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FORMATION OF A TERMINAL CONJUGATED DIENE SYSTEM BY THE PALLADIUM CATALYZED ELIMINATION REACTIONS OF ALLYLIC ACETATES AND PHENYL ETHERS

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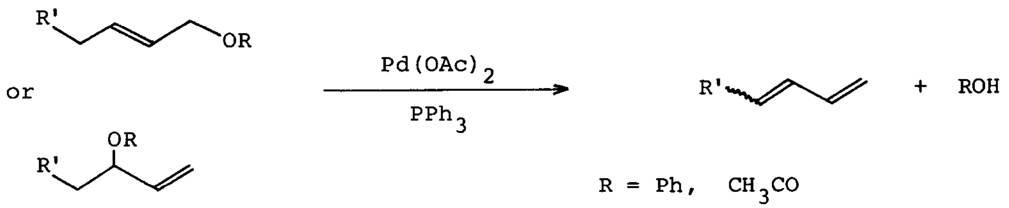
A terminal conjugated diene system is present in certain natural products. Also it can be converted to 2-olefin or 3-olefin by selective reduction. But there appeared few synthetic methods for this system. For example, a rapidly developing coupling reaction of vinyl halides with various vinyl metal reagents catalyzed by transition metal compounds is one acceptable method.[1] Also formation of 1,3-dienes from allylic alcohols *via* oxirane and enediol has been reported.[2] We now wish to report a simple preparative method for the terminal conjugated diene system based on the elimination of acetic acid and phenol from easily available allylic acetates and allylic phenyl ethers respectively using a palladium catalyst.



The reaction proceeds under mild conditions to give dienes in high yields. Thus allylic acetates and phenyl ethers can be regarded as useful synthons of dienes. As a related reaction, Smutny briefly reported the formation of 1,3,7-octatriene by distillation of a product of the telomerization of butadiene with phenol catalyzed by palladium.[3]

In a typical example, 8-acetoxy-6-octen-2-one (532 mg, 3.0 mmol) was heated in dioxane (3.0 ml) with $Pd(OAc)_2$ (6.7 mg, 0.03 mmol) and triphenylphosphine (78.6 mg, 0.3 mmol) at 100° for 1 h (entry 1). Gas chromatographic analysis of the reaction mixture showed complete conversion of the acetate to 5,7-octadien-2-one. The diene was isolated by distillation. (110-120°/19 Torr, Kugel rohr, 290 mg, 78%) ^{1}H NMR (CCl_4) δ 2.05 (s, 3H), 2.20-2.50 (m, 4H), 4.70-6.70 (m, 5H).

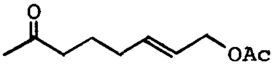
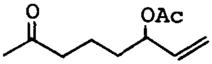
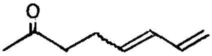
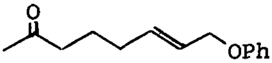
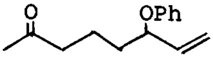
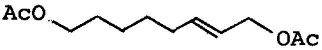
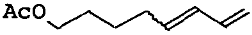
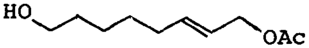
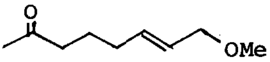
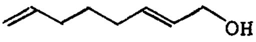
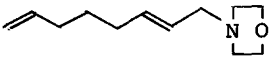
As shown in Table I, the reaction proceeded smoothly in boiling dioxane. Toluene is also a suitable solvent. But the results of the Table I may be explained by a temperature effect as well as a solvent effect. Slow elimination of phenol from allylic phenyl ethers was observed even at 50°.

Table I Effects of Solvents on the Reaction of 8-Acetoxy-6-octen-2-one[a]

Solvents	bp(°C)[b]	Time(hr)	Conversion(%)[c]
Toluene	110.6	1	94
Dioxane	101	2	99
n-Heptane	98.4	2	42
t-Butyl alcohol	82.4	1	72
Benzene	80.1	6	66
THF	66	44	55

a. $Pd(OAc)_2$, 1 mol%, PPh_3, 10 mol%.
b. Reactions were carried but at refluxing temperature.
c. Determined by gas chromatography.

