupled dimers was observed in the former spectra. The structures of the complexes in the reaction mixture were established by comparing with the NMR spectra of the authentic samples (Table 2). Even one hour after mixing, a substantial amount of π-allylic palladium acetate has been found in the two systems. It is interesting that the π-allylic complexes are formed from the reaction of these monoolefins and palladium acetate under such mild con ditions as those in this experiment. In contrast, most of the palladium acetate was recovered without reaction from the reaction mixture of methylenecyclohexane (after 1 h). No evidence for the formation of the π-allylic complex species was obtained, while a trace of the oxidative coupling products could be detected
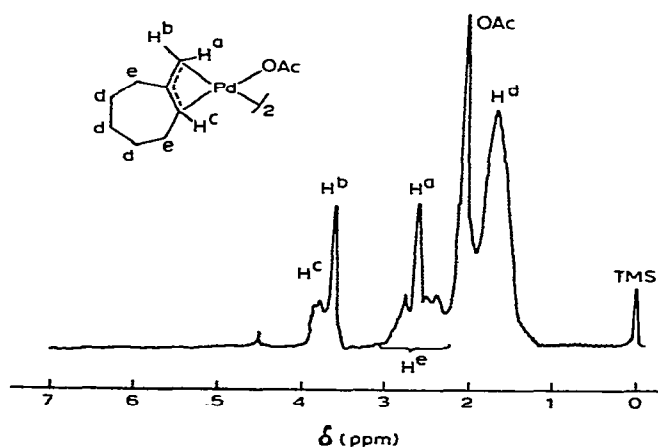

Fig. 2. NMR spectrum of reaction mixture of methylenecyclopentane with Pd(OAc)₂ concentrated under vacuum.

spectroscopically. These observations lead us to the supposition that the π-allylic palladium acetates do not play an important role in the current oxidative coupling reaction, because the olefins giving the complexes most readily (methylenecyclopentane and methylenecycloheptane) afforded none or only a small amount of the coupling products, while methylenecyclohexane which does not form the π-allylic complex gave the highest yield of the dimers.

It now seems well established for methylenecyclopentane and methylenecycloheptane that the prominent species of palladium in the oxidation mixture is the π-allylic palladium acetate, but the nature of the intermediate for methylenecyclohexane is still uncertain. With this in mind, the reactivity of the π-allylic complex, π-methylenecyclohexylpalladium acetate, was investigated. With low pressure carbon monoxide plus methanol in acetic acid the complex decomposed to allylic acetates (XVI and XVII in comparable yields) in a similar manner to the other π-allylic complexes in this study, and no carbonylated compounds were formed. Thus, with reference to the results in Table 4, the π-methylenecyclohexyl palladium complex at best explains only a part of the palladium species present in the actual oxidation mixture, and other palladium species which enable CO insertion must be considered for the intermediate. On the other hand, the reaction of the complex with methylenecyclohexane under similar conditions to those in Table III gave X (24%), XI (8%), and XII (12%) along with some higher oligomers (27% as trimer), a result which is fairly close to that in Table 3. This reactivity, which is formally an insertion of an olefin into the π-allylic C—Pd bond, is quite unusual as the reaction of π-allylic complex in general, and it is better considered as due to the reaction of the other palladium species which has been formed during the reaction. The π-methylenecyclohexylpalladium complex is quite similar in structure to the other π-allylic complexes (NMR spectra in Table 2) and behaves similarly in a rapid reaction such as decomposition under carbon monoxide pressure. However, this might not be the case for a slow reaction. It should be recalled that under certain conditions the formation of a π-allylic complex from a π-olefin complex is reversible [4, 5], and in fact the above experimental fact seems best explainable by considering such a process, which effectively eliminates the difference between the two reaction systems, Pd(OAc)₂—olefin and π-allylic complex—olefin.

Discussion

Notable features of the current oxidation of the methylene type olefins with palladium acetate (Table 3) as compared to those of ordinary terminal olefins [1, 7] are: (1) the severe conditions required to complete the oxidation, (2) the absence of enol acetate in the products for all the olefins, (3) the marked tendency of isobutene and methylenecyclohexane to yield oxidatively coupled products, and (4) the ready conversion of methylenecyclopentane or methylenecycloheptane to the π-allylic palladium acetate during the reaction. The acetoxylation of ordinary terminal olefins by palladium acetate proceeds principally via acetoxypalladation in a Markovnikov manner followed by 1,2-elimination of palladium hydride to form unsaturated acetates. With the olefins in this study both steric and electronic influences would strongly control the direction of Pd—OAc addition in such a way that the palladium atom becomes attached to the terminal carbon atom (Markovnikov type addition). Because of the absence of a β-hydrogen, the resultant adduct is un-

