

# Ruthenium/1,1'-Bis(diphenylphosphino)ferrocene-Catalysed Oppenauer Oxidation of Alcohols and Lactonisation of $\alpha,\omega$ -Diols using Methyl Isobutyl Ketone as Oxidant

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**Abstract:** A number of ruthenium catalysts, made *in situ* from  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$  and various monodentate and bidentate phosphorus ligands were screened in the double Oppenauer oxidation of 1,6-hexanediol to caprolactone using methyl isobutyl ketone as oxidant and potassium carbonate as base. The catalyst based on 1,1'-bis(diphenylphosphinyl)ferrocene gave this lactone in excellent yield. The same catalyst was

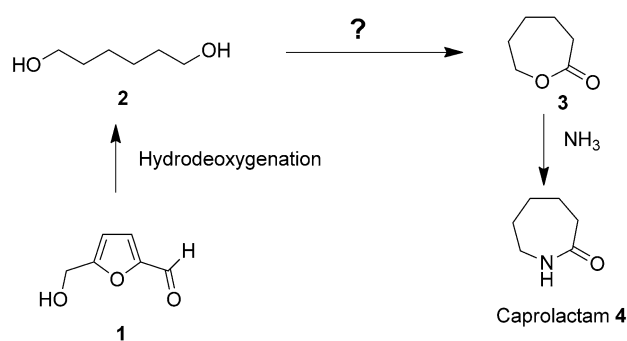
evaluated for the oxidation of other diols to their lactones, of primary alcohols to the corresponding aldehydes and of secondary alcohols to the ketones under the same reaction conditions. The products were obtained in moderate to excellent yields.

**Keywords:** alcohols; aldehydes; diols; homogeneous catalysis; ketones; lactones; ligand effects; oxidation

## Introduction

In synthetic organic chemistry, the oxidation of alcohols to carbonyl compounds plays a pivotal role. Traditionally, these reactions were performed using stoichiometric amounts of toxic reagents such as  $\text{CrO}_3$ .<sup>[1]</sup> Since this type of chemistry is no longer sustainable much effort has been put in the development of catalytic methods. Numerous transition metal-catalysed oxidations have been developed which can be achieved under mild conditions with high selectivity using benign oxidants such as oxygen or hydrogen peroxide.<sup>[2]</sup> Use of the Oppenauer oxidation usually leads to high selectivities.<sup>[3]</sup> As part of a study on the conversion of 5-hydroxymethyl-2-furfural, readily available from renewable resources, into caprolactam we wanted to investigate the dehydrogenative cyclisation of 1,6-hexanediol into caprolactone (Scheme 1).<sup>[4]</sup> Murahashi developed the acceptorless dehydrogenation of  $\alpha,\omega$ -diols such as 1,4-butanediol and 1,5-pentanediol into lactones, using  $\text{RuH}_2(\text{PPh}_3)_4$  as catalyst.<sup>[5]</sup> However, the conversion of 1,6-hexanediol to caprolactone was not reported. Use of other ruthenium catalysts<sup>[6]</sup> as well as an iridium pincer complex<sup>[7]</sup> and

a heterogeneous  $\text{CuO}:\text{ZnO}:\text{ZrO}_2:\text{Al}_2\text{O}_3$  catalyst<sup>[8]</sup> has been reported by others for this transformation, again without the use of 1,6-hexanediol as substrate. Several other groups have developed the oxidative cyclisation of 1,4- and 1,5-diols into lactones using a range of other catalysts and oxidants; some of these even use clean oxidants, such as  $\text{O}_2$  or hydrogen peroxide.<sup>[9]</sup> The catalytic oxidation of 1,6-hexanediol has been reported a number of times yielding caprolactone in



**Scheme 1.** Oxidative lactonisation of 1,6-hexanediol as part of the conversion of HMF to caprolactam.

good to excellent yields. Bamoharram and co-workers reported the use of polyoxometalates as catalysts with  $\text{H}_2\text{O}_2$  in chlorinated solvents (98% yield).<sup>[10]</sup> Park et al. used Shvo's catalyst and  $\text{CHCl}_3$  as unusual oxidant (90% yield).<sup>[11]</sup> Khusnutdinov and co-workers used several manganese and vanadium salts as catalysts and  $\text{CCl}_4$  as oxidant (82% yield).<sup>[12]</sup> Ishii and co-workers used tris(cetylpyridinium) 12-molybdophosphate as catalyst and  $\text{H}_2\text{O}_2$  as oxidant in  $\text{CHCl}_3$  as solvent (54% yield).<sup>[13]</sup> The same method was also used in *t*-BuOH (70% selectivity at 54% conversion after 24 h).<sup>[14]</sup> For a large-scale industrial process we would need selectivity to caprolactone in excess of 95%, preferably 99%. Use of chlorinated solvents is not an option for environmental reasons. As none of the reported methods would be useful for large-scale application we needed to develop a new catalytic method for the lactonisation of 1,6-hexanediol to caprolactone using a benign oxidant.

