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Nickel catalyzed hydrosilane reduction of (het)arenecarboxylic acids into aldehydes

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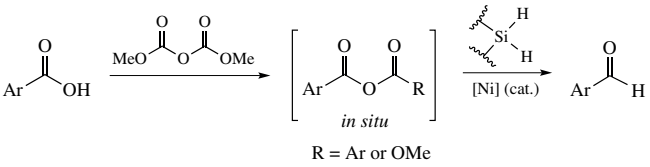
Nickel-catalyzed reduction of (het)arenecarboxylic acids with hydrosilanes in the presence of dimethyl dicarbonate as the activator affords the corresponding aldehydes. The role of the activator is the conversion of the acids into their anhydrides undergoing C–O cleavage. The good yields were achieved in case of substrates bearing electron-donating and electron-neutral groups.



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Aldehydes are most commonly prepared through the oxidation of the corresponding alcohols or selective reduction of carboxylic derivatives. The direct reduction of carboxylic acid derivatives is generally difficult since aldehydes are more easily reduced to alcohols than the starting reactants.[1] In this context, the Rosenmund reduction shows good application while some hydride reagents,[2] catalysts[3–6] as well as synthetic methodologies[7,8] have been developed. Despite these important advances, the reported methods still have some limitations including the limited substrate scope or practicality.[9]

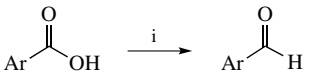
The use of acid derivatives such as their halides, anhydrides, esters, *etc*. instead of the very acids to prepare aldehydes attracted much attention. For example, Yamamoto and co-workers reported the synthesis of aldehydes from carboxylic acids *via* hydrogenation of the *in situ* generated anhydrides under the action of pivalic anhydride.[10,11] Gooßen and co-workers employed hydrophosphite salts as the reductants to achieve the similar process.[12] Later, Tsuji and co-workers developed a Pd-catalyzed reduction of carboxylic acids to aldehydes with hydrosilanes in the presence of pivalic anhydride.[13] Inspired by the success of Ni catalysis in cross-coupling reactions,[14–24] just recently, Bergman and co-workers reported a nickel-catalyzed selective reduction of carboxylic acids to aldehydes.[25] However, limited arenecarboxylic acid substrates were reported for their process. Inspired by the above contributions, herein we report an efficient protocol for the selective reduction of arenecarboxylic acids to aldehydes in detail.

Initially, we started to optimize the reaction conditions by employing those similar to other published Ni-hydrosilane reductive methods (Table 1; Tables S1 and S2 in Online Supplementary Materials) using benzoic acid **1a** as the substrate.[25–27] Briefly, reduction of benzoic acid **1a** in the presence of $Ni(COD)_2$, 4,4′-di-*tert*-butyl-2,2′-bipyridine (dtbbpy), zinc, dimethyl dicarbonate (DMDC), phenylsilane and 2,6-lutidine in ethyl acetate provided the desired benzaldehyde **2a** in 12% yield (Table 1, entry 1). Other nickel sources such as $NiCl_2$(dme) or $NiBr_2 \cdot 3H_2O$ provided better yields of product **2a** as 39 and 45%, respectively (entries 2 and 3). Switching the ligand to 2,2′-bipyridyl (bpy) or 1,10-phenanthroline (phen) led to lower yields (entries 4 and 5). The use of other organic or inorganic bases instead of 2,6-lutidine provided **2a** in lower yields (entries 6–8 as well as Table S1, entries 14–18). Lowering the catalyst loading to 5% still gave **2a** in 38% yield which was increased to 51% with 20% loading of the catalyst (see Table 1, entry 3, footnotes *c*, *d*). While screening hydrosilanes and their amount (entries 9, 10), we found the use of 2.25 equiv. Ph_2SiH_2 to be superior providing 77% yield of benzaldehyde **2a**. Variation of some other parameters (solvent, temperature, activator and reducing metal nature, see Online Supplementary Materials, Table S2) did not lead to improvement of the reaction outcome.

Table 1 Optimization of the reaction conditions for reduction of benzoic acid **1a** into bezaldehyde **2a**.[a]

Entry	[Ni] source	Ligand	Hydrosilane	Base	Yield (%)[b]
1	$Ni(COD)_2$	dtbbpy	$PhSiH_3$	2,6-lutidine	12
2	$NiCl_2$(dme)	dtbbpy	$PhSiH_3$	2,6-lutidine	39
3	$NiBr_2 \cdot 3H_2O$	dtbbpy	$PhSiH_3$	2,6-lutidine	45, 38,[c] 51[d]
4	$NiBr_2 \cdot 3H_2O$	bpy	$PhSiH_3$	2,6-lutidine	20
5	$NiBr_2 \cdot 3H_2O$	phen	$PhSiH_3$	2,6-lutidine	14
6	$NiBr_2 \cdot 3H_2O$	dtbbpy	$PhSiH_3$	2,4,6-collidine	31
7	$NiBr_2 \cdot 3H_2O$	dtbbpy	$PhSiH_3$	DBU	11
8	$NiBr_2 \cdot 3H_2O$	dtbbpy	$PhSiH_3$	DIPEA	24
9	$NiBr_2 \cdot 3H_2O$	dtbbpy	Ph_2SiH_2	2,6-lutidine	65,[d] 69,[d,e] 77,[d,f] 75[d,g]
10	$NiBr_2 \cdot 3H_2O$	dtbbpy	$MePhSiH_2$	2,6-lutidine	52[d]

