

Selective hydrogenation of exocyclic α,β -unsaturated ketones:

Part I. Hydrogenations over palladium

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Abstract

Exocyclic α,β -unsaturated ketones were hydrogenated to the corresponding saturated ketones with Pd catalysts. The effect of solvents, basic and poisoning additives and various supports on conversion and selectivity was investigated. The conditions, under which the reaction afforded the saturated ketones with complete selectivity and appropriate reaction rate, were determined. The highest selectivities were obtained over Pd/C, in toluene, at atmospheric pressure and in the presence of pyridine. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

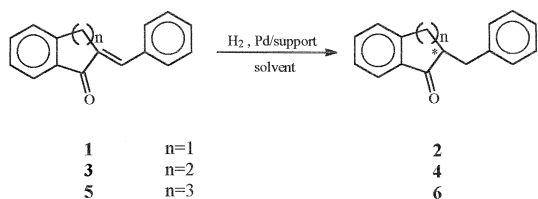
Selectivity in the hydrogenations of compounds containing more reducible functional groups is an important phenomenon. The selective hydrogenation of α,β -unsaturated carbonyl compounds was studied widely [1–3], but the reduction of exocyclic ones was rarely published in the literature.

In this work the heterogenous catalytic hydrogenation of (*E*)-2-benzylidene-1-indanone (**1**) to 2-benzyl-1-indanone (**2**), (*E*)-2-benzylidene-1-tetralone (**3**) to 2-benzyl-1-tetralone (**4**) and (*E*)-2-benzylidene-1-benzosuberone (**5**) to 2-benzyl-1-benzosuberone (**6**) were investigated in order to find the reaction conditions to obtain the highest selectivity (Scheme 1).

Here we report hydrogenations, which can be found in the literature. Compound **1** was reduced over 10% palladium on carbon, in methanol, at atmospheric pressure with 80.5% yield [4], as well as over Pd/BaSO₄, in ethanol, at 5 bar with 78.6% yield [5]. These examples demonstrate that some investigations were car-

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Scheme 1. The heterogeneous catalytic hydrogenation of (*E*)-2-benzylidene-1-indanone, (*E*)-2-benzylidene-1-tetralone and (*E*)-2-benzylidene-1-benzosuberone to the corresponding saturated ketones.

ried out with respect to the reduction of **1**, but no systematic research was done with compounds containing six- and seven-member rings.

Our further aim is to carry out the enantioselective hydrogenation of the above mentioned compounds. For this purpose we first had to determine the conditions under which these reactions are chemoselective.

In this paper the effects of the reaction conditions, such as catalyst support, solvent, additives and pressure on selectivity are discussed.

2. Experimental

2.1. Materials

Compounds **1** and **3** were prepared according to the procedure described in Ref. [6], while **5** was synthesized as described in Ref. [7].

The catalysts were partly commercial products: 10% Pd/C Selcat [8] (Fine Chemicals, Budapest, Hungary). Pd black catalyst was prepared as follows: 18 mmol (6.0 g) K_2PdCl_4 was dissolved in 50 ml water and reduced at boiling point with 74 mmol (5.0 g) HCOONa dissolved in 20 ml water. When the reduction was com-

plete, the pH of the suspension was basic (pH 11). The catalyst was filtered and washed several times with distilled water.

The 10% Pd/ Al_2O_3 , 10% Pd/ SiO_2 and 10% Pd/ TiO_2 catalysts were prepared by the same method. The calculated amount of the catalyst precursor (K_2PdCl_4) was added to the aqueous suspension of the support. The pH value of the solution was adjusted to 10–11 by addition of KOH . The suspension was boiled for 1 h then HCOONa was added to the boiling mixture. After half an hour the suspension was cooled, the catalyst was filtered and washed with distilled water.

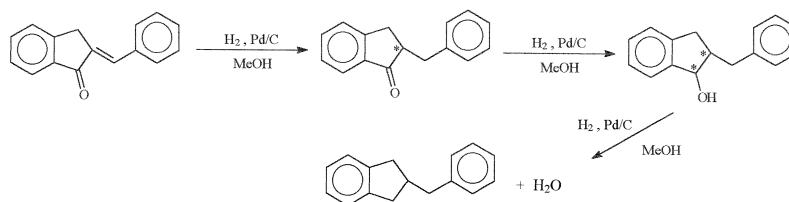
2.2. Hydrogenations

The hydrogenations were carried out either in a conventional apparatus with magnetic stirrer at atmospheric pressure or in a stainless steel autoclave equipped with magnetic stirrer and digital manometer, at 10 or 50 bar hydrogen pressure, at room temperature. During working-up procedure of the reaction mixtures, the catalyst was filtered and the solvent was removed in vacuum.

The reaction mixtures and the crude products were analyzed by GC. The products were identified by $^1\text{H-NMR}$ measurements.

