The Reaction of Open-chain Unconjugated Dienes with Palladium Acetate. Dependence of the Products on Disposition of the Two Double Bonds

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The reaction of open-chain unconjugated dienes with palladium acetate in acetic acid was investigated with particular reference to the behavior of the two double bonds in the course of the acetoxylation. 1,5-Hexadiene produced 3-acetoxymethylenecyclopentane (64%), but 2,6-octadiene bearing two terminal methyl groups gave open-chain acetoxylated products: 3-acetoxy-1,6-octadiene (46%) and 7-acetoxy-2,5-octadiene (47%). The reactions of 1,6-heptadiene and diallyl ether are found to proceed *via* abnormal anti-Markovnikov addition to afford *cis* and *trans* 1-acetoxy-1,6-heptadienes (63%) and γ-acetoxyallyl allyl ethers (84%), respectively. No participation of the second double bond has been observed in the reaction of 1,7-octadiene. The behaviors of these dienes to palladium acetate can be reasonably explained by assuming the formation of π,σ-palladium species possessing a stable pseudo-six membered ring.

Although considerable efforts have been devoted to the reaction of conjugated dienes, especially of 1,3-butadiene, with palladium salts, studies of unconjugated dienes seem to be limited to such compounds as 1,5-cyclooctadiene, dicyclopentadiene, norbornadiene and so on, in which the two double bonds are fixed in cyclic system and favorably located so that they can interact with palladium salt to form a diene-palladium complex of considerable stability. Moreover, the resultant complexes are known to react with several nucleophiles to give π,σ-palladium species.[1]

We previously reported[2] that in the reaction with palladium acetate 1,5-hexadiene underwent cyclization to form a methylenecyclopentyl acetate. This fact strongly suggests that a cyclic intermediate similar to the π,σ-palladium species is involved in the cyclization. This paper deals with the reactions of other open-chain unconjugated dienes and diallyl compounds containing oxygen, nitrogen and sulfur with palladium acetate, and presents a relationship between the structures of the dienes and the oxidation products.

Results

The oxidation of dienes with palladium acetate (1 g) was generally carried out in acetic acid (40 ml) at 50 °C in the presence of ten-fold excess of diene until precipitation of palladium metal was completed (5—7 hr). The principal products obtained from the reactions and their yields based on palladium acetate are tabulated in Table 1. Their analytical data are shown in Table 2. The crude reaction products were usually obtained in yields over 90%, and virtually consisted of monoacetates (or monoketone). The excess dienes were recovered free from isomerization of the double bonds.

The cyclization product obtained from 1,5-hexadiene had previously been assumed to be 2-acetoxymethylenecyclopentane, mainly on the basis of considerably large chemical shift (δ 5.15) of the proton at the carbon carrying an acetoxyl group.[2] However, comparison of its NMR spectrum with that obtained in the reactions of methylenecyclopentane with palladium acetate[5] or mercuric acetate led us to conclude the product to be 3-acetoxy isomer (**1**) (see Table 2, **1** and **1'**). 1,6-Heptadiene yielded a mixture consisting

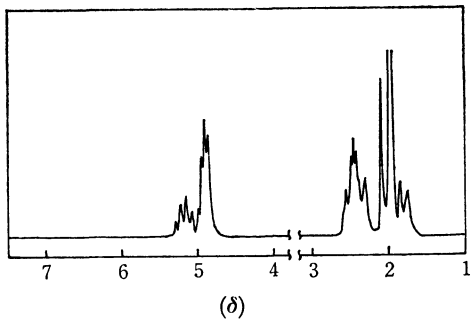


Fig. 1. NMR spectrum of **1**.

