Participation at the International Conference on Green Chemistry 2019 (ISGC) in La Rochelle
May 13-17

Two PhD students of our group, namely Michael Stricker and Alessa Hinzmann, attended the International Conference on Green Chemistry 2019 (ISGC) in La Rochelle, France. Alessa Hinzmann had the opportunity to give an oral presentation on TEMPO-oxidation in alternative solvent, while Michael Stricker presented a poster on TEMPO-oxidation of primary diols. His work was generously financed by the Europäische Fonds für Regionale Entwicklung (EFRE) (Grant no. EFRE-0400138). The ISGC is one of the biggest conferences within Green Chemistry and covers all topics of Sustainable Chemistry in industry and academia. Overall around 600 participants were present, 300 talks and 200 posters were presented.

Alessa Hinzmann (left) and Michael Stricker (right) in front of the Espace Encan (conference venue).
Selective TEMPO-oxidation of dialcohols to dialdehydes in alternative solvents

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Introduction
Oxidation of primary alcohols to aldehydes is still challenging in terms of selectivity, environmental friendliness and costs.[1] In contrast to the standard oxidation methods, which often require the use of toxic metal species, oxidation with 2,2,6-tetramethylpiperidine-1-oxyl radical (TEMPO) as catalyst offers a greener alternative.[2,3] Usually, TEMPO-oxidation takes place in a biphasic reaction medium consisting of water and dichloromethane, which is considered as very harmful to the environment. Replacing dichloromethane usually leads to selectivity problems, thus a reaction optimisation for each individual substrate is needed.[4] These disadvantages are even more problematic in the case of primary dialcohols, which are very sensitive in terms of over-oxidation.

Substrate Scope
The solvent screening indicated that aliphatic nitriles especially n-butyronitrile and n-octanenitrile, are suitable solvents for selective TEMPO-oxidations. In order to test the performance of these solvents, a substrate scope with PIPO as catalyst and a substrate concentration of 1 M was determined.

Mono alcohols. Overall ten primary mono alcohols and four secondary alcohols could be converted with high conversions of >93% and high selectivities of >91%.

Solvent Screening
Initially, we decided to optimise the TEMPO-catalysed oxidation of n-octan-1-ol in dichloromethane as described by Okada et al.[5] to obtain a benchmark system, which then can be used for a solvent screening. After a reaction optimisation, high conversions and selectivities could be achieved. Subsequently, a solvent screening with TEMPO and PIPO, a polymer-bound TEMPO-derivative, for the oxidation of n-octan-1-ol was performed.

<table>
<thead>
<tr>
<th>Product</th>
<th>1</th>
<th>Conversion/%</th>
<th>Selectivity/%</th>
<th>Yield/ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45</td>
<td>96</td>
<td>91</td>
<td>37</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>&gt;99</td>
<td>90</td>
<td>69</td>
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<td>3</td>
<td>40</td>
<td>&gt;99</td>
<td>93</td>
<td>56</td>
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<td>4</td>
<td>45</td>
<td>&gt;99</td>
<td>94</td>
<td>87</td>
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<tr>
<td>5</td>
<td>45</td>
<td>&gt;99</td>
<td>91</td>
<td>71</td>
</tr>
</tbody>
</table>

Outlook
Furthermore, the TEMPO-oxidation of dialcohols to dialdehydes will be used as a first step in a cascade reaction towards dinitriles. Dialcohols will be oxidised using PIPO, followed by a condensation with hydroxylamine hydrochloride in a sequential one-pot process. In a final step the dialdoxime will be dehydrated with aldoxime dehydratases to the dinitriles. This will open up a green synthetic route towards dinitriles, which could also be suitable for industrial applications.

References

Acknowledgment
We gratefully acknowledge generous support from the Europäische Fonds für Regionale Entwicklung (EFRE) (Grant no. EFRE-0400138). We also gratefully acknowledge generous support from the Fachagentur Nachwachsende Rohstoffe (FNR) (Grant No. 22001716).

![Chemical structures and reaction schemes](image-url)