[a] Reaction conditions: **1a** (0.2 mmol), [Ni] (10 mol%), ligand (20 mol%), Zn (20 mol%), hydrosilane (1.5 equiv.), DMDC (2 equiv.), base (1.2 equiv.), EtOAc (4 ml), 60 °C, 24 h. [b] GC yield using *n*-dodecane as the internal standard. [c] 5 mol% catalyst. [d] 20 mol% catalyst. [e] 2.0 equiv. Ph_2SiH_2. [f] 2.25 equiv. Ph_2SiH_2. [g] 2.5 equiv. Ph_2SiH_2. For more optimization experiments (*e.g.*, solvent, temperature and reagent variation), see Online Supplementary Materials, Tables S1 and S2.

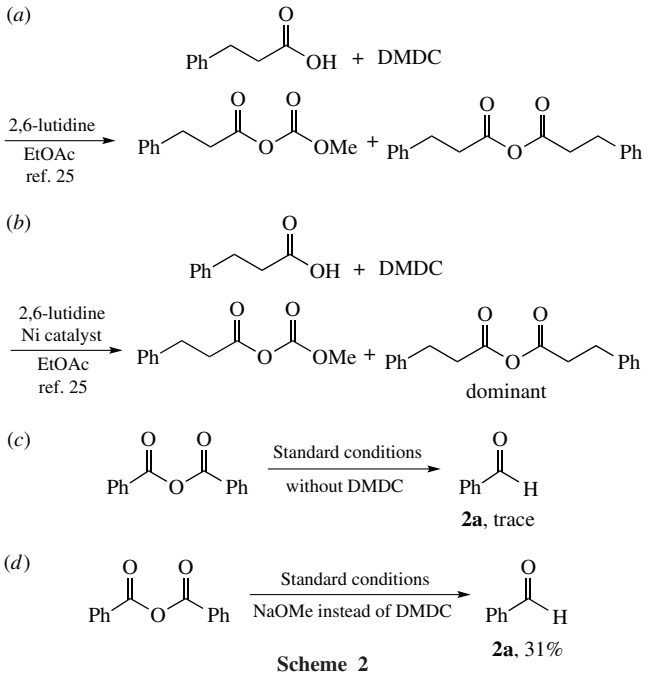


1a–p **2a–p**

a Ar = Ph, 77%
b Ar = 4-MeC_6H_4, 78%
c Ar = 4-EtC_6H_4, 76%
d Ar = 4-$MeOC_6H_4$, 80%
e Ar = 4-$Bu^tC_6H_4$, 74%
f Ar = 4-$Me_2NC_6H_4$, 81%
g Ar = 4-$MeSC_6H_4$, 72%
h Ar = 2-$MeOC_6H_4$, 75%
i Ar = 2-MeC_6H_4, 74%
j Ar = 3-MeC_6H_4, 75%
k Ar = 3,4-$(MeO)_2C_6H_3$, 79%
l Ar = 2-naphthyl, 71%
m Ar = 4-$MeO_2CC_6H_4$, 42%
n Ar = 1-methylindol-3-yl, 54%
o Ar = 2-furyl, 39%
p 'Ar' = PhCH=CH, 31%

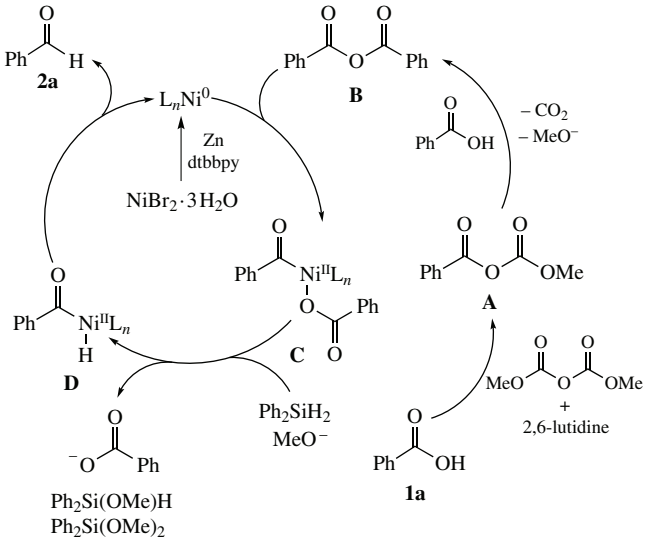
Scheme 1 *Reagents and optimized conditions*: i, **1** (0.2 mmol), $NiBr_2 \cdot 3H_2O$ (20 mol%), dtbbpy (20 mol%), Zn (20 mol%), Ph_2SiH_2 (2.25 equiv.), $(MeO)_2C_2O_3$ (2 equiv.), 2,6-lutidine (1.2 equiv.), EtOAc (4 ml), 60 °C, 24 h, GC yields. For Ar = 4-$F_3CC_6H_4$, 4-$O_2NC_6H_4$ and 3-pyridyl, trace yields; for Ar = 4-BrC_6H_4, product mixture was formed.

