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REDUCTION BY A MODEL OF NAD(P)H. 44. TRANSITION METAL CATALYZED REDUCTION OF ALLYLIC ACETATE

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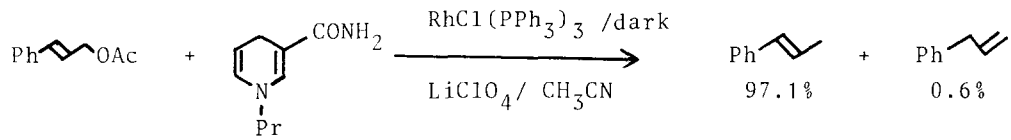
Summary : Allylic acetates were reduced regioselectively to alkenes by a model of NAD(P)H via catalytic activation with transition metal complexes.

In enzymatic systems, NAD(P)H reduces various kind of substrates with the aid of dehydrogenases. In NAD(P)H model systems, some cationic species such as proton,[1] Lewis acid,[2] or magnesium ion[3] have been known to catalyze reductions although their effects are far from that of enzymes and a new active catalyst has been awaited. In this paper, we report a new type of reduction by a model of NAD(P)H ; reduction of allylic acetates catalyzed by transition metals.[4,5]

Cinnamyl acetate (1) was inert against the reduction by NAD(P)H model compounds. However, the reduction proceeded quantitatively when 10 mol% of $RhCl(PPh_3)_3$ was added to the system. Thus, in the presence of Rh(I), 1 was reduced to trans-β-methylstyrene in 97% yield by N-propyl-1,4-dihydronicotinamide (PNAH) in acetonitrile. Results are summarized in the table.



Other transition metals such as palladium or ruthenium can catalyze this reduction but their abilities are inferior to that of rhodium both in the yield of alkene and in the product selectivety. The effects of added salts are important ; lithium perchlorate promotes the reduction but magnesium perchlorate inhibits it. Lithium acetate exerts no effect on the reduction. Thus, anionic species plays an important role in the reaction. It is well known that magnesium ion promotes the reduction of ketones with NAD(P)H models. The role of magnesium ion in the reduction of carbonyl compounds is to catalyze the initial electron transfer step,[6] and the reduction of a cationic or a reactive substrate is retarded by magnesium ion because it stabilized the intermediate.[7] The effect of Mg^{2+} in the present reaction suggests that an attack of an NAD(P)H model to a cationic or a reactive species is involved in the reduction.

The chemoselectivity of this reduction is important. Acetophenone, methyl benzoate and benzyl acetate were neither reduced nor degraded under the reaction condition. Allylic acetates with aliphatic moiety such as geranyl acetate and

neryl acetate were not reduced. The present system demonstrates a different feature from palladium catalyzed reactions[5] in its mildness.

Details about the mechanism are ambiguous in the present time and our efforts on this point are now under progress in our laboratory.

Table. Reduction of allylic acetates by PNAH[a]

Substrate	Catalyst[b]	Addendum (mmol)	Solvent	yield (%)[c]	
					
	$RhCl(PPh_3)_3$	$LiClO_4$, 0.15	CH_3CN	97.1[d]	0.6
"	"	none	"	53.6	0.6
"	"	$Mg(ClO_4)_2$, 0.1	"	2.6	—
"	"	LiOAc, 0.15	"	53.1	0.6
"	"	$LiClO_4$, 0.15	benzene	18.3	1.0
"	"	" "	THF	10.7	2.5
"	$PdCl_2(PPh_3)_2$	" "	CH_3CN	18.9	13.3
"	$Pd(PPh_3)_4$	" "	"	15.4	30.8
"	$NiCl_2(PPh_3)_2$	" "	"	no reaction	
"	$RuCl_2(PPh_3)_3$	" "	"	0.5	7.4
	$RhCl(PPh_3)_3$	" 0.3	"	95.9	0.4
	"	" 0.5	"	79.0	5.5
	"	" 0.15	"	70.9	6.0
	"	" "	"	76.8[e]	
neryl acetate	"	" "	"	no reaction	

a) Reaction condition : [substrate] = 0.1mmol, [PNAH]= 0.15mmol, 70°C, 17h.
b) 0.01mmol. c) Determined by glpc. d) Isolated yield 87.3%. e) Isolated yield.

References and notes

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3) Ohno, A., Ikeguchi, M., Kimura, T., and Oka, S., *J. Am. Chem. Soc.*, 101, 7036 (1979) and references cited therein.
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