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A Strategy for Accessing Aldehydes *via* Palladium-Catalyzed C-O/C-N Bond Cleavage in the Presence of Hydrosilanes

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Abstract. We report the catalytic reduction of both active esters and amides by selective C(acyl)–X (X = O, N) cleavage to access aldehyde functionality *via* a palladium-catalyzed strategy. Reactions are promoted by hydrosilanes as reducing reagents with good to excellent yields and with excellent chemoselectivity for C(acyl)–N and C(acyl)–O bond cleavage. Carboxylic acid C(acyl)–O bonds are activated by 2-chloro-4,6-dimethoxy-1,3,5-triazine (CDMT) to form triazine ester intermediates, which further react with hydrosilanes to yield aldehydes in one-pot two-step procedures. We demonstrate that C(acyl)–O cleavage/formylation offers higher yields and broader substrate scopes compared with C(acyl)–N cleavage under the same reaction conditions.

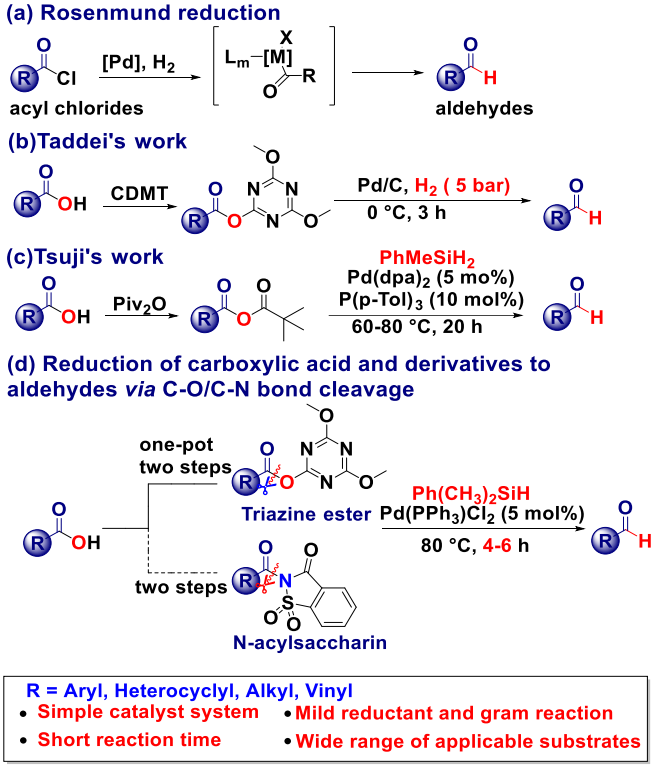
Keywords: C-O/C-N bond cleavage; Hydrosilanes; Palladium-catalyzed; Reduction; Aldehydes;

Aldehydes play an important role in constructing different kinds of organic molecules, and they have a wide range of applications in pharmaceuticals, agrochemicals, and perfumes as vital intermediates[1]. A simple and efficient approach to aldehydes preparations remains a challenge in organic chemistry[2], and the classic methods used to prepare aldehydes mainly include the oxidation of primary alcohols or the reduction of carboxylic acids and their derivatives[3]. The Oxidation of primary alcohols requires careful handling to avoid overoxidation and the creation of carboxylic acid byproducts. In the case of carboxylic acid derivatives, there are two possible reduction products: an aldehyde and an alcohol. Carboxylic acids or their derivatives can be reduced in a variety of ways, and aluminum-H, boron-H, and H_2 are the most powerful reductants[4]. Compared with hydrosilanes, these traditional reagents are flammable and unstable due to their pyrophoric nature[5]. Furthermore, the process produces aldehydes in moderate yields with the isolation of the corresponding alcohols as overreduction byproducts. To obtain aldehydes efficiently, carboxylic acids are first converted into highly reactive derivatives such as acyl chlorides[6], then further converted to aldehydes with high chemoselectivity. Rosenmund reduction has been the general method for the transformation of acyl chlorides into aldehydes (**Scheme 1a**)[7].