able to undergo palladium hydride elimination, which is usually a quite facile product even at room temperature. Thus, the features noted under (1) and (2) above are obviously related to the inability of the olefins to enter the ordinary addition— elimination mechanism, and the features (3) and (4) seem to be a manifestation of the secondary reactivity in the system which is uncovered after the ordinary reactant has been blocked. All of these logically follow if the palladium in the adduct is increase bound to the terminal carbon. If the direction of Pd—OAc addition had been the opposite, then the products expected from the ordinary route would have resulted This anticipation was partially substantiated by the reaction of methylenecyclo- hexane with a phenylpalladium reagent which is known to add to olefins in an anti— Markovnikov manner [9, 13]. 1-Benzylcyclohexene (16%) and benzylidenecyclo- hexane (28%) were obtained and none of the oxidatively coupled dimers was detected.

Reaction intermediates

Several mechanism have been proposed for the oxidative coupling of 1,1-di- substituted ethylenes effected by palladium acetate [14, 15]. A 1-alkenyl palla- dium(II) acetate, for example, is proposed as the reaction intermediate in the coupling of α-methylstyrene. In the present study two types of oxidation were disclosed, the first leading to allylic acetates and the second to oxidative coupling of the olefin. The first is exemplified by the reaction of methylenecycloheptane where allylic acetates are the sole product, and the second is most clearly seen in the reaction of methylenecyclohexane which gave only oxidative coupling product In order to account for the results we propose the following scheme which is in- tended for a general usage with other olefins and includes the reactions which were not realized with methylenecyclohexane.

SCHEME 1

POSTULATED REACTION PROCESS
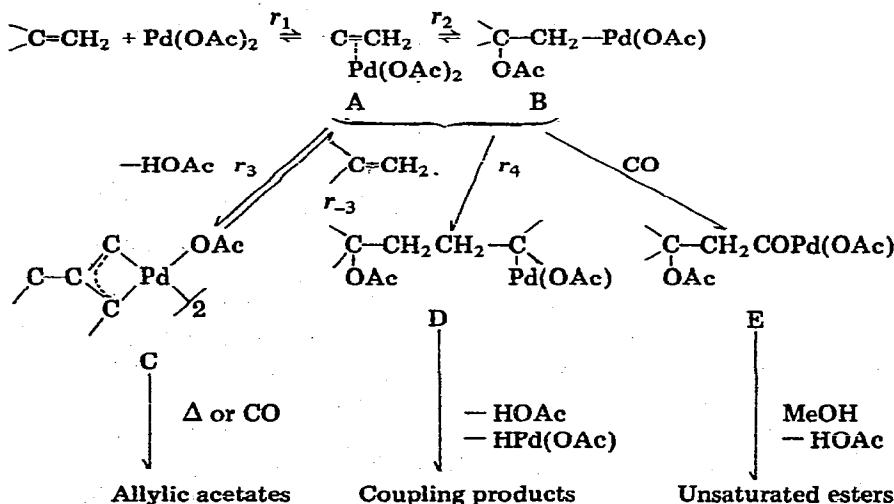
The oxidation of methylenecycloheptane by palladium acetate is most reason ably explained by considering the intermediate formation of π-methylenecyclo-

heptylpalladium acetate. Both the NMR and the quenching (by carbon monoxide) studies support the intermediacy of the complexes. The resultant solution of the π-allylic complex C is stable at room temperature and decomposes to the allylic acetates and metallic palladium only at elevated temperatures. This is exactly the behavior of the π-methylenecyclohexylpalladium acetate observed in an independent study.

The situation is more complicated for methylenecyclohexane. It is to be emphasized that while the introduction of carbon monoxide into the reaction mixture immediately produced a substantial amount of carbonylated organic compounds (which meant the insertion of carbon monoxide into the C—Pd bond of some intermediate complex), a simple concentration of the reaction mixture (without carbon monoxide introduction) left most of palladium acetate and none of the complex was detected. These facts lead us to the idea that the complex species being responsible for the carbon monoxide insertion* (and probably also for the olefin insertion) is in rapid equilibrium with the olefin and palladium acetate. The intermediate (or precursor) complexes having σ-(2-alkenyl)-(XXVII) and/or
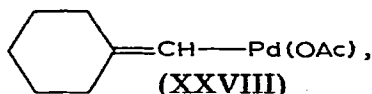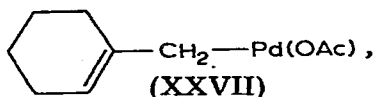
1-alkenylpalladium (XXVIII) structures seem inadequate to account for the observed results. The former structure must be in a very rapid equilibrium with the π-allylic structure (so-called σ-π interconversion of π-allylic complexes), and does not represent the structure of the precursor we are seeking since the π-methylenecyclohexylpalladium complex proved unable to undergo the insertion of carbon monoxide. The 1-alkenylpalladium species or cyclohexylidenemethylpalladium acetate (XXVIII) appears attractive since it can explain the formation of the carbonylated compound XXI (but not XX) as well as some of the oxidatively coupled dimers. However, it is hardly acceptable that such a complex can be in a fast equilibrium with methylenecycloalkane and palladium acetate. Moreover, the formation of such a methylenecycloalkane type complex should be less favored for the six-membered homolog as compared with the five- or seven-membered homologs from the concept of the internal strain [16]. In other words, if cyclohexylidenemethylpalladium acetate indeed took part in the reaction to a considerable extent, a difficulty would arise to account for the fact that such an intermediate was not detected in the reaction of methylenecyclopentane or methylenecycloheptane.

