Catalytic Hydrogenation

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Direct Ruthenium-Catalyzed Hydrogenation of Carboxylic Acids to Alcohols**

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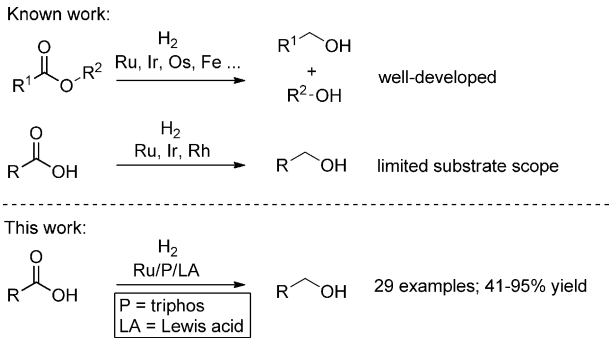
Abstract: *The "green" reduction of carboxylic acids to alcohols is a challenging task in organic chemistry. Herein, we describe a general protocol for generation of alcohols by catalytic hydrogenation of carboxylic acids. Key to success is the use of a combination of $Ru(acac)_3$, triphos and Lewis acids. The novel method showed broad substrate tolerance and a variety of aliphatic carboxylic acids including biomass-derived compounds can be smoothly reduced.*

Aliphatic alcohols are basic building blocks for organic synthesis, life science and material industry, some of them being annually applied up to multimillion-ton scale. Among the various methods for preparation of alcohols,[1] hydrogenation of carboxylic acids to alcohols represents a straightforward and atom-efficient procedure. Despite the apparent simplicity of this transformation, common methods rely on the use of (over)stoichiometric amounts of metal hydrides[2,3] or silanes,[4] which inevitably generate large amounts of waste. Until to date, the hydrogenation of carboxylic acids has seriously lagged behind related reductions of other carbonyl compounds.[5,6] For example, elegant examples for the synthesis of alcohols from esters were developed in the last decade using catalysts based on Ru,[5,7] Ir,[8] Os,[9] or Fe.[10]

Contrary to ester hydrogenation, interaction of carboxylic acids with the active transition metal center may result in the crucial deactivation of the active catalyst. Thus, only few molecularly defined complexes have been reported for the hydrogenation of "simple" carboxylic acids, for example, acetic, levulinic and benzoic acid.[5c,11] Interestingly, recently a biocatalytic hydrogenation proved to be effective for hydrogenation of some carboxylic acids, too.[12] Despite this important progress, there is a need for more general catalysts for such reactions (Scheme 1). In fact, the selective hydrogenation of carboxylic acids in the presence of different functional groups has not been addressed in detail.

Herein, we demonstrate a general method for hydrogenation of carboxylic acids to alcohols using $Ru(acac)_3$/triphos (acac = acetylacetonate) in the presence of Lewis acids. This work was inspired by the efficient hydrogenation of carbon dioxide[13] and the recently developed methodology for the synthesis of ethers from esters.[14]



Scheme 1. Homogeneous hydrogenation of carboxylic acid derivatives.

Initially, the catalytic hydrogenation of phenylacetic acid was investigated as a model reaction. The resulting alcohol occurs widely in nature and is also found in a variety of essential oils. Variation of 8 phosphine ligands with different structures reveal significant activity only for the tridentate ligand 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos: **4a**) (see the Supporting Information). Hence, in the presence of $Ru(acac)_3$ and $Sn(OTf)_2$ 2-phenylethan-1-ol is obtained in 49% GC yield. In addition, phenethyl 2-phenylacetate is observed as the sole by-product, which results from condensation of the product with the substrate.

To avoid this unwanted condensation process, water was added as co-solvent. Indeed, under these conditions (48 h reaction time) full conversion of the substrate occurred and 95% yield of the desired alcohol is produced (Table 1, entry 12). In the presence of other phosphine ligands **4b**–**4h** much lower or no activity on the formation of 2-phenylethan-1-ol was observed.