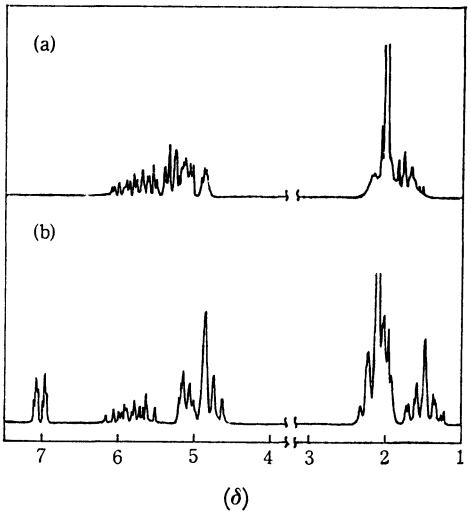
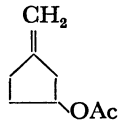


Fig. 2. NMR spectra of **2**(a) and **3**(b).

of three monoacetoxydienes bearing a terminal vinyl group (δ_{CH} 990—980 and 910 cm^{-1}, and multiplet at δ 4.8—6.2). Two of them were characterized by the presence of higher carbonyl absorption (1765—1770 cm^{-1}) and a doublet absorption at around δ 7 region (Fig. 2b) indicating the presence of $\underset{\text{OAc}}{\text{CH}}$=CH– group.

By considering coupling constants of the doublet absorptions, they were assigned to be *cis* (**3**, J=6.5 Hz) and *trans* (**4**, J=12 Hz) isomers of 1-acetoxy-1,6-heptadiene. The structure of the other one was tentatively assigned to 3-acetoxy-1,6-heptadiene (**2**) on the basis of $\nu_{C=C}$ at 1648 cm^{-1} (refer to $\nu_{C=C}$: 1653

Table 1. Acetoxylation of unconjugated dienes

Diene	Product, (%)[a]
1,5-Hexadiene	 **1** (64)
1,6-Heptadiene	$CH_2=CHCH(CH_2)_2CH=CH_2$, OAc **2** (13); $CH=CH(CH_2)_3CH=CH_2$, OAc **3** (*cis*, 32), **4** (*trans*, 31)
2,6-Octadiene	$CH_2=CHCH(CH_2)_2CH=CHCH_3$, OAc **5** (46); $CH_3CHCH=CHCH_2CH=CHCH_3$, OAc **6** (47)
1,7-Octadiene	$CH_2=CH(CH_2)_4CCH_3$, O **7** (7); $CH_2=C(CH_2)_4CH=CH_2$, OAc **8** (72); $CH_2CH=CH(CH_2)_3CH=CH_2$, OAc **9** (14)
Diallyl ether	$CH=CHCH_2OCH_2CH=CH_2$, OAc **10** (*cis*, 41), **11** (*trans*, 43)

a) Yields are based on $Pd(OAc)_2$ and obtained by glc analyses.