After we had finished the research described here, a paper was published by Endo and Bäckvall using the Shvo catalyst in a relay system using 2,6-dimethoxybenzoquinone as intermediate oxidant and oxygen as terminal oxidant.<sup>[15]</sup> They obtained caprolactone from 1,6-hexanediol in 86% NMR yield. After finishing the manuscript, the Pd-catalysed oxidative lactonisation of diols was reported by Waymouth and co-workers.<sup>[16]</sup>

## Results and Discussion

The oxidative condensation of 1,6-hexanediol to caprolactone was investigated with a variety of catalytic systems (Table 1). Initial experiments trying Murahashi's dehydrogenative conditions gave very poor selectivities. The same was true for reactions using oxygen or air as oxidants. Thus we started our screening in refluxing acetone as solvent and oxidant in an Oppenauer variant.

It was apparent that the reaction did not proceed at all without the catalyst (entry 1). Fujita et al. reported a  $[\text{Cp}^*\text{IrCl}_2]_2$  complex-catalysed oxidation of primary and secondary alcohols to give carbonyl compounds.<sup>[17]</sup> Surprisingly, in this system, low conversion and selectivity were observed (entry 2). Nozaki also demonstrated a selective oxidation of alcohols to aldehydes using  $\text{RuCl}_2(\text{PPh}_3)_3$  as catalyst.<sup>[18]</sup> Also with this catalyst the oxidation proceeded rather slowly (entry 3). None of the heterogeneous Ru catalyst showed any appreciable catalytic activity for this reaction (entries 4 and 5). Gratifyingly,  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$  in the presence of 1.1 equivalents (with respect to ruthenium) of diphenylphosphinopropane (DPPP) gave excellent conversion with high selectivity (entry 6). Other ruthenium precursors such as  $\text{RuCl}_3$  and  $\text{Ru}(\text{acac})_3$  did not catalyse this reaction (entries 7 and 8).

An optimisation study including three different solvents and bases was performed (Table 2). It was found that MIBK is an excellent solvent/oxidant for

shi's dehydrogenative conditions gave very poor selectivities. The same was true for reactions using oxygen or air as oxidants. Thus we started our screening in refluxing acetone as solvent and oxidant in an Oppenauer variant.

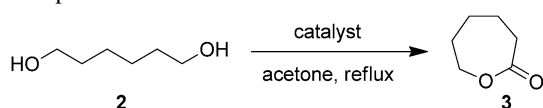
**Table 2.** Effect of solvent and base in the oxidation of 1,6-hexanediol.<sup>[a]</sup>

Entry	Solvent	Base	Conversion [%] <sup>[b]</sup>	Selectivity [%] <sup>[b]</sup>
1	acetone	$\text{K}_2\text{CO}_3$	54	87
2	butyl acetate	$\text{K}_2\text{CO}_3$	–	–
3	MIBK	$\text{K}_2\text{CO}_3$	87	90
4	MIBK	NaOAc	58	86
5	MIBK	$\text{Cs}_2\text{CO}_3$	100	0
6	MIBK	<i>t</i> -BuOK	100	0

<sup>[a]</sup> The reaction was performed at reflux temperature for 24 h with 1,6-hexanediol (1.0 mmol),  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$  (1.0 mol%), DPPP (2.2 mol%) and base (0.2 mmol) in solvent (30 mL)

<sup>[b]</sup> Determined by GC based on the starting material. MIBK = methyl isobutyl ketone