Next, the effect of different Lewis acids was explored. The best yield of the desired product is achieved in the presence of $Sn(OTf)_2$ using a mixture of toluene and water. In contrast, almost no desired alcohol is observed in the absence of water, which demonstrates the striking influence of water in this hydrogenation. Consistently, the use of molecular sieves has a negative effect for this reaction. Using other organic solvents such as THF, xylene and methylene instead of toluene has no improvement on the activity (Table S1 in the Supporting Information). Different Sn-based Lewis acids such as Me_2SnCl, Me_2SnO and Bu_3SnO showed significantly lower activity in this transformation compared to $Sn(OTf)_2$ (Table 1, entries 4–7). Similarly, other triflates with different cations showed lower activities than tin triflate in this transformation (Table S1). We also examined different ruthe-

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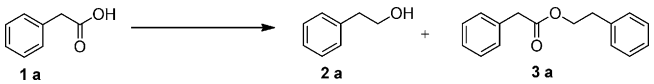
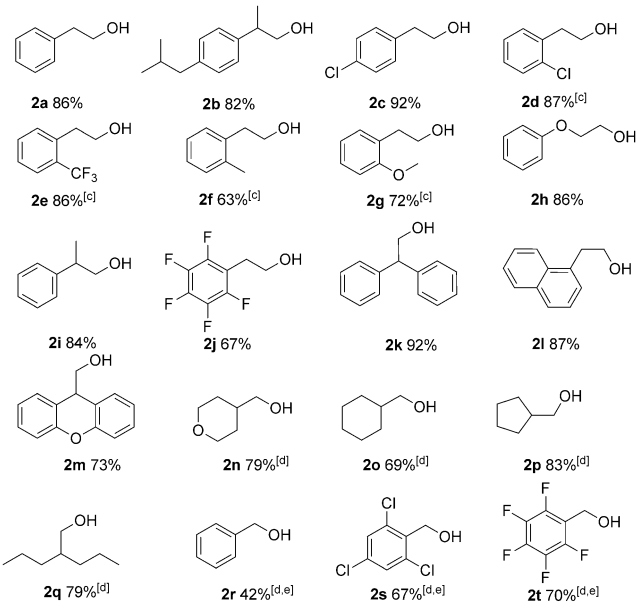
Table 1: Hydrogenation of phenylacetic acid by H_2 in the presence of triphos.[a]



Entry	Catalyst	Additive 1	Additive 2	Yield[b] **2a** [%]	Yield[b] **3a** [%]
1	$Ru(acac)_3$	–	H_2O	4	0
2	$Ru(acac)_3$	$Sn(OTf)_2$	H_2O	0	0[c]
3	$Ru(acac)_3$	$Sn(OTf)_2$	–	0	26
4	$Ru(acac)_3$	Me_2SnCl	H_2O	19	6
5	$Ru(acac)_3$	Me_2SnO	H_2O	7	14
6	$Ru(acac)_3$	Bu_3SnO	H_2O	4	9
7	$Ru(acac)_3$	$Sn(OTf)_2$	H_2O	49	20
8	$[Ru(triphos)(CO)H_2]$	$Sn(OTf)_2$	H_2O	10	10[c]
9	$[Ru(p\text{-cymene})Cl_2]_2$	$Sn(OTf)_2$	H_2O	0	8[c]
10	$Ru[CH_3S(O)CH_3]_4Cl_2$	$Sn(OTf)_2$	H_2O	0	7[c]
11	$Ru(PPh_3)_3Cl_2$	$Sn(OTf)_2$	H_2O	0	11[c]
12	$Ru(acac)_3$	$Sn(OTf)_2$	H_2O	95	2[d]

[a] Reaction conditions: 0.5 mmol substrate, catalyst (4 mol%), ligand (5 mol%), additive 1 (10 mol%), 2 mL toluene, 0.5 mL H_2O, 60 bar H_2, reaction temperature (160°C), 24 h. [b] GC yields. [c] Ligand-free. [d] 48 h.

Table 2: A general catalytic hydrogenation of carboxylic acids.[a,b]



[a] Reaction conditions: 0.5 mmol substrate, $Ru(acac)_3$ (4 mol%), triphos (5 mol%), $Sn(OTf)_2$ (10 mol%), 2 mL toluene, 0.5 mL H_2O, 60 bar H_2, 160°C (reaction temperature), 48 h. [b] Isolated yields. [c] 165°C. [d] GC yields. [e] Reaction conditions: 0.5 mmol substrate, $Ru(acac)_3$ (4 mol%), triphos (5 mol%), $Al(OTf)_3$ (10 mol%), 2 mL toluene, 0.1 mL H_2O, 0.3 mL methanol, 60 bar H_2, 160°C (reaction temperature), 24 h.

nium complexes in the hydrogenation of phenylacetic acid to 2-phenylethan-1-ol under the previously optimized conditions. Among the tested complexes only $[Ru(triphos)(CO)H_2]$ also catalyzed this hydrogenation producing **2a** in 10% yield. This demonstrates the importance of the triphos ligand.

