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Platinum-Catalyzed Selective Hydration of Hindered Nitriles and Nitriles with Acid- or Base-Sensitive Groups

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Hindered tertiary nitriles can be hydrolyzed under neutral and mild conditions to the corresponding amides using platinum(II) catalysts with dimethylphosphine oxide or other secondary phosphine oxides (SPOs, phosphinous acids) as ligands. We have found that this procedure also works well for nitriles with acid- or base-sensitive groups, which is unprecedented in terms of yield and selectivity. The catalyst loading can be as low as 0.5 mol %. Amides are isolated as the only product in high yield, and no further hydrolysis to the corresponding acids takes place. Reactions are carried out at 80 °C but take place even at room temperature. When enantiopure secondary phosphine oxide ligands are used in the hydrolysis of racemic nitriles, no kinetic resolution is observed, presumably due to racemization of the ligand during the reaction.

Introduction

The hydrolysis of nitriles to amides and carboxylic acids is an important transformation in organic chemistry. Many industrial examples are known, such as the hydrolysis of amino nitriles to amino acids, acrylonitrile to acrylamide and acetone cyanohydrin to the corresponding amide, en route to methyl methacrylate. Using specific conditions, it is possible to stop at the amide stage. Frequently used methods for nitrile hydrolysis to amides are strong acid (96% H₂SO₄) or base (50% KOH/t-BuOH). A simple and versatile method has been reported by Katritzky and co-workers who used a combination of 30% H₂O₂/K₂CO₃/DMSO at 0 °C for 5–10 min to obtain high yields of pure amides. However, in general, selective hydrolysis of nitriles to amides is troublesome and yields are reasonable at best for two reasons:

(1) It is difficult to stop the hydrolysis at the amide stage and further hydrolysis to the carboxylic acid often takes place, as the rate constant of amide hydrolysis is usually larger than that for nitrile hydrolysis, especially under basic conditions (Scheme 1).

(2) Since the nitrile group is not very reactive, harsh conditions using strong acids or bases are required, which precludes the presence of acid- or base-sensitive functional groups.

Tertiary nitriles are a special class as they are particularly resistant toward hydrolysis. There are only a few successful examples known in the literature. Use of 96% H₂SO₄ at 140 °C for 3 h yields tertiary amides with yields ranging from 10% to 90% depending on the substrate. Strong basic conditions have also been used, but this leads to much lower yields. For instance, tributylacetoni-trile could be converted into tributylacetamide in 15% yield after 100 h of reflux with 50% KOH in tert-butyl alcohol. Due to these difficulties, tertiary amides are generally prepared from the corresponding acid chloride and NH₃. Furthermore, the method of

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SCHEME 1. Nitrile Hydrolysis

\[
\text{R-CN + H}_2\text{O} \xrightarrow{\text{slow}} \text{R-OH} + \text{NH}_3 \xrightarrow{\text{fast}} \text{R-OH} + \text{NH}_3
\]

Katritzky and co-workers mentioned above does not work for tertiary nitriles.\(^{11}\) No efficient method for the hydrolysis of tertiary nitriles has been reported so far.

To reduce salt formation in industrial nitrile hydrolysis, a number of methods based on the use of enzymes and transition-metal catalysts have been developed. Enzymatic hydrolysis takes place under exceptionally mild conditions.\(^{12}\) A number of examples have been reported, with some of them showing good enantioselectivity in the kinetic resolution of racemic nitriles or in the conversion of meso-dinitriles.\(^{13}\) A restriction, however, is the low reactivity of the enzymes, although DeSantis and co-workers have reported very high rates of hydrolysis with less hindered nitriles, such as mandelonitrile.\(^{14}\)

Transition-metal catalysts have also been successful in the hydrolysis of nitriles to amides. Several classes of heterogenous catalysts\(^{15}\) have been used, such as supported metals (Cu, Ni, Ag, Pd),\(^{16}\) metal oxides, (\(\text{MnO}_2, \text{TiO}_2, \text{SiO}_2, \text{Al}_2\text{O}_3\)), and zeolites\(^{18}\) (\(\text{NaY}, \text{Al}, \text{Zn}\)). Yields and selectivities generally are poor.