Table 2. Spectral data of the products

Compound	NMR,[b] ppm (no. of proton)	IR, cm^{-1}
1	1.90m (2), 1.95 s (3), 2.40m (4), 4.90 bs (2), 5.15m (1)	$\nu_{C=O}$ 1730, $\nu_{C=C}$ 1655, δ_{CH} 970, 900 sh, 880
1'[a]	1.80m (4), 2.0 s (3), 2.35m (2), 5.05 b and 5.15 b (2) 5.42 bs (1)	$\nu_{C=O}$ 1730, $\nu_{C=C}$ 1655, δ_{CH} 965, 910 sh, 900
2	1.75m (2), 2.0 s and 2.0m (5), 4.8—6.1m (7)	$\nu_{C=O}$ 1740, $\nu_{C=C}$ 1648, δ_{CH} 990, 910
3	1.55m (2), 2.10 s and 2.10m (7), 4.8—6.2m (3), 4.75 t (1), 7.0 d (1, J=6.5 Hz)	$\nu_{C=O}$ 1770, $\nu_{C=C}$ 1680, 1650 δ_{CH} 980, 910, 745
4	1.55m (2), 2.05 s and 2.10m (7), 4.45 d (1), 4.8—6.1m (3), 7.05 d (1, J=12 Hz)	$\nu_{C=O}$ 1765, $\nu_{C=C}$ 1680, 1650 δ_{CH} 990, 930, 910
5	1.68m (5), 2.0 s and 2.0m (5), 5.0—5.8m (6)	$\nu_{C=O}$ 1735, $\nu_{C=C}$ 1653, δ_{CH} 995, 965, 930
6	1.26 d (3), 1.68m (3), 1.95 s (3), 2.70m (2), 5.2—5.7m (5)	$\nu_{C=O}$ 1730, $\nu_{C=C}$ 1670, δ_{CH} 965, 845
7	1.50m (4), 2.05 s (3), 2.25m (4), 4.8—6.2 (3)	$\nu_{C=O}$ 1718, $\nu_{C=C}$ 1648, δ_{CH} 995, 910
8	1.45m (4), 2.05 s and 1.85—2.3m (7), 4.65 bs (2), 4.8—6.2m (3)	$\nu_{C=O}$ 1765, $\nu_{C=C}$ 1670, 1650, δ_{CH} 995, 966, 910, 865
9	1.55m (2), 2.0 s and 1.9—2.3m (7), 4.45 d (2), 4.8—6.1m and 5.6m (5)	$\nu_{C=H}$ 1745, $\nu_{C=C}$ 1670, 1645, δ_{CH} 985, 965, 910
10	2.10 s (3), 4.0m (4), 4.8—6.1m (3), 7.1 d (1, J=7 Hz)	$\nu_{C=O}$ 1765, $\nu_{C=C}$ 1670, ν_{COC} 1090, δ_{CH} 925, 910
11	2.05 s (3), 3.90 bd (4), 4.9—5.6m (3), 7.25 d (1, J=13 Hz)	$\nu_{C=O}$ 1765, $\nu_{C=C}$ 1675, ν_{COC} 1080, δ_{CH} 935, 905

a) 2-Acetoxymethylenecyclopentane. b) Bs and bd stand for broad singlet and doublet, respectively.

Anal. **1**, Found: C, 68.33; H, 8.66%. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63%.
3, Found: C, 69.92; H, 9.20%.
4, Found: C, 69.93; H, 9.21%.
Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15%.
10, Found: C, 60.94; H, 8.08%.
11, Found: C, 60.96; H, 7.95%.
Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75%.

cm^{-1} for **5**, but 1670 cm^{-1} for **6** and **9**) and the presence of a methylene group at δ 1.75, although an ambiguity remains in excluding the another isomer, 7-acetoxy-1,5-heptadiene. Two products were obtained from *trans,trans*-2,6-octadiene in nearly equal amount. One of them contained a methyl group (δ 1.68) and a vinyl group, and the other showed the presence of two methyl groups (3H each, δ 1.26 and 1.68). Their NMR and IR spectra were most reasonably explained by assigning their structure to 3-acetoxy-1,6-octadiene (**5**) and 7-acetoxy-2,5-octadiene (**6**), respectively (Figs. 3a and 3b). 1,7-Octadiene afforded a methyl ketone and two acetoxylated dienes (Figs. 4a, 4b, and 4c). Examination of their NMR spectra showed that the structures corresponded to those which were made up by replacing the terminal ethyl group (C7 and C8) with a vinyl group from 2-octanone, 2-acetoxy-1-octene and 1-acetoxy-2-octene, respectively, which were produced in the reaction of 1-octene.[2] Thus, they were concluded to be 1-octen-7-one (**7**), 2-acetoxy-1,7-octadiene (**8**) and 1-acetoxy-2,7-octadiene (**9**), respectively.