Then, the most active catalyst system, $Ru(acac)_3$/triphos/$Sn(OTf)_2$, was used to examine the scope and limitations of this methodology. As shown in Table 2, the reduction of a broad range of aliphatic and aromatic carboxylic acids proceeded well. In case of phenyl acetic acids, sterically more hindered substrates and electron-donating groups showed slightly lower reactivity (Table 2, **2d**–**2g**). However, increasing the reaction temperature led to good yields, too. Interestingly, perfluorophenyl acetic acid is transformed into the corresponding alcohol in 67% yield (Table 2, **2j**). Diphenylacetic acid and naphthylacetic acid were also successfully converted to the respective alcohols in excellent yields (Table 2, **2k** and **2l**). Moreover, hydrogenations of cyclic aliphatic carboxylic acids proceeded smoothly to the desired alcohols in 69–83% yields (Table 2, **2n**–**2p**). Similarly, 2-propylpentanol is obtained in 79% yield by hydrogenation of 2-propylpentanoic acid (Table 2, **2q**).

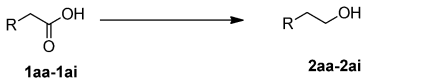
Notably, no catalytic hydrogenation occurred for benzoic acid under the previously optimized conditions. Nevertheless, small amounts of benzyl alcohol is formed using $Al(OTf)_3$ instead of $Sn(OTf)_2$ as the co-catalyst, albeit with dibenzyl ether as the main product. Gratifyingly, hydrogenation of benzoic acid led to benzyl alcohol in 42% yield using 10 mol% $Al(OTf)_3$ in the presence of H_2O and CH_3OH at 160°C (Table 2, **2r**). Furthermore, 2,4,6-trichlorobenzoic acid and 2,3,4,5,6-pentafluorobenzoic acid gave the corresponding alcohols in 70% and 67% yields, respectively, using $Ru(acac)_3$/triphos/$Al(OTf)_3$ (Table 2, **2s** and **2t**).

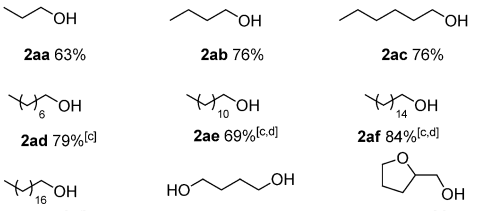
In the context of biorefinery, the selective hydrogenation of carboxylic acids, which are easily obtained by biological or chemical treatment of biomass,[15] is an important process and offers new opportunities.[16] For example, fatty alcohols, which are widely used in the production of surfactants, polymers and solvents, can be easily accessed from the corresponding acids.

Thus, we examined the reactivity of different bio-relevant carboxylic acids (Table 3). Indeed, the novel $Ru(acac)_3$/triphos/$Sn(OTf)_2$ catalyst system showed good activity for the hydrogenation of 9 renewable carboxylic acids to the corresponding alcohols. More specifically, the reduction of low and medium chain aliphatic acids such as propionic, butyric, hexanoic and octanoic generated the desired products in 63–79% yields under the optimized conditions (Table 3, **2aa**–**2ad**). For the longer-chain acids the yields of the products decreased with increasing length of the alkyl chain, which may be caused by the insufficient solubility in toluene. However, dodecan-1-ol, hexadecan-1-ol and octadecan-1-ol are obtained in preparative useful yields (69–84%) by increasing the reaction temperature to 165°C (Table 3, **2ae**–**2ag**). Moreover, the catalytic transformation of succinic acid to the desired diol was realized (Table 3, **2ah**). Finally, tetrahydro-2-furoic acid, which is a useful intermediate and is used for the preparation of several drugs, gave tetrahydrofurfuryl alcohol[17] in 80% yield (Table 3, **2ai**).

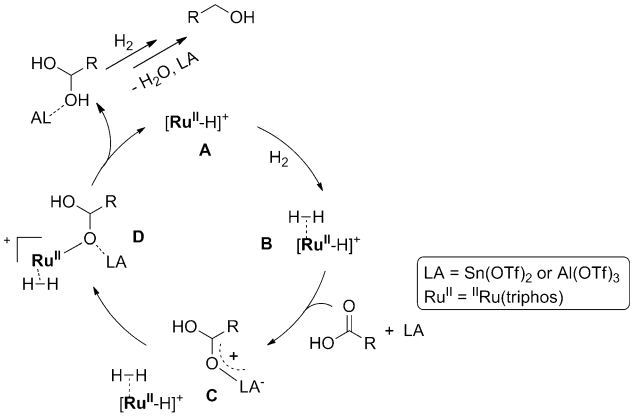
To investigate the reaction mechanism, a time–concentration profile of the model hydrogenation under the

Table 3: The hydrogenation of bio-relevant carboxylic acids.[a,b]





[a] Reaction conditions: 0.5 mmol substrate, $Ru(acac)_3$ (4 mol%), triphos (5 mol%), $Sn(OTf)_2$ (10 mol%), 2 mL toluene, 0.5 mL H_2O, 60 bar H_2, 160°C (reaction temperature), 48 h. [b] GC yields. [c] Isolated yields. [d] 165°C. [e] 24 h.