**Table 1.** Catalyst screening for the oxidation of 1,6-hexanediol to caprolactone.<sup>[a]</sup>

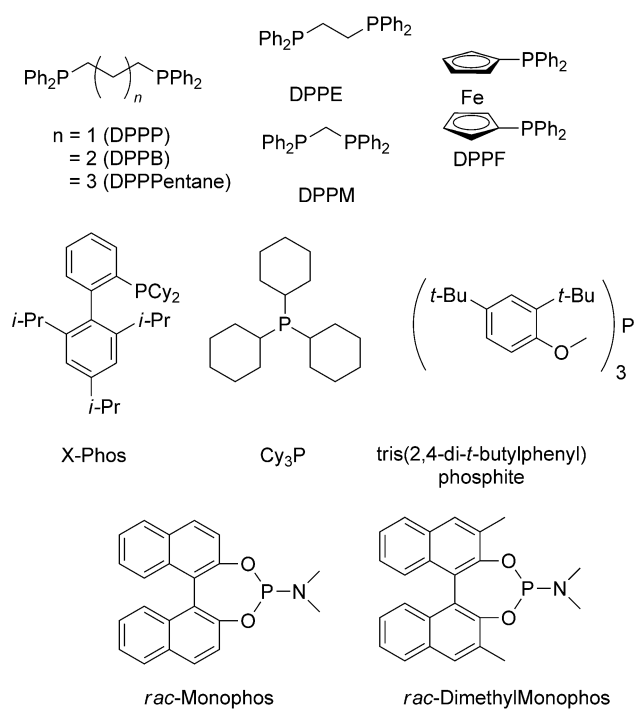


Entry	Catalyst	Conversion [%] <sup>[b]</sup>	Selectivity [%] <sup>[b]</sup>
1	–	–	–
2	$[\text{Cp}^*\text{IrCl}_2]_2$	44	33
3	$\text{RuCl}_2(\text{PPh}_3)_3$	31	81
4	Ru/C	–	–
5	Ru/TiO <sub>2</sub>	3	90
6	$[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2/\text{DPPP}$	54	87
7	$\text{RuCl}_3/\text{DPPP}$	3	90
8	$\text{Ru}(\text{acac})_3$	–	–

<sup>[a]</sup> The reaction was performed at reflux temperature for 24 h with 1,6-hexanediol (1.0 mmol), catalyst (2.0 mol%) and  $\text{K}_2\text{CO}_3$  (0.2 mmol) in acetone (30 mL).

<sup>[b]</sup> Determined by GC based on the starting material.

this reaction due to its higher boiling point (entry 3). Use of butyl acetate as solvent confirmed that this is an Oppenauer oxidation, rather than a dehydrogenation (entry 2).  $\text{K}_2\text{CO}_3$  is the most suitable base for this catalytic system (entries 1–3). Surprisingly, when  $\text{Cs}_2\text{CO}_3$  or *t*-BuOK were used, the selectivity decreased dramatically, due to formation of polymerised product (entries 5 and 6). It was found that presence of water is detrimental to the yield of the reaction and for this reason the  $\text{K}_2\text{CO}_3$  used has to be dried before use. Next, a ligand screening was carried out in



**Figure 1.** Evaluation of commercially available ligands for the oxidative condensation of 1,6-hexanediol.

order to determine the effect of the ligand on the catalytic activity and the selectivity (Figure 1, Table 3). A number of diphosphine ligands with different bridge lengths and some monodentate ligands were screened in the ruthenium-catalysed oxidation of **2** (Table 3). The reaction was stopped after 30 min to

**Table 3.** Ligand screening in the Ru-catalysed oxidation of 1,6-hexanediol.<sup>[a]</sup>

Entry	Ligand	Yield [%] <sup>[b]</sup>
1	–	–
2	DPPPPentane	74
3	DPPPB	70
4	DPPP	79
5	DPPE	88
6	DPPM	79
7	DPPF	100 (79) <sup>[c]</sup>
8	X-Phos (1 equiv.)	54
9	X-Phos (2 equiv.)	71
10	Cy <sub>3</sub> P	50
11	tris(2,4-di- <i>tert</i> -butylphenyl) phosphite	15
12	<i>rac</i> -Monophos	29
13	<i>rac</i> -DimethylMonophos	54

<sup>[a]</sup> The reaction was performed at reflux temperature for 0.5 h with 1,6-hexanediol (1.0 mmol), [Ru(*p*-cymene)Cl<sub>2</sub>]<sub>2</sub> (1.0 mol%), ligand (2.2 mol%) and K<sub>2</sub>CO<sub>3</sub> (0.2 mmol) in MIBK (30 mL)

<sup>[b]</sup> Determined by GC based on the starting material.

