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REGIOSELECTIVE SYNTHESIS OF 1-OLEFINS BY PALLADIUM-CATALYZED HYDROGENOLYSIS OF TERMINAL ALLYLIC COMPOUNDS WITH AMMONIUM FORMATE

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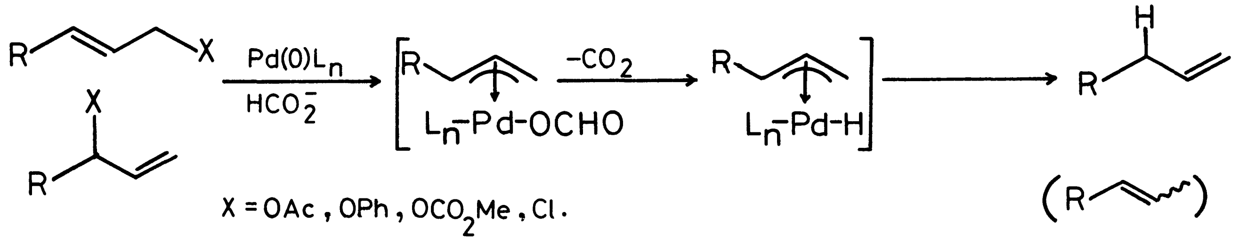
Various terminal allylic compounds such as allylic esters, phenyl ethers, carbonates, chlorides, and vinyl epoxides react with ammonium or sodium formate to give 1-olefins with high regioselectivity by using palladium-tributylphosphine complex as a catalyst. The reaction offers a useful synthetic method for 1-olefins.

In 1979, we have reported a new preparative method for 1-olefins by the hydrogenolysis of terminal allylic acetates and phenyl ethers with ammonium formates using palladium-PPh_3 complex as a catalyst.[1] The reaction can be understood by the attack of hydride formed by the decarboxylation of formate on the more substituted site of π-allylpalladium intermediate.



This is a simple synthetic method for 1-olefins. However, in this reaction, 2-olefins are also formed in 6-20% depending on structure of allylic compounds. Since separation of 1-olefins from 2-olefins is not easy, the method needs further improvement.[2-7] In our effort to improve the selectivity for 1-olefins, we have found a profound effect of ligands on the regioselectivity. In this paper we wish to report that various terminal allylic compounds can be converted to 1-olefins in nearly 100% selectivity by using $P(n\text{-}Bu)_3$ as the ligand. This method offers a very good synthetic method for 1-olefins.

The hydrogenolysis of various allylic compounds was carried out in boiling dioxane using several phosphines and phosphites as the ligands. Results are shown in the Table. The selectivity for 1-olefins changes in wide range depending on the ligands. Alkyl phosphines show the higher selectivity than aryl phosphines. Phosphites are not satisfactory. Among various phosphines and phosphites, $P(n\text{-}Bu)_3$ gives the best results. In most cases, the reaction proceeded completely in 0.5-2 h and 1-olefins were obtained in nearly 100% selectivity with $P(n\text{-}Bu)_3$. No other product was detected by gas chromatography.

Table 1. Palladium-Catalyzed Hydrogenolyses of Allylic Compoumds with Ammonium Formate[a]

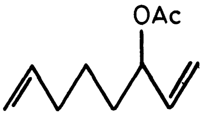
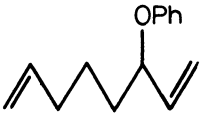
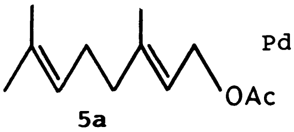
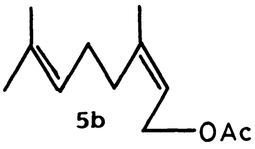
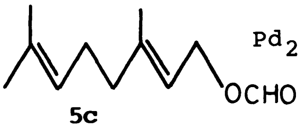
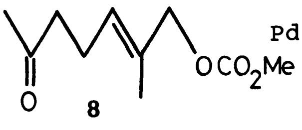
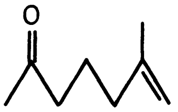
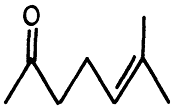
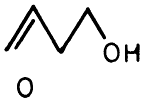
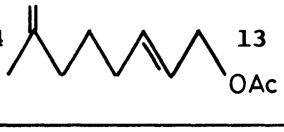
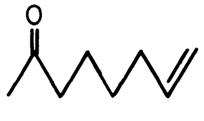
Run	Allylic compounds	Catalysts	Products (Selectivity/%)[b]	
1	 **1a**	$Pd_2(dba)_3CHCl_3$-P^nBu_3	 **2** (100)	 **3** (0)
2	**1a**	$PdCl_2$-P^nBu_3	**2** (100)	**3** (0)
3	**1a**	$Pd(PPh_3)_4$-P^nBu_3	**2** (100)	**3** (0)
4	**1a**	$Pd(OAc)_2$-P^nBu_3	**2** (94)	**3** (6)
5	**1a**	$Pd_2(dba)_3CHCl_3$-PPh_3	**2** (93)	**3** (7)
6	**1a**	$Pd(PPh_3)_4$	**2** (70)	**3** (30)
7	**1a**	$Pd_2(dba)_3CHCl_3$-$P(OEt)_3$	**2** (74)	**3** (26)
8	 **4a**	$Pd_2(dba)_3CHCl_3$-P^nBu_3	**2** (96)	**3** (4)
9	 **1b**	$Pd_2(dba)_3CHCl_3$-P^nBu_3	**2** (98)	**3** (2)
10	 **4b**	$Pd_2(dba)_3CHCl_3$-P^nBu_3	**2** (99)	**3** (1)
11	 **1c**	$Pd_2(dba)_3CHCl_3$-P^nBu_3	**2** (99)	**3** (1)
12[c]	 **1d**	$Pd_2(dba)_3CHCl_3$-P^nBu_3	**2** (100)	**3** (0)