In recent decades, transition-metal-catalyzed reactions have engendered a central transformation in organic synthesis[8]. Recently, tremendous progress has been made on the selective C-O/C-N bond cleavage of active esters/amides. The Garg[9], Szostak[10], Rueping[11], Yamaguchi[12], Shi[13], Huang[14] and Zou[15] groups have reported many works in this field, providing a powerful strategy to obtain target molecules in organic synthesis. These activated esters/ amides can be converted from carboxylic acids directly and used in transition-metal-catalysis, which indicates that they can provide a new protocol for the synthesis of aldehydes.

To the best of our knowledge, the one-pot conversion process of carboxylic acids to aldehydes has been well developed. In 1998, the Yamamoto group[16] first reported a catalytically hydrogenated approach to obtain aldehydes from carboxylic acids in the presence of Piv_2O. They carried out the reduction under 30 bar of flammable hydrogen. Later, Professor Gooßen[17] modified the catalyst system to conduct a reaction under 5 bar of hydrogen. In 1999, the Taddei group[18] first reduced triazine esters to aldehydes from carboxylic acids in the presence of 5 bar of hydrogen, but an overreduced alcohol byproduct was obtained (**Scheme 1b**). In 2013, the Tsuji group

developed a palladium-catalyzed reduction of carboxylic acids to corresponding aldehydes in the presence of hydrosilanes (**Scheme 1c**)[19]. These exceptional works provided a straightforward approach for the efficient synthesis of aldehydes from carboxylic acids. Despite the significant progress that has been achieved in the reduction of carboxylic acids, limits remain, such as the production of overreduced alcohol, longer reaction times, and the presence of explosively flammable hydrogen.



Scheme 1. Reduction of carboxylic acids and derivatives

Our group has a continuing interest in C-O/C-N bond cleavage by metal catalysis[20], as carboxylic acids/amides can now be used in several important transformations, including Suzuki-Miyaura couplings, C–H functionalization, and transamidation. Here, we hypothesize that triazine ester or *N*-acylsaccharins can be utilized in the synthesis of aldehydes by highly chemoselective C(acyl)–X (X=O, N) cleavage. (**Scheme 1d**). The characteristics of our study include: (a) proof of a general and facilitating path for the formylation of carboxylic acids; (b) a simple catalytic system for the direct reduction of a wide range of carboxylic acids *via* C(acyl)–X (X=O, N) cleavage; and (c) utilization of a mild reductant instead of flammable hydrogen to avoid overreduced alcohol and provide a gram-scale reaction in the laboratory.

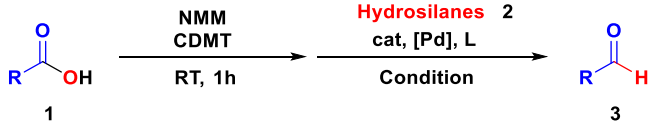
Triazine esters were synthesized efficiently from carboxylic acids in high yield, and then further transformed to aryl ketones through a one-pot two-step procedure in our previous report. We anticipate the use of this one-pot procedure to investigate the reduction of carboxylic acids to aldehydes by C-O bond cleavage. The proposed C-O/formylation was first surveyed in a model reaction between benzoic acid and hydrosilanes. The catalysts, ligands, solvents, temperature, and hydrosilanes, were systematically screened in this reaction, and their data are summarized in **Table 1**. Initially, we attempted to achieve this transformation in the presence of a 5 mol% $Pd(PPh_3)_4$ catalyst, resulting in corresponding aldehydes in 78% yield (**Table 1**, Entry 1). After several experiments in different catalyst systems (**Table 1**, Entries 2-9), we found that the ligand is essential and influences the yield; PPh_3 was found to be the most efficient ligand, whereas tri(cyclohexyl)phosphine (PCy_3), 1,4-bis(diphenylphosphino)butane (dppb), 1,1'-bis(diphenylphosphino)ferrocene (dppf), 2-(dicyclohexylphosphino)-3,6-dimethoxy-2'-4'-6'-tri-i-propyl-1,1'-biphenyl (Brettphos), and 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos) delivered the product in low yields. With this condition in hand, we selected the $Pd(PPh_3)_2Cl_2$ as the catalyst system.