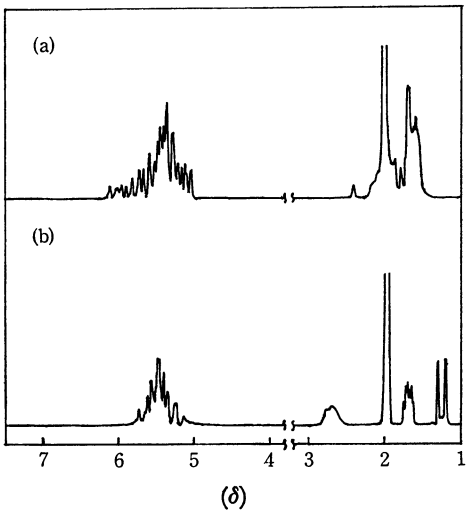


Fig. 3. NMR spectra of **5**(a) and **6**(b).

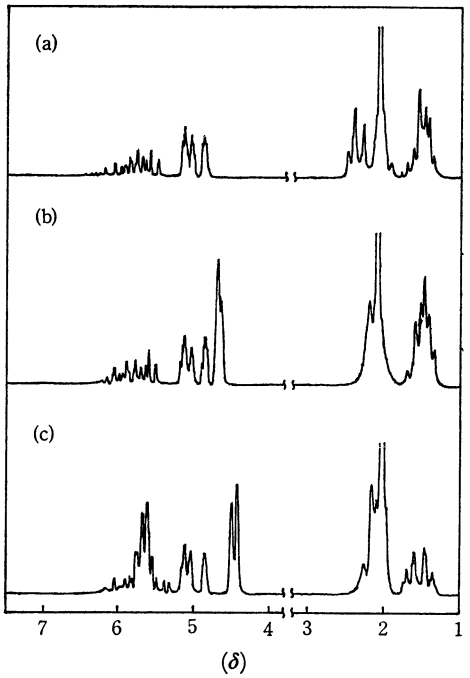


Fig. 4. NMR spectra of **7**(a), **8**(b), and **9**(c).

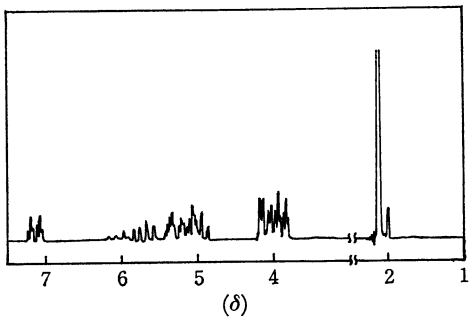


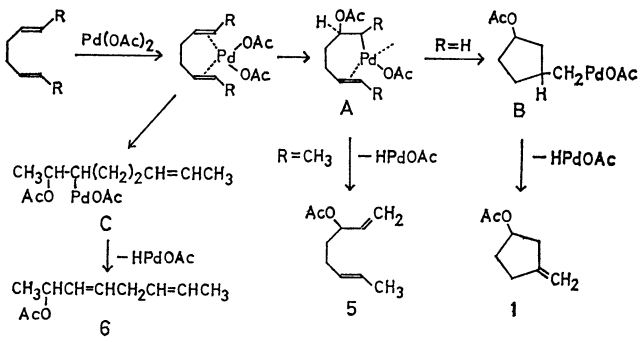
Fig. 5. NMR spectrum of **10**.

Diallyl ether reacted like other dienes to produce two acetoxylated products. They were assigned to *cis* and *trans* γ-acetoxyallyl allyl ethers (**10** and **11**) by their NMR spectra (Fig. 5) and elementary analyses.

The reactions of diallylamine and diallyl sulfide with palladium acetate proceeded in markedly different manner from the other dienes, and produced little liquid product but a considerable amount of intractable solid materials containing palladium. Since normal acetoxylation attended by precipitation of palladium metal was scarcely observed, the reactions were not examined further.