Table (continued)

13	 **5a**	$Pd_2(dba)_3CHCl_3$-P^nBu_3	 **6** (100)	 **7** (0)
14	**5a**	$Pd(OAc)_2$-PPh_3	**6** (94)	**7** (6)
15	**5a**	$Pd(OAc)_2$-$P(OEt)_3$	**6** (51)	**7** (49)
16	 **5b**	$Pd_2(dba)_3CHCl_3$-P^nBu_3	**6** (100)	**7** (0)
17[d]	 **5c**	$Pd_2(dba)_3CHCl_3$-P^nBu_3	**6** (100)	**7** (0)
18	 **8**	$Pd(OAc)_2$-P^nBu_3	 **9** (99)	 **10** (1)
19	**8**	$PdCl_2[P$-⬡$_3]_2$	**9** (93)	**10** (7)
20	**8**	$PdCl_2(PPh_3)_2$-PPh_3	**9** (90)	**10** (10)
21	**8**	$PdCl_2$-$P(o\text{-}Tol)_3$	**9** (34)	**10** (66)
22	**8**	$Pd(OAc)_2$	**9** (34)	**10** (66)
23	 **11**	$Pd_2(dba)_3CHCl_3$-P^nBu_3	 **12** (100)[e]	
24	 13	$Pd_2(dba)_3CHCl_3$-P^nBu_3	 **14** (100)[f]	

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a) All reactions were carried out using allylic compound (1 mmol), palladium catalyst (0.025-0.05 mmol, Pd:P=1:4) and ammonium formate (2 mmol) in boiling dioxane (3 cm^3) for 0.5-2 h. b) GLC analysis. c) Sodium formate (2 mmol) was used instead of ammonium formate. d) Reaction without ammonium formate. e) The vinyl epoxide **11** (15%) was recovered. f) Isolated yield 79%.

For this reaction various terminal allylic compounds can be used. Allylic esters, phenyl ethers, and carbonates reacted smoothly with ammonium formate to give satisfactory results. Good result was obtained by the reaction of allylic chloride **1d** with sodium formate, instead of ammonium formate (Run 12). Allylic formate **5c** was converted to 1-olefin without addition of ammonium formate (Run 17). 3-Acetoxy and 3-phenoxy compounds, **4a** and **4b**, were similarly converted to the terminal olefin **2** selectively (Runs 8 and 10). These results indicate that similar π-allylpalladium complexes are formed as intermediates from **1a, 1b, 4a,** and **4b.** 1,3-Butadiene monoepoxide (**11**) was converted selectively to 3-butenol (**12**) without forming 2-butenol (Run 23).$^{8)}$

A typical experiment for the preparation of 1-octen-7-one (**14**) from 1-acetoxy-2-octen-7-one (**13**) is as follows. A mixture of $Pd_2(dba)_3CHCl_3$$^{9)}$ (0.0125 mmol), PBu_3 (0.1 mmol), ammonium formate (2 mmol) and the allylic acetate **13** (1 mmol) in dioxane (3 mL) was stirred at 100 °C for 1 h and then filtered (florisil). Removal of the solvent followed by elution on SiO_2 with ether-hexane (1:20) gave the 1-olefin **14** in 79% yield (100% selectivity by GLC analysis).

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References

1) J. Tsuji and T. Yamakawa, Tetrahedron Lett., 1979, 613.
2) H. Hey and H. J. Arpe, Angew. Chem., Int. Ed. Engl., 12, 928 (1973).
3) Palladium catalyzed hydrogenolyses of allylic compoumds with several hydrides have been reported.$^{4-7)}$ But 2-olefins are major products.
4) R. O. Hutchins, K. Learn, and R. P. Fulton, Tetrahedron Lett., 21, 27 (1980).
5) a) E. Keinan and N. Greenspoon, Tetrahedron Lett., 23, 241 (1982);
b) E. Keinan and N. Greenspoon, J. Org. Chem., 48, 3545 (1983).
6) H. Matsushita and E. Negishi, J. Org. Chem., 47, 4161 (1982).
7) K. Nakamura, A. Ohno, and S. Oka, Tetrahedron Lett., 24, 3335 (1983).
8) Reaction of **11** with HCO_2NH_4 using Pd-PPh_3 catalyst to give the homoallyl alcohol **12** was briefly presented orally in the 30th symposium on organometallic chemistry, in Nov., 1983 by T. Tsuda.
9) T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet, and J. A. Ibers, J. Organomet. Chem., 65, 253 (1974).

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