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SELECTIVE REDUCTION OF CONJUGATED DOUBLE BONDS WITH MOLECULAR HYDROGEN AND PALLADIUM(II) COMPLEXED TO FERROCENYLAMINE SULFIDE CATALYSTS

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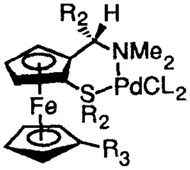
Abstract. Highly catalytic chemo- and regioselectivity have been achieved for the reduction of carbon-carbon double bonds conjugated to different unsaturated functional groups by molecular hydrogen and palladium(II) complexes of ferrocenylamine sulfides. Chemical yields and selectivities were more than 99% in many cases.

Selective reduction of carbon-carbon double bonds conjugated to different functional groups is an important transformation in organic synthesis and has recently gained considerable interest.[1] Stoichiometric amounts of $LiAlH_4$,[2] diisobutylaluminum hydride (DIBAH),[3] (Mg/MeOH),[4] and several transition metal hydrides have been utilized.[5] There are several examples of the cartalytic reduction of carbon-carbon double bonds by using $PdCl_2$ complexed to other ligands[6]. $PdCl_2(PPh_3)_2$ has been used as a catalyst for selective reduction of 3-methyl-2-cyclohexane-1-one and carvone to saturated ketones[7], however, it is necessary to use $CF_3SO_3SnBu_3$ as co-catalyst. $PdCl_2$ reduced by borohydride is also an effective hydrogenation catalyst for reduction of some conjugated aldehydes[8].

Here we wish to report the reduction of carbon-carbon double bonds conjugated to α-β-unsaturated carbonyl, carboxylic acid, ester, amide, nitrile, and lactone groups by using molecular hydrogen and catalyzed by $PdCl_2$ complexes 1-4. These compounds are synthesized in a few steps from inexpensive starting materials[9-11]. They are extremely air stable and can be used as catalysts at room temperature under mild pressure (60-100 Psi). In addition, they showed high selectivity for the hydrogenation of conjugated dienes or styrene derivatives under the same moderate conditions.[12]

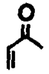
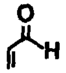
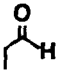
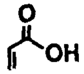
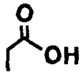
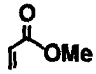
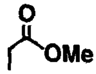
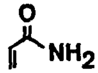
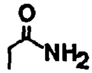
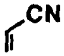
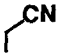
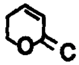
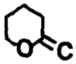
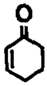
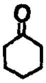
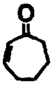
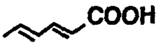
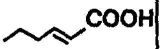
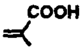


1 R_1 = H, R_2 = 4-Tolyl, R_3 = H[6]
2 R_1 = H, R_2 = 4-Tolyl, R_3 = S-4-Tolyl[7]
3 R_1 = H, R_2, = 4-Tolyl, R_3 = 4-Tolyl[7]
4 R_1 = Me, R_2 = *n*-Pr, R_3 = H[8]

Table 1 (entries 1-12) shows that selective reduction of double bonds could be achieved quantitatively in 0.25 - 12h. No reduction of any of the functional groups was observed; moreover, isolated double bonds are much less reactive.[9,11-12] Selective hydrogenation of methyl vinyl ketone, 2-cyclopentenone, and 2-cyclohexenone by using $K_3[Co(CN)_5H]$ as a catalyst gave the hydrogenation products in 70%, 10%, and 75% yields respectively.[13] The reduction of 2-cyclohexenone was also reported by using $Mo(CO)_6/PhSiH_3$[14] and $Co(CO)_6(PBu_3)_2/H_2$[15] to give cyclohexanone in 25% and 86% yields respectively. In this work, these substrates were hydrogenated to 100%, 48%, and 100% respectively. Crotonic acid (entry 17) was not hydrogenated under these conditions; however, extension of the conjugation, as in 2,4-hexadienoic acid (entry 18), allows 100% reduction of the γ-δ-double bond. Hydrogenation of methyl-2,4-hexadienoate recently reported gave a 1:1 mixture of α-β- and γ-δ-hydrogenated products by using Mg/MeOH.[4b] Table 1 also shows that double bonds conjugated to more basic carbonyl (i.e. amide or acid) react more rapidly than those conjugated to more electron withdrawing groups. (i.e. carboxyl or nitrile). Flexible ketones (entries 1,2) that can adopt either transoid or cisoid have been reduced much faster than those locked in transoid conformations (entries 13-16) and suggest that both the double bond and the carbonyl group simultaneously interact with palladium.[14]

The catalysts described in this work are superior to the other $PdCl_2$ based catalysts[7,8] because they are more selective, more general, and most important they are air and moisture stable.

Table 1: Conjugate Reduction with Molecular M_2/Pd(II)

Entry	Starting Material	Catalyst	Time(h)	Product	Yield (%)
1		2	0.5		100
2	"	3	0.5	"	100
3		2	1		100
4	"	3	2	"	100
5		2	6		100
6	"	3	1.25	"	100
7		2	0.25		100
8	"	3	0.75		100
9		3	0.25		100
10		2	1		100
11	"	3	2.5	"	100
12		1	10		100
13		1	8		48
14	"	4	11	"	26
15		4	6.5		100
16		3	8		95
17		1	48	**no reaction**	
17		1	12		100
19		1	10		41

General procedure:

The palladium catalyst (1x10^{-5} mol), acetone (4.5 mL), and substrate (3.725 x 10^{-3} mol) were placed in a 100 mL pressure bottle equipped with a pressure gauge and a stirring bar. The bottle was evacuated and filled with H_2 several times, then fixed at 80 Psi. At the end of the reaction, the product was distilled from the catalyst and analyzed by GC and ^{1}H NMR.

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