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Homogeneous catalysts of Pd(II),\(^{19}\) Pt(II),\(^{20}\) Pt(0),\(^{21}\) Co(III),\(^{22}\) Cu(II),\(^{23}\) Zn(II),\(^{24}\) Rh(I),\(^{26}\) Rh(III),\(^{27}\) Ru(II),\(^{28}\) Ru(III),\(^{26}\) Ni(II),\(^{24}\) Ni(II),\(^{24}\) Zn(II),\(^{24}\) Rh(I),\(^{26}\) Rh(III),\(^{27}\) Ru(II),\(^{26}\) Ru(III),\(^{26}\) Re(II),\(^{29}\) or Mo(I)\(^{30}\) and others.\(^{11}\) Limitations of these catalysts are as follows:

1. There is need for additional base or acid, which precludes the hydrolysis of nitriles containing sensitive functional groups,\(^{20a,b,22a,e}\)
2. Some catalysts are only effective for nitriles containing an additional coordinating group,\(^{22,24,27}\)
3. Some of the applied ligands are not easily synthesized.\(^{22a-c}\)

The two reported catalysts that stand out in terms of reactivity and selectivity are \(\text{[PdH (PMe}_3\text{)2(H}_2\text{O)}]\text{[OH]}\)\(^{20b}\) and \(\text{[Pd(PMe}_3\text{OH)} (\text{PMe}_3\text{O})\text{⋅H}_2\text{O}]\text{[OH]}\)\(^{20b,d}\) (Figure 3).

In the hydrolysis of acetonitrile, the turnover frequencies (TOF) of these two catalysts are 178 and 380 h\(^{-1}\), respectively. Both catalysts are surprisingly active as attested by their turnover numbers (TON) of \(6 \times 10^2\) mol/mol. Thus far, catalyst 1, developed by Parkins and co-workers,\(^{20,26}\) has been shown to be the most active and versatile one. In the hydrolysis of acetonitrile, with 0.015 mol % of 1, 91% isolated yield of acetamide was obtained after 15.5 h of reflux in water. The applied secondary phosphine oxide ligands are possibly involved in the hydrolysis reaction by intramolecular nucleophilic attack on the coordinated nitrile.\(^{26}\) The hydrolysis of tertiary nitriles and acid- or base-sensitive nitriles using this catalyst has not been reported, however.

Secondary phosphine oxide ligands (SPOs) have found application in Pt-catalyzed hydroformylation,\(^{32}\) in Pt-catalyzed hydrolytic amination of nitriles,\(^{33}\) and in Pd-catalyzed aromatic substitution reactions.\(^{34}\) We recently...
reported the preparation of enantiopure SPOs and their application as ligands in the Ir(I)-catalyzed asymmetric imine hydrogenation. The ligands are prepared by the addition of a Grignard reagent to a solution of RPCl₂ in THF at -20 °C, followed by hydrolysis with water. They are readily obtained enantiopure by preparative chiral HPLC. In particular, t-BuPHPO L₁ (Figure 2) is easy to separate by preparative chiral HPLC with a 4.3 min retention time difference between the two enantiomers. Classical resolution has also been used to obtain enantiopure SPOs.

More recently, this ligand has also been used by Dai and co-workers in palladium-catalyzed allylic alkylation reactions.

In view of the above, we decided to further investigate the hydrolysis of nitriles that are not easy to hydrolyze by other means, such as tertiary nitriles and nitriles containing acid- or base-sensitive groups. In addition, the availability of the enantiopure L₁ prompted us to investigate the possibility of kinetic resolution of racemic nitriles.

Results and Discussion

Catalyst 1 has been prepared from Pt(PPh₃)₄ and 5 equiv of Me₂POH in toluene. The same procedure could be used with Ph₂POH to form 3. Unfortunately, with L₁, this procedure failed to give the analogous complex. For this reason, we explored the preparation of complexes starting from PtCl₂ instead of Pt(PPh₃)₄. Gratifyingly, reaction of PtCl₂ with 5 equiv of Me₂POH in toluene gave a white solid, the structure of which was determined by X-ray analysis after crystallization from DCM/Et₂O (Figure 2).