<sup>[c]</sup> Isolated yield

allow discrimination since we found in the previous study that use of a diphosphine ligand led to 100% conversion within 24 h. No reaction was observed in the absence of ligand (entry 1). In the presence of 1.1 equivalents of diphosphine ligand (with respect to Ru) such as DPPPPentane, the reaction satisfactorily proceeded to give 74% of the desired product (entry 2). Surprisingly, there is no clear correlation between the bite angle of the ligand and the yield of this reaction (entries 2–6). Note that DPPPB and DPPF have very similar bite angles. However, some caution is warranted as we base ourselves on yields rather than rates. The yield is not only determined by the rate, but also by the stability of the catalyst. When DPPF was used, the reaction went to completion within the time period; no other products were found (entry 7). The product was isolated by means of column chromatography in yields varying between 79–86%. Use of 1 equivalent of the monodentate ligand X-Phos led to 54% yield. When 2 equivalents of X-Phos were employed, the yield increased to 71%. Use of other monodentate phosphine, phosphite or phosphoramidite ligands did not lead to any improvement (entries 10–13).

In conclusion, the catalyst made in situ from [Ru(*p*-cymene)Cl<sub>2</sub>]<sub>2</sub> and DPPF was extremely effective in converting 1,6-hexanediol into caprolactone in the Oppenauer oxidation with MIBK.

Iridium complexes have been used as highly effective catalysts for Oppenauer oxidations of alcohols to aldehydes and ketones.<sup>[19]</sup> In view of the high cost of iridium, ruthenium is more preferred. However, most oxidations using ruthenium are limited to secondary alcohols or benzylic alcohols.<sup>[20]</sup>

Encouraged by our results in the lactonisation we decided to test this catalyst also in the Oppenauer oxidation of a number of primary and secondary alcohols under the same conditions as used before (Table 4). As may be expected from an Oppenauer oxidation, no formation of carboxylic acids was observed in these reactions. Surprisingly, we also did not find esters that could have formed *via* hemiacetal formation and further oxidation. Gratifyingly, no condensation products of the aldehydes were observed either. Benzylic alcohols were selectively transformed into the corresponding benzaldehydes (entries 1–8). The yields of the reaction after 0.5 h are strongly influenced by the substituents on the aromatic ring. Not surprisingly, higher yields are obtained with substrates that contain electron-donating groups and lower yields with substrates containing electron-withdrawing groups such as chloro and nitro. In cases where the conversion was incomplete longer reaction times did not lead to further conversion. Apparently, catalyst deactivation occurs. The problem of catalyst deactivation can be countered to a large extent by slowly dosing the preformed ruthenium-bisphosphine com-

**Table 4.** Oxidation of primary and secondary alcohols to aldehydes and ketones catalysed by  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$  and DPPF.<sup>[a]</sup>

Entry	Alcohol	Yield [%] <sup>[b]</sup>
1	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	60
2	4-Cl- $\text{C}_6\text{H}_4\text{CH}_2\text{OH}$	28
3	4- $\text{O}_2\text{N-C}_6\text{H}_4\text{CH}_2\text{OH}$	6
4	4-Me- $\text{C}_6\text{H}_4\text{CH}_2\text{OH}$	70 (86) <sup>[c]</sup>
5	4-HO- $\text{C}_6\text{H}_4\text{CH}_2\text{OH}$	81
6	4-MeO- $\text{C}_6\text{H}_4\text{CH}_2\text{OH}$	85
7	3-MeO- $\text{C}_6\text{H}_4\text{CH}_2\text{OH}$	52
8	2-MeO- $\text{C}_6\text{H}_4\text{CH}_2\text{OH}$	43
9	1-octanol	49
10	cyclohexylmethanol	62
11	1-phenylethanol	70
12	2-octanol	58

<sup>[a]</sup> The reaction was performed at reflux temperature for 0.5 h with alcohol (2.0 mmol),  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$  (1.0 mol%), DPPF (2.2 mol%) and  $\text{K}_2\text{CO}_3$  (0.4 mmol) in MIBK (30 mL).

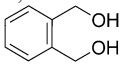
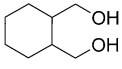
<sup>[b]</sup> Isolated yields (after purification *via* column chromatography or bulb-to-bulb distillation).