Table II Elimination Reactions of Various Allylic Compounds[a]

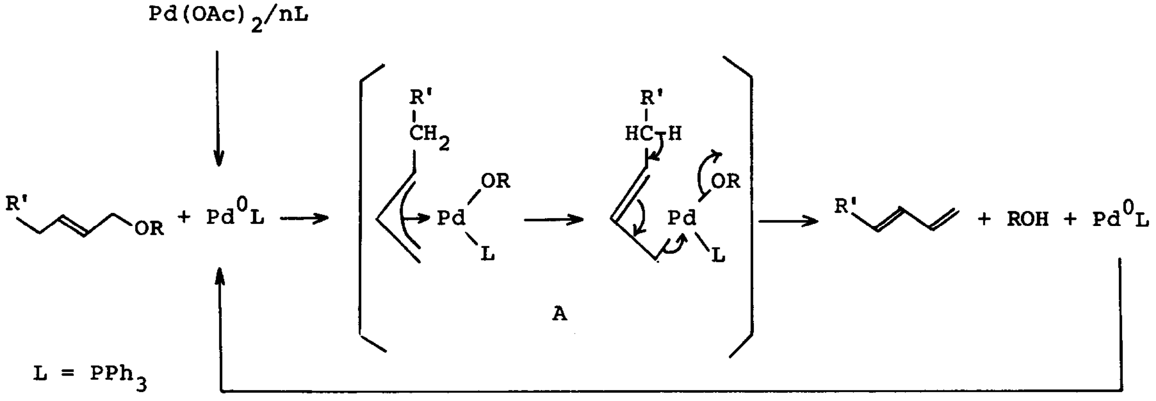
No.	Substrates	Products	Conversion(%)[b]	Isolated yields(%)[c]
1			100	78
2			100	71
3			98	63
4			98	62
5			100	77
6			100	84
7			0	0
8			0	0
9			0	0

a. Carried out in refluxing dioxane.
b. Determined by gas chromatography (PEG, 3mmX3m).
c. Distilled by a Kugel rohr.

For this reaction, $Pd(OAc)_2$ combined with triphenylphosphine is a suitable catalyst. The presence of an excess of triphenylphosphine (about 8-10 mols for one mol of Pd) is desirable for maximum catalytic activity. About one mol% of the catalyst for the substrate was found to be enough. $PdCl_2(PPh_3)_2$ was not an active catalyst.

As the substrates, allylic acetates and phenyl ethers were found most satisfactory. As shown in Table II, no elimination was observed with allylic methyl ether (entry 7), allylic alcohol (entry 8) and amine (entry 9). Also a simple acetate was not eliminated (entry 5). The allylic isomers (entries 1-2 and 3-4) were converted to the same products in the same yields.

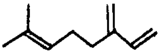
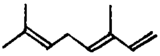
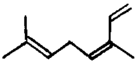
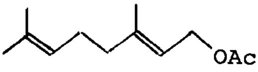
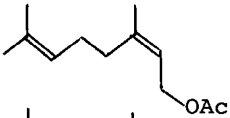
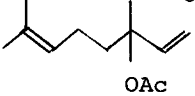
This elimination reaction can be explained *via* the formation of a π-allylic complex A by the oxidative addition of allylic compounds to zerovalent palladium. Elimination of acetic acid or phenol from the complex A liberates the diene and regenerates the zerovalent palladium, which recycles.



It is known that thermal or base-promoted decomposition of π-allylic complexes of palladium affords conjugated dienes.[4-6] This is a stoichiometric model reaction related to the present catalytic reaction. The selective reduction of the terminal double bond of dienes with diimide formed from hydrazine and hydrogen peroxide[7] afforded a mixture of nearly equal amounts of Z and E isomers.[8] This result indicates that the original dienes also consist of the Z and E isomers. Thus the elimination of hydrogen from the π-allylic complex A is not selective.

Three isomeric monoterpenol acetates, geranyl acetate (entry 10), neryl acetate (entry 11), and linalyl acetate (entry 12) were subjected to the elimination and a mixture of myrcene, *trans*- and *cis*-ocimene was obtained. As shown in Table III, nearly the same product distribution was observed with these acetates.

Table III Elimination Reactions of Geranyl acetate, Neryl acetate and Linalyl acetate[a]

			Products		
No.	Substrates	Conversion (%)	myrcene 	*trans*-ocimene 	*cis*-ocimene 
10		100	60	20	20
11		100	74	8	18
12		100	74	12	14

a. Refluxed in dioxane for 1 h.

Application of this method to natural product synthesis will be reported shortly.

References and Note:

1. H. P. Dang and G. Linstrumelle, Tetrahedron Lett., 191 (1978), and references cited therein.
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7. C. R. Scholfield, R. O. Butterfield, T. L. Mounts, and H. J. Dutton, J. Am. Oil Chem. Soc., 46, 323 (1969).
8. The experiment was carried out by Dr. R. Yamaoka and Prof. H. Fukami (Pesticide Research Institute, Kyoto University).

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