Discussion

The reaction of 1-octene with palladium acetate in acetic acid yielded 2-acetoxy-1-octene and 1-acetoxy-2-octene in a ratio of 5 : 1 along with 2-octanone and the other minor acetoxylated products.[2] This fact is understood to indicate that in the reaction of palladium acetate with a terminal olefin Markovnikov addition prefers considerably to anti-Markovnikov addition in view of the established route to the palladium acetate oxidation of olefins involving 1,2-addition of PdOAc (acetoxypalladation) and the subsequent *cis* 1,2-elimination of HPdOAc.[3] The formation of **8** and **9** from 1,7-octadiene in a ratio of nearly 5 : 1 as well as of **7** strongly suggests that one of the terminal double bonds reacts like 1-octene without being affected by the presence of the second double bond. However, other dienes utilized in this study afforded characteristic products which reflect the structures of the starting dienes. 1,5-Hexadiene gave the cyclic product **1**, while

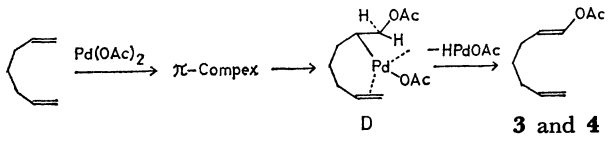


Scheme 1.

2,6-octadiene yielded two open-chain oxidation products **5** and **6**. The marked difference in the products between the two dienes could be reasonably explained in terms of the following scheme.

Addition of one mole of palladium acetate to the dienes would result in the formation of a cyclic π,σ-Pd intermediate since the coordination of the second double bond to palladium can stabilize the initial σ-bonded palladium species. It is noteworthy that in the intermediate (A, R=H) from 1,5-hexadiene β-hydrogen is forced to locate in anti or anti-periplanar position to PdOAc group and cannot enter into the usual *cis* 1,2-elimination of HPdOAc. There are several experimental facts that in the absence of β-hydrogen to be eliminated σ-Pd species enters into another slower processes, such as insertion of a double bond to σ-Pd–C bond[4,5] or formation of π-allylic palladium species.[5,6] Thus, the reaction of 1,5-hexadiene could be depicted that the second double bond in the π,σ-Pd intermediate reacts with σ-Pd–C bond intramolecularly to lead to B, which then undergoes 1,2-elimination to give **1**. On the other hand, in the intermediate (A, R=CH_3) from 2,6-octadiene, a terminal methyl group can act as a β-hydrogen source for the facile 1,2-elimination. Thus, the presence of the methyl group can be regarded as a contributing factor to the formation of **5**, in place of cyclization product. In contrast to the preference for Markovnikov addition of palladium acetate to a terminal double bond, palladium acetate can add to an internal double bond in two alternative ways with much less selectivity.[2] The anti-Markovnikov addition of palladium acetate to 2,6-octadiene is considered to give the intermediate C, which then collapses directly to **6** without forming any cyclic intermediate, since the pseudo-five membered ring species expected by π-donation to palladium must be subjected to considerable steric strain due to a methyl group at C–7 and an α-acetoxyethyl group (–$\underset{\displaystyle CH_3}{\overset{|}{C}}$HOAc) at C–3.

The rationalization of the reaction pathway based on the formation of the stable π,σ-Pd intermediate of pseudo-six membered ring is also applicable to account for the products obtained from 1,6-heptadiene or diallyl ether. Formation of **3** and **4** seems somewhat curious since in the palladium acetate oxidation of simple olefins (except for ethylene) there is no previous example describing the formation of the product bearing 1-acetoxy-1-enyl structure in a considerable yield. If palladium acetate adds to one of the double bonds of 1,6-heptadiene in Markovnikov manner, it would be expected to form either 2-acetoxy-1,6-heptadiene (and/or its isomeric allylic acetates) or a cyclic product through an intermediate of pseudo-seven membered ring. However, it is not the case with the present result except for the formation of a relatively small amount of **2**. On the other hand, a pathway through the pseudo-six membered ring intermediate (D) formed *via* anti-Markovnikov addition is consonant well with the formation of **3** and **4**, because D can not only receive the similar stabilizing effect as was discussed in the reactions of 1,5-hexadiene and 2,6-octadiene, but also possesses β-hydrogen at C–1 available for the facile 1,2-elimination (Scheme 2).



Scheme 2.