While none of the above arguments constitutes a conclusive proof against the intermediacy of cyclohexylidenemethylpalladium species, it seems more proper at present to regard the π-olefin complex A or the acetoxypalladation adduct B as the intermediate undergoing the insertion reactions. The formation of the complex D is formally an addition of the adduct B to another olefin molecule, and the mode of addition is in line with that observed in the reaction of phenyl-

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* A possibility may be considered that a methoxycarbonylpalladium species (—PdCOOMe) initially forms under carbon monoxide atmosphere and reacts with methylenecyclohexane to give XX and XXI. However, this process cannot explain the behavior of the other methylene type olefins under the similar reaction conditions (Table 4).

palladium reagent with methylenecyclohexane. Recently, it has been reported
that an alkylpalladium species which lacks a β-hydrogen to palladium, such as ber
or neopentylpalladium acetate, adds to olefins in a manner similar to that observe
for phenylpalladium reagent [17]. It should be noted that the complex B is struc
turally similar to these alkylpalladium reagents. The reaction of D leading to the
coupling products constitutes a complicated process involving the elimination
of both acetic acid and palladium hydride. At first sight the elimination of acetic
acid from D may appear unusual, but in the presence of palladium such a reactior
could well be postulated since it has a parallel in the facile reaction of A or B to
form π-allylic intermediate C for methylenecyclopentane or methylenecyclo-
heptane, though the mechanism involved is still uncertain. Similarily the reaction
of E leads to the unsaturated esters XX and XXI.

Behavior of the other olefins

The reaction of methylenecyclopentane with palladium acetate resembles
that of methylenecycloheptane in that the formation of the π-allylic complex is
complete in the initial stage of the reaction. However, the resultant solution of
the π-allylic complex does not give allylic acetates on further reaction but gives
dark brown, intractable, polymeric precipitates. A small amount of oxidative
coupling product also is obtained, but the most of it is formed in the very early
stages of the reaction (probably in parallel with the formation of the π-allylic
complex) and prolonged reaction times do not increase the yield. Thus, the forma
tion of the coupled product is again related to complex A or B and not directly
to complex C. A structural study on the precipitates has remained unsuccessful
and the detailed mode of decomposition of the π-allylic complex under the
current condition is still uncertain. One of the possibilities would be that the
oxidative coupling product is continuously produced from the adduct B which
is in equilibrium with the complex C, but the diene enters into further complicate
reactions with the complexes in Scheme 1.

Isobutene resembles methylenecyclohexane in that the major products are
the oxidative coupling products. The reaction of π-(2-methylallyl)palladium acetat
with isobutene under similar conditions to those in Table 3 gives only methallyl
acetate and none of the coupling products. This indicates that the π-allylic comple
is not the intermediate leading to the coupled products but is the precursor to the
minor product, methallyl acetate. It also means that π-(2-methylallyl)palladium
acetate, unlike the π-allylic complex from methylenecyclohexane, is unable to
follow the reverse way to give isobutene and palladium acetate under the current
conditions. The structure of the dimer III is unique in that the acetate group is re-
tained.

Difference among the methylene type olefins

Scheme 1 represents the summary of the reactions studied in the present wor
For all the olefins the formation of A or B from the olefin and palladium acetate
is reversible. The marked difference in reactivity among the four olefins results
from the next step. The formation of C is a rapid process for methylenecyclo-
pentane and methylenecycloheptane, i.e., $r_3 \gg r_4$ for the two olefins, while the
opposite is true for isobutene and methylenecyclohexane. Further, the equilibrium
(r_3/r_{-3}) favors the π-allylic complex C for isobutene, methylenecyclopentane

and methylenecycloheptane; for methylenecyclohexane A and B predominate over C. The stability and the relative ease of formation of the π-allylic complex C for methylenecyclopentane and methylenecycloheptane over methylenecyclohexane are no doubt related to the strain released on forming the π-allylic complex from the parent olefin and palladium acetate. Thus, it would be concluded that the conformational strain associated with the system is a major contributing factor which controls the oxidation of these olefins to either acetoxylation to allylic acetates or leads to oxidative coupling to form dienes.

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