The structure of this complex (2), [PtCl₂(PMe₂OH)(PMetoH⋅H−OPMe₂)], is comparable to the structure of 1 (Figure 3). In particular, it shares with 1 the deprotonation of one of the hydroxyl groups of the Me₂POH ligands. The P−O is hydrogen-bonded to the adjacent Me₂POH. Thus, a neutral Pt(II) complex is the net result. In view of the above, we decided to further investigate the hydrolysis of hindered nitriles, especially those with acid or base-sensitive groups. In addition, the availability of the enantiopure L₁ prompted us to investigate the possibility of kinetic resolution of racemic nitriles.

Me₂POH. Thus, a neutral Pt(II) complex is the net result. Again, no well-defined complex could be obtained using L₁. It turned out, however, that in situ preparation of the catalyst by using PtCl₂ in combination with 3 equiv of racemic or enantiopure L₁ gave comparable results in the hydrolysis reactions.

Initially, acetonitrile and α-methylbenzyl cyanide 4k (Scheme 3) were applied as model substrates in the hydrolysis reactions. Catalysts 1–3 all gave full conversion to the corresponding amide as the sole product, being the most active catalyst. Their catalytic activities decrease as follows: 1 > 3 > 2. With 0.5 mol % of 1, the reaction took 3 h at 80 °C in EtOH/H₂O (TOF 67 h⁻¹), whereas using 3, a reaction time of 20 h (TOF 10 h⁻¹) was required. With 2 mol % of catalyst 2, 18 h was needed for complete conversion (TOF 3 h⁻¹). When 4k was used as substrate, similar trends were found. The somewhat reduced rate of 2 is due to the presence of chloride anion, which can still compete with the nitrile for the binding site. This can be remedied by the addition of AgBF₄, as shown by Parkins. This presumably creates the same cationic complex as the one obtained by hydrolysis of 1.

To expand the scope of this reaction, a number of sterically hindered tertiary nitriles and nitriles with acid or base-sensitive groups were hydrolyzed with the catalysts mentioned above (Figures 4 and 5).

Using catalyst 1, all substrates were smoothly converted to the corresponding amides in over 95% isolated yield except for trimethylacetonitrile 4f (Scheme 2, Table 1).

Catalyst 1 is more active than 2 and the in situ complexes made from PtCl₂ and ligand L₁, especially with the sterically hindered tertiary nitriles. With unhindered nitriles, the difference is less pronounced. All nitriles (4a–j) except 4c were completely converted to

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**Figure 1.** Structure of L₁.

**Figure 2.** Perspective PLUTO drawing of catalyst 2.

**Figure 3.** Structures of preformed catalysts.

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hydrolysis of unhindered nitriles (catalyst 1) the corresponding amides (Scheme 2).

**FIGURE 4.** Structures of tertiary nitriles.

**FIGURE 5.** Structures of nitriles with acid- or base-sensitive groups.

**SCHEME 2.** Platinum-Catalyzed Nitrile Hydrolysis

\[ R-CN + H_2O \xrightarrow{\text{Catalyst}} R-CNH_2 \]

**TABLE 1.** Platinum-Catalyzed Hydrolysis of Nitriles to Amides

<table>
<thead>
<tr>
<th>entry</th>
<th>nitrile</th>
<th>catalyst</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>product</th>
<th>isolated yield (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>4a</td>
<td>1</td>
<td>80</td>
<td>1</td>
<td>5a</td>
<td>99</td>
</tr>
<tr>
<td>2</td>
<td>4b</td>
<td>1</td>
<td>80</td>
<td>12</td>
<td>5b</td>
<td>99</td>
</tr>
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<td>1</td>
<td>80</td>
<td>48</td>
<td>5c</td>
<td>96</td>
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<tr>
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<td>4d</td>
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<td>5d</td>
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<tr>
<td>13</td>
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<tr>
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<td>25</td>
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<tr>
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<tr>
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<td>PtCl_2 + L1</td>
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<td>21</td>
<td>5a</td>
<td>85</td>
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<tr>
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<td>4b</td>
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<td>80</td>
<td>33</td>
<td>5b</td>
<td>74</td>
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<tr>
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<td>4d</td>
<td>PtCl_2 + L1</td>
<td>80</td>
<td>48</td>
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<td>43</td>
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<tr>
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<td>PtCl_2 + L1</td>
<td>80</td>
<td>48</td>
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<td>41</td>
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<td>5g</td>
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<td>4g</td>
<td>1</td>
<td>25</td>
<td>20</td>
<td>5g</td>
<td>96</td>
</tr>
</tbody>
</table>