Thus, it can be concluded that the formation of a stable π,σ-Pd intermediate of pseudo-six membered ring controls not only the orientation of palladium acetate addition to double bond, but also alters the direction of 1,2-palladium hydride elimination.

The formation of **2** is unusual in view of the normal palladium acetate oxidation involving 1,2-addition and 1,2-elimination, and cannot be explained at present. Although a route involving π-allylic species in place of the σ-Pd bond in D might be an explanation, it is hardly compatible with the formation of **3** and **4**.

Cis and *trans* γ-acetoxyallyl allyl ethers are considered to be produced from diallyl ether in the same route discussed for 1,6-heptadiene, though none of α-acetoxyl isomer was observed. It is to be noted that in the absence of the second double bond the acetoxylation proceeded in a normal manner under the same reaction conditions as evidenced by the formation of β-acetoxyallyl ethyl ether[7] from allyl ethyl ether as a principal product.

It has been reported that allylamines[8] and allyl sulfides[9] gave stable complexes with palladium chloride. The strong dative power of nitrogen and sulfur to palladium could be a principal factor for the present results that diallylamine and diallyl sulfide did not undergo normal acetoxylation with palladium acetate, but afforded intractable solid materials.

Experimentals

Materials. 1,5-Hexadiene[10] and diallylamine[11] were synthesized by the standard methods. 1,7-Octadiene and diallyl sulfide were commercial grade and distilled before use. 1,6-Heptadiene was obtained by the coupling of 4-butenylmagnesium bromide with allyl chloride in the presence of a catalytic amount of ferric chloride,[12] bp 89.0—90.0 °C (lit,[13] bp 91 °C). *Trans,trans*-2,6-octadiene was prepared by the method reported by Webb and Borcherdt[14] consisting of the coupling of crotyl bromide in the presence of nickel carbonyl, bp 123.2—124.0 °C (lit,[14] bp 124.5 °C). Diallyl ether was prepared by the method reported by Skrabal.[15] Palladium acetate was prepared according to the procedure of Wilkinson.[16]

Reaction Procedure. Palladium acetate (1 g, 4.3 mmol) in 40 ml of acetic acid was placed in a 100 ml flask equipped with a reflux condenser and a magnetic stirrer. After the addition of ten-fold excess of diene (43 mmol), the mixture was stirred at 50 °C for 5—7 hr until precipitation of palladium metal was completed. The palladium metal was separated from the reaction mixture by centrifuge, and the supernatant solution was mixed with 300 ml of ether. The ethereal solution was washed successively with water, 30% sodium bicarbonate solution, and saturated sodium chloride solution and dried. Ether and the excess diene were recovered by distillation, and the residue was distilled under reduced pressure to give the following amounts of crude products from the dienes indicated (yields were calculated

as monoacetate and based on the quantity of palladium acetate utilized). 1,5-Hexadiene; 0.58 g (94%), 1,6-heptadiene; 0.68 g (103%), *trans,trans*-2,6-octadiene; 0.72 g (92%), 1,7-octadiene; 0.74 g (100%), and diallyl ether; 0.61 g (100 %).

The crude products were analyzed by glc using one of the 3 mm×2 m columns of Ucon Oil 50HB5100 (10%)-Celite or Reoplex 400 (10%)-Celite. After separation of the main components from the products by glc, their structures were determined by the measurements of IR, NMR and elementary compositions as shown in Table 2.

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7) The product was obtained in a yield of 16% (bp 60—63 °C/10 mmHg) on a $Pd(OAc)_2$ basis, together with the formation of a considerable amount of higher boiling complex mixture (bp 90 °C/3 mmHg—93 °C/1 mmHg). After purification by glc, it showed the following analytical data. IR: 1760, 1665, 1200, 1120, 1030, 890 cm^{-1}, NMR: 1.16 (t, 3H), 2.08(s, 3H), 3.47(q, 2H), 3.90(bs, 2H), 4.88 (bs, 2H), MW: 143 (cryoscopy in benzene).
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