2.3. Analysis

Gas-chromatographic analyses were carried out using a 1 m column, filled with SE-30 5% on Chromosorb W 100–120 mesh, at 230°C with FID. The chromatograms were recorded and the peak areas were calculated with Chro-



Scheme 2. The possible consecutive reactions in the hydrogenation of **1**.

Table 1

The effect of different solvents on the selectivity. Conditions: 0.5 g substrate, 0.05 g Pd/C (Selcat), 20 ml solvent, atmospheric pressure, 25°C

Entry	Solvents	Substrates					
		1		3		5	
		Reaction rate (ml H ₂ /g _{cat} min)	Selectivity to 2 (%)	Reaction rate (ml H ₂ /g _{cat} min)	Selectivity to 4 (%)	Reaction rate (ml H ₂ /g _{cat} min)	Selectivity to 6 (%)
1	MeOH	59	0	103	0	56	73.6
2	Toluene	34	95.5	47	95.5	58	100
3	EtOAc	20	94.1	17	70.6	75	97.3
4	DCM ^a	17	0	16	79.7	14	96.2
5	DMF	64	0	46	0	36	100

^aDichloromethane.

matography Station for Windows™ v1.7 (DataApex, Prague, Czech Republic).

The NMR spectra were recorded on a Bruker DRX500 spectrometer, in CDCl₃.

saturation of the C=C double bond, the next mol hydrogen reduces C=O double bond and, finally, the hydroxy group is hydrogenolyzed, and, moreover, the five-member molecule loses its chirality.

3. Results and discussion

The substrates can take up to 3 mol hydrogen in consecutive reactions according to Scheme 2. Uptake of the first mol hydrogen results in the

3.1. Effect of solvents

The effect of solvents on the selectivity in the Pd/C catalyzed hydrogenations is summarized in Table 1. In the hydrogenation of **1**, the

Table 2

The influence of different catalyst additives on selectivity. Conditions: 0.5 g substrate, 0.05 g Pd/C (Selcat), 20 ml solvent, 0.25 g additive, atmospheric pressure, 25°C

Entry	Solvents	Additives	Substrates					
			1		3		5	
			Reaction rate (ml H ₂ /g _{cat} min)	Selectivity to 2 (%)	Reaction rate (ml H ₂ /g _{cat} min)	Selectivity to 4 (%)	Reaction rate (ml H ₂ /g _{cat} min)	Selectivity to 6 (%)
1	MeOH	Et ₃ N	68	100	130	87.3	133	100
2	MeOH	Pyridine	14	100	68	100	37	100
3	MeOH	KOAc	100	100	14	95.2	63	100
4	DCM	Et ₃ N	23	100	108	95.3	–	–
5	DCM	Pyridine	10	100	21	100	–	–
6	DCM	KOAc	18	100	22	98.1	–	–
7	DMF	Et ₃ N	17	100	37	81.0	–	–
8	DMF	Pyridine	37	100	22	100	–	–
9	DMF	KOAc	16	100	43	100	–	–
10	EtOAc	Et ₃ N	–	–	71	75.6	–	–
11	EtOAc	Pyridine	–	–	41	98.1	–	–
12	EtOAc	KOAc	–	–	28	98.2	–	–

selectivity to **2** was high only in toluene and in ethyl acetate. The reaction of **3** was also selective in toluene, but in ethyl acetate and in dichloromethane the selectivity to **4** decreased. All solvents were suitable for the selective reduction of C=C double bond of **5**, but in methanol the selectivity to **6** was lower.

Applying solvents of different polarity the selectivity changed, but the conversion of the starting materials was 100% in every case. In toluene, which is an apolar solvent, the selectivity was nearly 100% for all compounds. Using methanol, which is a polar and protic solvent, these values were much lower.

The initial rate of the hydrogenation was also changed with solvents, the lowest rate values were observed in DCM. During hydrogenations in methanol, high reaction rate was accompanied with low selectivity. On the contrary, in toluene the selectivity was high, but the rate much lower.

3.2. Effect of additives

In order to increase the selectivity, three type of additives were given to the reaction mixtures (Table 2). In solvents, where the selectivity was low, the catalyst was poisoned with triethylamine or pyridine, as well as the pH of the solution was increased with potassium acetate to avoid the reduction of carbonyl groups.

Comparing the corresponding data of Table 1 with that of Table 2, it can be seen that addi-

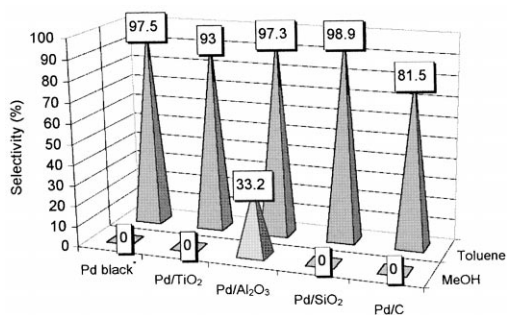


Fig. 1. Hydrogenation of **1** with different catalysts: selectivity of the reaction to **2**. Conditions: 0.5 g substrate, 0.05 g catalyst, 20 ml solvent, 10 bar, reaction time: 4 h, 25°C. *50 bar.