A series of aromatic acids **1a–p** were then tested under the optimized reaction conditions (Scheme 1).† In general, most of the reactions proceeded smoothly to afford the corresponding aldehydes **2a–p** in moderate to good yields. Aromatic acids bearing electron-donating and electron-neutral groups such as alkyl, methoxy, dimethylamino and methylthio were found to be good substrates. However, reduction of benzoic acids bearing strong electron-withdrawing groups gave trace amounts of the desired products. Similarly, electron-deficient monomethyl terephthalate **1m** afforded product **2m** in 42% yield. It was also worth noting that the reduction of 4-bromobenzoic acid was not selective to produce a mixture of 4-bromobenzaldehyde, benzoic



Scheme 2

† *General procedure for the synthesis of aldehydes* **2**. In an oven-dried 10 ml vial, $NiBr_2 \cdot 3H_2O$ (11 mg, 0.04 mmol) was stirred vigorously with ligand dtbbpy (11 mg, 0.04 mmol) in a dry solvent (4 ml) for 10 min. Then acid **1** (0.2 mmol) and Zn (3 mg, 0.04 mmol) were added to a 10 ml Schlenk flask with a magnetic stir bar. The flask was evacuated and backfilled with nitrogen three times. To this the solution of the Ni/ligand prepared above, 2,6-lutidine (0.24 mmol) and DMDC (0.4 mmol) were added. Then, Ph_2SiH_2 (0.45 mmol) was added *via* microsyringe, and the reaction mixture was stirred at 60 °C for 24 h. After cooling to room temperature, the mixture was diluted with diethyl ether (5.0 ml) and *n*-dodecane as an internal standard was added. The yield of product **2** was analyzed by gas chromatography using *n*-dodecane as the internal standard.



Scheme 3

acid and benzaldehyde. Reduction of 2-naphthoic acid **1l** also proceeded well, giving 2-naphthaldehyde **2l** in 71% yield. Heterocyclic aromatic acids such as 1-methyl-1*H*-indole-3-carboxylic acid **1n** and furan-2-carboxylic acid **1o** gave the corresponding products **2n**,**o** in relatively moderate yields (54 and 39%, respectively). Finally, cinnamic acid **1p** was converted into cinnamaldehyde **2p** in 31% yield.

Some control experiments were performed to gain insight into the mechanism. Bergman and co-workers previously showed that both mixed and symmetrical anhydrides were generated during the reaction in the presence of the base and the Ni catalyst.[25] Importantly, formation of symmetrical anhydride is more prevalent than mixed anhydride in the presence of Ni catalyst (Scheme 2, experiments *a* and *b*). These results suggested that the anhydride may be the active intermediate in this reaction. Next, the benzoic anhydride was tested as the substrate under the standard reaction conditions in the absence of DMDC. However, only trace amounts of the desired product **2a** were formed (see Scheme 2, experiment *c*). When 1 equiv. of NaOMe was added to mimic our catalytic conditions, aldehyde **2a** was obtained in 31% yield (experiment *d*). These results indicate that methoxide anion (MeO^-) is indispensable for this transformation.

A mechanism outlined in Scheme 3 is proposed based on the control experiments and the literature data. Initially, benzoic acid **1a** reacts with DMDC in the presence of 2,6-lutidine to generate non-symmetrical anhydride **A**, which reacts with another molecule of **1a** in the presence of Ni catalyst to give symmetrical anhydride **B**.[25] Then, compound **B** undergoes oxidative addition to a Ni^0 species,[28] which are formed *in situ* by the reduction of Ni^{II} with Zn, to deliver the intermediate **C**. Under the assistance of methoxide, transmetalation with diphenylsilane occurs and hydrometallide intermediate **D** is generated.[29] Finally, reductive elimination within **D** provides product **2a** and the Ni^0 species are regenerated.[30]

In summary, we have accomplished a Ni-catalyzed selective reduction of (het)arenecarboxylic acids to aldehydes in the presence of hydrosilane and DMDC as the activator. Aromatic carboxylic acids containing electron-donating and electron-neutral groups showed good reactivities. Some heterocyclic aromatic acids were also successfully converted to the corresponding aldehydes albeit with moderate reactivities. This procedure provided a direct way for the selective reduction of (het)arenecarboxylic acids.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.03.043.

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