Scheme 2. Proposed catalytic cycle and mechanistic studies: Comparison of the hydrogenation of phenylacetic acid with possible reaction intermediates.

optimized conditions in the presence of $Ru(acac)_3$/triphos/$Sn(OTf)_2$ was performed. As shown in Figure S1 phenylacetic acid is almost fully converted into the corresponding 2-phenylethan-1-ol within 48 h. It is interesting to note that within the first 10 h only small amounts of the desired alcohol **2a** and the ester **3a** (phenethyl 2-phenylacetate) are detected. Then, the reaction becomes faster and both **2a** and **3a** are increasing. After 20 h, we observe a maximum amount of phenethyl 2-phenylacetate (25%) and subsequently mainly conversion of **3a** to **2a** takes place, most likely by hydrolysis because of the water present.

Moreover, we explored the hydrogenation of phenethyl 2-phenylacetate and phenylacetic acid anhydride, which might be formed as intermediates at higher temperature (Scheme S1). While the reaction of phenylacetic acid gave 2-phenylethan-1-ol **2a** (49% yield) and phenethyl 2-phenylacetate **3a** (20% yield), under similar conditions the ester **3a** reacted sluggishly to give **2a** in lower yield (23%). This result is consistent with the above study of the reaction profile and it implies that the corresponding ester is not involved as a reaction intermediate in the major catalytic cycle. Notably, without any water present only low conversion is observed. This demonstrates clearly that there is a striking difference between the present system and the known ester hydrogenation catalysts.[18] In addition, it confirms that the carboxylic acid is directly activated and not reduced via the ester. Interestingly, using anhydride **4a** as the starting material, which should be more reactive, there is no alcohol **2a** generated. However, small amounts of the ester **3a** are formed (10%). Therefore, the hydrogenation of in situ generated anhydrides can also be excluded as major reaction pathway. It is more likely that in both cases, the ester and anhydride are slowly hydrolyzed to the free acids followed by reduction. In addition, pivalic acid (**1u**) was converted smoothly to the corresponding alcohol (**2u**) in 78% yield. Hence, this result suggested that in situ formation of ketene intermediates is unlikely.

Based on the results obtained above, a preliminary mechanism for the hydrogenation of carboxylic acids to alcohols with molecular hydrogen is proposed in Scheme 2: Firstly, $Ru(acac)_3$ and triphos are converted into the active cationic Ru^{II}-hydride species **A** in the presence of water and/or acid. After activation of the carboxylic acid by coordination to the Lewis acid reduction by **A** constitutes a crucial step in the catalytic cycle. The subsequent hydrogenation forms the hemiacetal intermediate **D** followed by protonation. The desired alcohol product is supposed to be formed according to known reductions of aldehydes and acetals. In case of benzoic acid, which forms benzyl alcohol, the corresponding ether was observed as side product. Due to the slower reduction of the ester compared to the respective carboxylic acid we believe that ester formation and ester hydrogenation do not constitute major reaction pathways in this transformation. This is also supported by the fact that small amounts of water act as a promotor for the desired reduction (see Table 1, entry 3). The formation of the acidic Ru-H species is in agreement with the results suggested for the hydrogenating methylation of amines and the reductive etherification of esters.[13,14] In addition to water, a similar phenomenon can be observed when using *t*BuOH as the proton source (Table S2). Expectedly, the pre-catalyst could also be activated in the presence of methanol resulting in **2a** with 100% conversion and 96% yield. As for the hydrogenation of benzoic acids, methyl esters may be formed firstly and reduced to the corresponding of alcohols subsequently.

In summary, we have developed the first general and efficient direct hydrogenation of carboxylic acids to the desired alcohols in the presence of in situ formed catalyst from $Ru(acac)_3$/triphos/$Sn(OTf)_2$. A series of aromatic alcohols and aliphatic alcohols are obtained successfully from the corresponding carboxylic acids with broad substrate scope by tuning Lewis acids and the ratio of water to methanol. Notably, a crucial proton effect is observed. Based on the in situ analysis of intermediates, a preliminary mechanism was proposed. In view of the importance of this reaction in both organic synthesis and industrial production, we hope this procedure can provide some inspiration for future research on the direct hydrogenation of carboxylic acids to alcohols with H_2.

Keywords: alcohols · carboxylic acids · homogeneous catalysis · hydrogenation · ruthenium

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