*a General conditions: 0.5 mol % preformed catalyst, 5 mmol of nitrile, 4 mL of EtOH, 2 mL of H_2O, and heating to 80 °C.  
*b 3.5 mol % catalyst, 1 mmol of substrate.  
*c 1 mol % catalyst.  
*d 1 mmol of substrate, pure H_2O as solvent.  
*e 2 mol % catalyst.  
*f 4 mol % catalyst.

the corresponding amides (5a–j) using only 0.5 mol % of catalyst 1 in EtOH/H_2O mixtures at 80 °C (Table 1). The hydrolysis of unhindered nitriles (4g–j) is completed in 3–4 h but the sterically hindered tertiary nitriles (4a,b, 4d–f) need reaction time up to 41 h to give full conversion under these conditions. Increasing the catalyst loading to 2 mol % reduced the reaction time to 5–18 h.

Nitrile 4c remained unchanged with 0.5 mol % of 1 even after prolonged reaction time. Increasing the catalyst loading to 3.5 mol %, however, did result in its hydrolysis to amide 5c (entry 3). This sluggish reaction might be due to the conformation of the substrate in which the cyano group occupies an axial position where its suffers severe steric hindrance (e.g., 1,3-diaxial interaction).

The nitriles possessing acid- or base-sensitive groups (4g–j) were all smoothly converted to the corresponding amides without any side reactions (entries 7–10, 20, and 21). Even the sensitive d-amygdalin (4j) was converted to the amide without racemization of any of the stereoergic centers in the sugar moieties in 98% yield. The stereochemical integrity of the product was confirmed by COSY and NOESY NMR experiments. All substrates could even be hydrolyzed at room temperature, although a long reaction time was needed (entries 13 and 21).

Because of the poor solubility of the catalysts in most organic solvents, the products can be extracted with THF or DCM after evaporation of the ethanol/water mixture. The recycled catalysts could be used at least one more time in subsequent reactions and were found to largely retain their activity.

There are very few reported examples of enantioselective hydration of nitriles, other than those catalyzed by enzymes. With the enantiopure ligand L1, we attempted a kinetic resolution of racemic nitriles. Using the in situ formed complex of (R)-(+) t-BuPhPHO (L1) and PtCl_2, nitrile 4k and sterically hindered tertiary nitriles 4d,e were hydrolyzed under the standard conditions. The hydrolysis of 4d,e did not go to completion (55% conversion determined by GC). The ee's of both the remaining substrate and the product were determined during the reaction by HPLC. However, in all cases (4k, 4d,e) both the nitrile and the product amide were found to be racemic. To exclude the possibility of racemization of the nitriles or amides an experiment was performed using D_2O instead of H_2O. Upon D-NMR analysis only a small signal due to the ND_2 group was observed and no D-deuteration was found neither in the nitrile nor in the amide (Scheme 3). These findings exclude racemization of the substrates or products.

After careful chiral HPLC–MS analysis of the hydrolysis samples, we discovered that the ligand L1 had largely racemized during the reaction. This explains the disappointing results in the kinetic resolution experiments.

**SCHEME 3.** Deuteration Experiment with Catalyst 1

\[ 4k \xrightarrow{D_2O} 5k \]

Conclusión

By broadening the scope of the nitrile hydrolysis reaction reported by Parkins and co-workers, a catalytic...
method has been developed for the hydrolysis of tertiary nitrites and nitrites containing sensitive groups to their corresponding amides. To the best of our knowledge, the excellent yields and chemoselectivity of these hydration reactions are unprecedented in the literature. An attempted kinetic resolution failed and the ligand was found to racemize during the reaction.