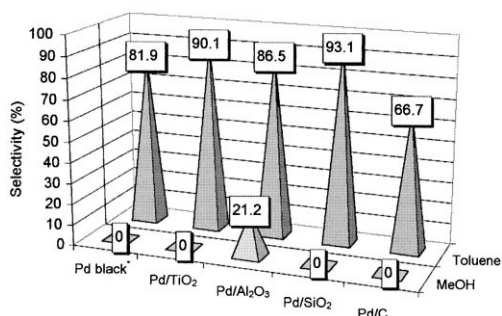


Fig. 2. Hydrogenation of **3** with different catalysts: selectivity of the reaction to **4**. Conditions: 0.5 g substrate, 0.05 g catalyst, 20 ml solvent, 10 bar, reaction time: 4 h, 25°C. *50 bar.

tives were fully efficient in the reduction of **1** and **5**. In the hydrogenation of **3**, pyridine was the best additive in all solvents. Nevertheless, in the presence of pyridine the rate of the hydrogenation was significantly lower than without it.

3.3. Effect of catalyst supports

The effect of palladium on different supports on selectivity was also investigated. The results of the hydrogenation of **1**, **3** and **5** in methanol and in toluene are shown in Figs. 1–3.

As seen, almost similar low selectivities were achieved over Pd black, Pd/Al₂O₃, Pd/SiO₂, Pd/TiO₂ and Pd/C in methanol. On the contrary, in toluene almost similar high selectivities were obtained over these catalysts, i.e., the catalyst support has no influence on selectivity. Furthermore, similarly to the atmospheric hy-

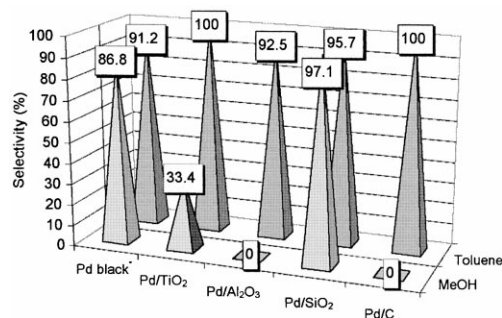


Fig. 3. Hydrogenation of **5** with different catalysts: selectivity of the reaction to **6**. Conditions: 0.5 g substrate, 0.05 g catalyst, 20 ml solvent, 10 bar, reaction time: 4 h, 25°C. *50 bar.

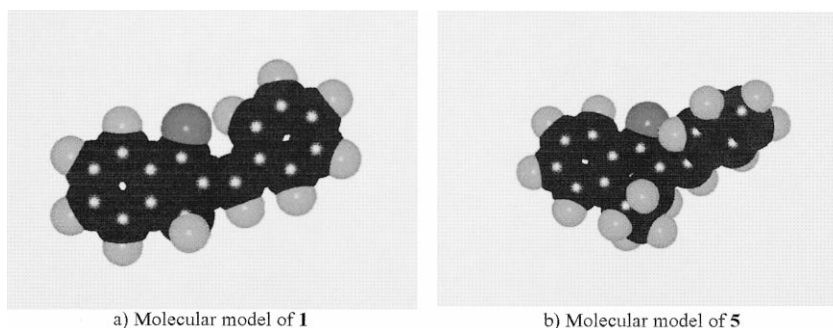


Fig. 4. Molecular models of the substrates **1** and **5**.

drogenations, higher selectivities were also obtained in toluene than in methanol, at both 10 and 50 bar pressures.

4. Conclusion

Exocyclic α,β -unsaturated ketones were converted to the corresponding saturated ketones over palladium on various supports with high selectivity. As known [9], the selectivity of hydrogenations could be influenced by solvents and by addition of poisoning or basic compounds. The best results were achieved with a palladium on carbon catalyst, in toluene, in the presence of pyridine, and at atmospheric pressure.

The selectivity and the rate of the hydrogenation of compounds containing five-, six- or seven-member saturated ring were different under the same reaction conditions. These significant differences between the selectivity values can be attributed to structural causes. Due to the rigidity of the five-member ring, compound **1** is nearly planar [6], therefore the carbonyl group and the C=C double bond can adsorb on the catalyst surface at the same time. This results in low selectivities to saturated ketones, contrary to the high selectivity values of the hydrogenation of **7**, where the molecule is rather flexible

in consequence of the seven-member ring (Fig. 4).

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