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A CONVENIENT METHOD FOR THE PREPARATION OF 1-OLEFINS BY THE PALLADIUM CATALYZED HYDROGENOLYSIS OF ALLYLIC ACETATES AND ALLYLIC PHENYL ETHERS WITH AMMONIUM FORMATE

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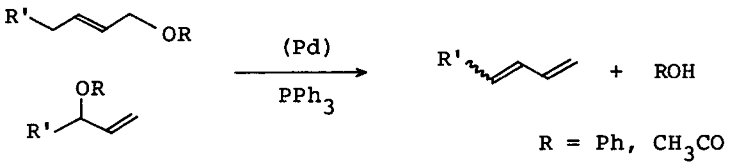
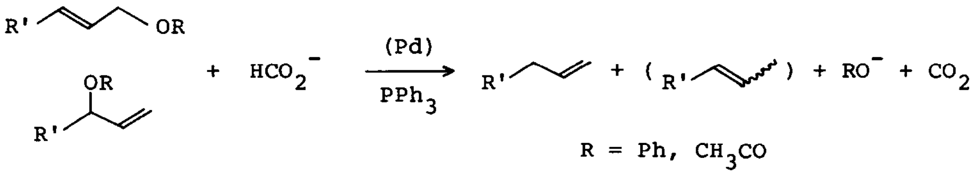
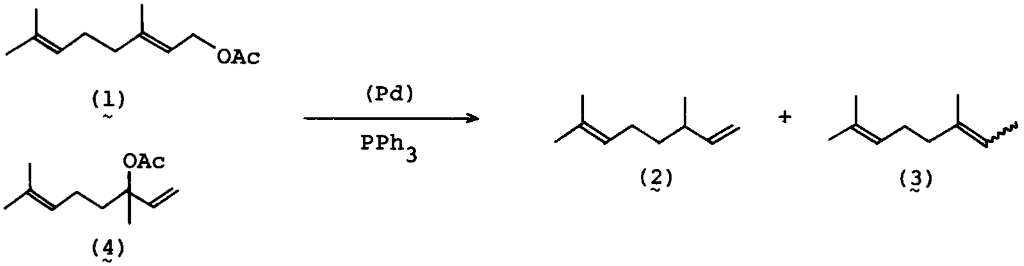
In a previous paper we have reported the formation of conjugated dienes by the palladium catalyzed elimination reaction of allylic acetates and allylic phenyl ethers,[1] and the method has been applied to a simple synthesis of 12-acetoxy-1,3-dodecadiene.[2]



We now wish to report that these allylic compounds are converted to 1-olefins in high yields under mild conditions by the reaction of ammonium formate using a palladium catalyst. In this reaction, 1-olefins were obtained predominantly from following isomeric allylic compounds. 2-Olefins are minor products. Thus allylic acetates and phenyl ethers can be regarded as useful synthons of 1-olefins.



In a typical example, a mixture of geranyl acetate (392 mg, 2 mmol) (1) and ammonium formate (252 mg, 4 mmol) was refluxed in dioxane in the presence of $PdCl_2(PPh_3)_2$ (1 mol%) for 1 h. Gas chromatographic analysis of the reaction mixture with an internal standard showed nearly quantitative conversion of geranyl acetate to give 1-olefin [dihydromyrcene (2)] and 2-olefin [*cis*-and *trans*-dihydromyrcene (3)] in a ratio of 94 : 6. Similar product ratio was obtained by the reaction of linalyl acetate (4).



Another usefulness of this method is that allyl esters can be used as a protecting group of carboxylic acids. Octanoic acid was obtained in 82% yield from allyl octanoate by the treatment with the palladium catalyst.

$$CH_3(CH_2)_6CO_2CH_2CH=CH_2 \xrightarrow[\text{[Pd]}]{HCO_2NH_4} CH_3(CH_2)_6CO_2H$$

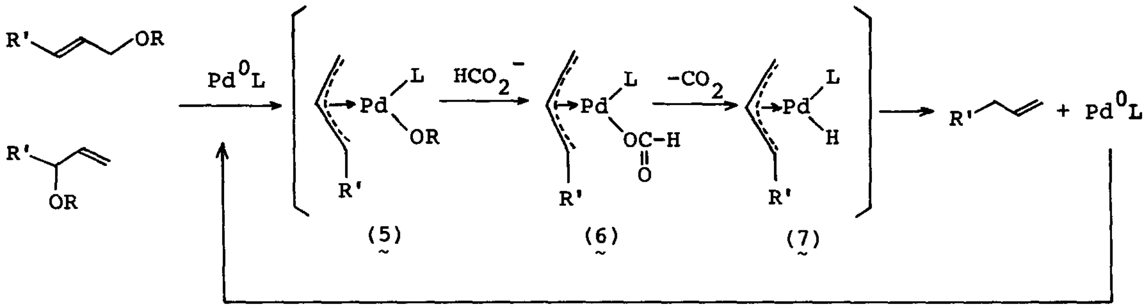
Similarly allyl cinnamate was treated with ammonium formate in the presence of the palladium catalyst, and cinnamic acid was obtained in 93% yield. In this reaction, the allyl group was removed by hydrogenolysis, but the double bond in the acid molecule remained intact. Therefore, the palladium catalyzed removal of the allyl protecting group is superior to the commonly used method of removing benzyl ester group by hydrogenation.