Experimental Section

For general methods and details of experimental procedures, see Supporting Information.

General Procedure for Catalytic Nitrite Hydrolysis Reaction. To a 25 mL round-bottom flask equipped with magnetic stirrer were added preformed catalyst (0.011 g, 0.0256 mmol, 0.5 mol %), nitrite (5 mmol), EtOH (4 mL), and the solution was heated to 80 °C (in air). After the required reaction time (conversion was checked by TLC and GC), the reaction was allowed to come to room temperature and the solvent was removed under vacuum. After redissolution in DCM or THF, the solution was filtered, the solvent removed, and the solid product was dried overnight under vacuum to yield the corresponding amides, generally pure enough for analysis. If further purification was needed, the products were recrystallized from THF or DCM.

1-(4-Methylphenyl)cyclopropanecarboxamide (5a) was isolated as a white crystalline compound: yield 99%; mp 76–77.5 °C; ^1H NMR (CDCl3) δ 1.05 (t, J = 3.4 Hz, 2H), 1.58 (t, J = 3.7 Hz, 2H), 2.34 (s, 3H), 5.35 (br, 1H), 5.92 (br, 1H), 7.16 (d, J = 7.3 Hz, 2H), 7.30 (d, J = 7.6 Hz, 2H); ^13C NMR (CDCl3) δ 175.5, 136.2, 135.4, 129.2, 128.1, 21.8, 19.4, 14.5; HRMS (EI) m/z 239.1308, 239.1304, 239.1304. Anal. Calcld for C16H17NO: C, 73.40; H, 7.76. Found: C, 73.51; H, 7.66; N, 7.96.

2-(4-Methylphenyl)cyclocaptonecarboxamide (5b) was isolated as a white crystalline compound: yield 99%; mp 112–114 °C; ^1H NMR (CDCl3) δ 1.69–1.74 (m, 2H), 1.75–1.81 (m, 2H), 1.92–2.12 (m, 2H), 2.33 (s, 3H), 2.36–2.52 (m, 5H), 5.48 (br, 1H), 7.15 (d, J = 6.6 Hz, 2H), 7.26 (d, J = 6.4 Hz, 2H); ^13C NMR (CDCl3) δ 177.7, 138.8, 134.9, 128.0, 124.9, 48.9, 32.9, 24.3, 21.3, 19.4; HRMS (EI) m/z 239.1321, 239.1354, calcld for C16H17NO: C, 76.81; H, 8.43; N, 6.69. Found: C, 76.88; H, 8.61; N, 6.91.

2-Phenyl-2-propyl-9-oxypentanoic acid (5c) was isolated as an off-white solid: yield 80%; mp 142 °C; ^1H NMR (CDCl3) δ 5.22 (t, 7.29 Hz, 1H), 5.62 (d, 7.15 Hz, 1H), 1.71 (m, 10H), 3.73 (m, 1H), 5.20 (m, 2H), 1.38 (m, 2H), 1.58 (m, 2H), 1.52 (m, 2H), 5.20 (m, 2H), 1.38 (m, 2H), 1.58 (m, 2H), 1.52 (m, 2H), 5.20 (m, 2H), 1.38 (m, 2H), 1.58 (m, 2H), 1.52 (m, 2H), 5.20 (m, 2H), 1.38 (m, 2H), 1.58 (m, 2H), 1.52 (m, 2H).

2-Furamide (5g) was isolated as an off-white solid: yield 95%; mp 140–142 °C; ^13C NMR (CDCl3) δ 146.6, 148.6, 148.6, 127.1, 127.1, 127.1, 127.1, 127.1, 127.1.

Acknowledgment. We thank Ms. T. Tietmersma for GC and HPLC analysis and Dr. A. Meetsma for X-ray analysis. Financial support from DSM and the Dutch Ministry of Economic Affairs for a subsidy under the EET scheme (Grant No. EETK97107 and EETK99104) is gratefully acknowledged.

Supporting Information Available: General experimental procedure; ^1H, ^13C, 2D COSY, and NOESY NMR spectra of 5j and 5a – c; selected X-ray data of catalyst 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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