<sup>[c]</sup> The value in parentheses is the isolated yield of the slow addition reaction.

plex to the reaction mixture using a syringe pump over a period of 1 h, followed by another half hour at reflux. Using this method the isolated yield of *p*-methoxybenzaldehyde could be increased from 70 to 86% (entry 4). The reaction is highly sensitive to steric effects, since the conversion was lower if the methoxy substituent was introduced at the *meta*- (entry 7) rather than the *para*-position (entry 6) and much lower with the methoxy substituent in the *ortho*-position (entry 8). The catalyst could also be used for the oxidation of aliphatic primary alcohols (entries 9 and 10) but the reaction gave much lower conversions. Nevertheless, these oxidations are selective and no acid or ester was formed. Secondary alcohols could be easily oxidised to the corresponding ketones under the same reaction conditions. 1-Phenylethanol and 2-octanol were transformed into the corresponding ketones in good yields (entries 11 and 12).

Finally, we also tested the  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2/\text{DPPF}$  catalyst in the oxidative cyclisation of other diols (Table 5). Both 1,5-pentanediol as well as 1,4-butanediol were converted quantitatively into the respective lactones and isolated after column chromatography in good yields (entries 1 and 2). 1,2-Benzenedimethanol underwent oxidative cyclisation to give 1-isobenzofuranone in 73% isolated yield (entry 3). *cis*-1,2-Cyclohexanedimethanol was oxidised to the lactone which could be isolated in 92% yield (entry 4).

**Table 5.** Oxidative condensation of diols to lactones catalysed by  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2/\text{DPPF}$ .<sup>[a]</sup>

Entry	Alcohol	Yield [%] <sup>[b]</sup>
1	1,5-pentanediol	80
2	1,4-butanediol	82
3		73
4		92

<sup>[a]</sup> The reaction was performed at reflux temperature for 0.5 h with diol (2.0 mmol),  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$  (1.0 mol%), DPPF (2.2 mol%) and  $\text{K}_2\text{CO}_3$  (0.4 mmol) in MIBK (30 mL).

<sup>[b]</sup> Isolated yield.

## Conclusions

In conclusion, we have found a novel ruthenium catalyst based on  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$  and DPPF for the double Oppenauer oxidation of 1,6-hexanediol to caprolactone in excellent yield. The high selectivity obtained in this reaction makes it a good candidate for large-scale production. Further development should be aimed at increasing the substrate/catalyst ratio and investigation of possible catalyst deactivation mechanisms. The same catalyst is also very useful for the conversion of other diols into lactones, primary alcohols into aldehydes and secondary alcohols into ketones *via* Oppenauer oxidation with MIBK as oxidant under mild reaction conditions. Selectivities of these reactions were mostly excellent, although with less reactive substrates incomplete conversion occurred. This is due to catalyst deactivation. This problem could be countered by slowly metering the catalyst into the reaction mixture. The very high selectivity of these reactions is truly remarkable.

## Experimental Section

All reactions and manipulations were carried out under an atmosphere of nitrogen by means of standard Schlenk techniques. Gas chromatography (GC) analyses were performed on an HP5890 Series II GC gas chromatograph with a solgel capillary column (CP) and coupled with an MSD 5972 Series detector. Dried methyl isobutyl ketone was purchased from Sigma Aldrich. Other reagents were used as obtained from commercial sources. Potassium carbonate was dried in an oven and stored in a desiccator or in the glove box.

### Typical Catalytic Reaction

To a flame-dried Schlenk flask were added  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$  (12.2 mg, 0.02 mmol), DPPF (24.4 mg, 0.044 mmol) and MIBK (5 mL). The suspension was stirred at room temperature for 15 min. Then, a solution of the sub-

strate (2 mmol) in MIBK (10 mL), the analytical standard (dodecane, 100  $\mu$ L), anhydrous  $K_2CO_3$  (55.3 mg, 0.4 mmol) and finally excess solvent (MIBK, 15 mL) were added to the preformed catalyst. The Schlenk flask was equipped with a condenser and the reaction mixture was put in a preheated oil bath (140 °C) and refluxed for 30 min. After cooling to room temperature, the conversion was checked by GC, the reaction mixture was filtered through a plug of silica, concentrated and purified by bulb-to-bulb distillation or column chromatography. For the products purified by bulb-to-bulb distillation, the reaction was carried on a 5 mmol scale. The products were identified by comparison of their NMR data with those of authentic samples.

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Ruthenium/1,1'-Bis(diphenylphosphino)ferrocene-Catalysed Oppenauer Oxidation of Alcohols and Lactonisation of  $\alpha,\omega$ -Diols using Methyl Isobutyl Ketone as Oxidant

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