$$PhCH=CHCO_2CH_2CH=CH_2 \xrightarrow[PPh_3]{\text{[Pd]}} PhCH=CHCO_2H$$

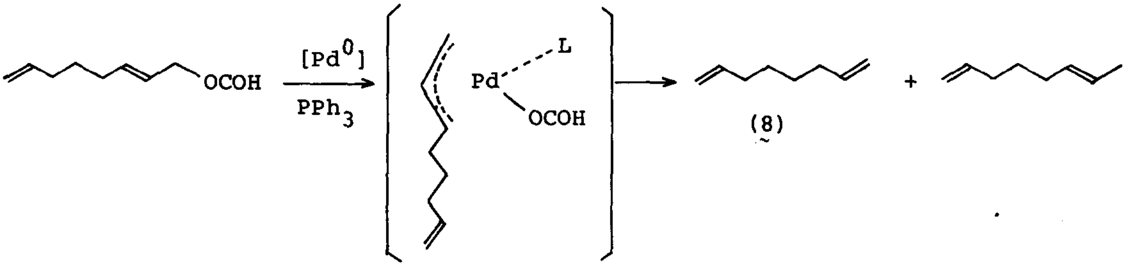
For this reaction, easily available $PdCl_2(PPh_3)_2$ is an active catalyst. Also $Pd(OAc)_2$ can be used with PPh_3. About one mol% of the catalyst was found to be enough. Hey and Arpe briefly reported that the palladium catalyzed reaction of allyl acetate with formic acid produced propylene.[3] We found that amine salts of formic acid rather than formic acid itself gave the better results Ammonium, triethylammonium and pyridinium salts of formic acid were found to be satisfactory. Some results of the reaction are shown in the Table.

The present reaction can be explained by the following mechanism. Oxidative addition of the allylic compounds to Pd^0 species takes place to form the π-allylic complex 5. Displacement reaction by formate affords the formate complex 6, which is then converted to the palladium-hydride 7 with generation of carbon dioxide. Then the olefins are liberated by the reductive elimination with regeneration of the Pd^0 species. In this step, the hydride attacks preferentially the more substituted side of the π-allylic system 7 to afford 1-olefins predominantly. The oxidative addition of isomeric allylic compounds such as geranyl and linalyl acetates forms the same π-allylic complex, from which olefins are formed in the same ratio by the reductive elimination. The selectivity to 1-olefins above 90% was observed with geranyl and linalyl acetates

(Exp. No. 2-9), but it was 80% with the less substituted 3-phenoxy- or 3-acetoxy-1,7-octadiene (Exp. No. 10-12). 2-Methyl group somewhat lowered the selectivity (Exp. No. 15). 2-Acetoxy-3-decene afforded nearly equal amounts of 2- and 3-decene (54 : 46) as expected.



In order to obtain a supporting evidence for the formation of the formate complex 6 in the above mechanism, 2,7-octadienyl formate was treated with the palladium catalyst in the absence of ammonium formate, and 1,7-octadiene (8) was obtained as a main product.



It is known that a palladium-hydride species is formed by the reaction of a palladium catalyst with formic acid.[4] A catalytic system composed of palladium salt/PPh_3/HCO_2H/amine was used for the reductive elimination of aromatic halogens.[5,6] As a related reaction, allylic methyl ethers were hydrogenolyzed with metal hydride species formed by the reaction of $TiCl_4$/$LiAlH_4$.[7]

References

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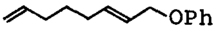
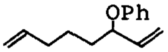
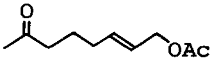
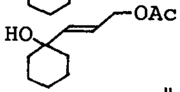
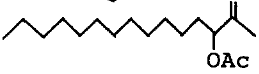
TABLE. THE PALLADIUM-CATALYZED HYDROGENOLYSIS OF VARIOUS ALLYLIC COMPOUNDS[a)]

Exp. No.	Substrate	Pd cat.	Reducing reagent	Solvent	Yield[b)] (%)	Ratio[c)] 1-olefin : 2-olefin
1	geranyl acetate	$pd(OAc)_2$[d)]	HCO_2H	dioxane	78	71 : 29
2	geranyl acetate	$Pd(OAc)_2$[d)]	HCO_2NH_4	dioxane	100	94 : 6
3	geranyl acetate	$Pd(OAc)_2$[d)]	HCO_2HNEt_3	dioxane	100	92 : 8
4	geranyl acetate	$Pd(OAc)_2$[d)]	HCO_2HPyr	dioxane	100	92 : 8
5	linalyl acetate	$Pd(OAc)_2$[d)]	HCO_2NH_4	dioxane	100	93 : 7
6	geranyl acetate	$PdCl_2(PPh_3)_2$	HCO_2NH_4	dioxane	100	92 : 8
7	linalyl acetate	$PdCl_2(PPh_3)_2$	HCO_2NH_4	dioxane	100	92 : 8
8	geranyl acetate	$PdCl_2(PPh_3)_2$	HCO_2NH_4	THF	3	-------
9	geranyl acetate	$PdCl_2(PPh_3)_2$	HCO_2NH_4	t-BuOH	70	93 : 7
10		$PdCl_2(PPh_3)_2$	HCO_2HNEt_3	dioxane	100	80 : 20
11		$PdCl_2(PPh_3)_2$	HCO_2HNEt_3	dioxane	100	81 : 19
12		$PdCl_2(PPh_3)_2$	HCO_2HNEt_3	dioxane	100	79 : 21[e)]
13		$PdCl_2(PPh_3)_2$	HCO_2NH_4	dioxane	100	94 : 6
14		$PdCl_2(PPh_3)_2$	HCO_2NH_4	dioxane	100	89 : 11
15		$PdCl_2(PPh_3)_2$	HCO_2NH_4	dioxane	100	83 : 17

a) Reactions were carried out at refluxing temperature with 1 mol% of Pd catalysts.

b) Determined by gas chromatography.

c) Selectivity was determined by glc analyses.

d) 10 mol% of PPh_3 was added.

e) This was determined by NMR spectroscopy of the purified product.

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