Furthermore, the solvents were also screened with toluene being the best choice (**Table 1**, Entries 10-13). Based on the above conditions, the reaction temperature was further optimized. Surprisingly, the target compound could be obtained in good yield at 80 °C (**Table 1**, Entries 14-15).

In addition, decreasing the amount of $Pd(PPh_3)_2Cl_2$ resulted in a significant decrease in yield while increasing the catalyst loading from 3 mol% to 8 mol% did not obviously affect the yield. (**Table 1**, Entries 16-18). Finally, we compared various hydrosilanes and found that $Ph(CH_3)_2SiH$ gave the best result (**Table 1**, Entries 18-21).

Based on these experiments, the optimized reaction conditions were set as 5 mol% $Pd(PPh_3)_2Cl_2$, $Ph(CH_3)_2SiH$ (1.5 equiv) in toluene at 80 °C for 6 h.

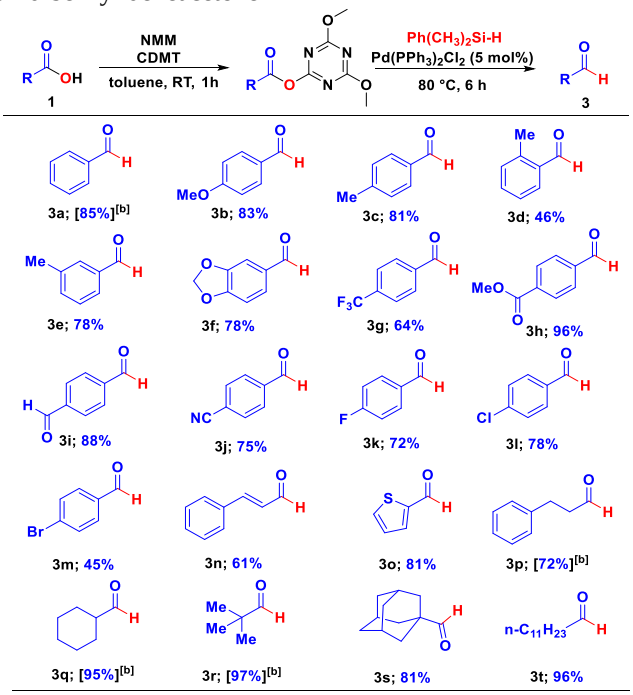
Table 1. Optimization studies for the reduction of carboxylic acids[a]



Entry	Catalyst(mol%)	Ligand	Solvent	Yield[b]
1	$Pd(PPh_3)_4$ (5)	none	toluene	78
2	$Pd_2(dba)_3$ (5)	none	toluene	<5
3	$PdCl_2$ (5)	none	toluene	<5
4	$PdCl_2$ (5)	PCy_3	toluene	50

5	$PdCl_2$ (5)	dppb	toluene	<5
6	$PdCl_2$ (5)	dppf	toluene	<5
7	$PdCl_2$ (5)	brettphos	toluene	62
8	$PdCl_2$ (5)	Xantphos	toluene	29
9	$Pd(PPh_3)_2Cl_2$ (5)	none	toluene	85
10	$Pd(PPh_3)_2Cl_2$ (5)	none	DMSO	27
11	$Pd(PPh_3)_2Cl_2$ (5)	none	DMF	30
12	$Pd(PPh_3)_2Cl_2$ (5)	none	dioxane	71
13	$Pd(PPh_3)_2Cl_2$ (5)	none	CH_3CN	75
14[c]	$Pd(PPh_3)_2Cl_2$ (5)	none	toluene	56
15[d]	$Pd(PPh_3)_2Cl_2$ (5)	none	toluene	78
16	$Pd(PPh_3)_2Cl_2$ (3)	none	toluene	81
17	$Pd(PPh_3)_2Cl_2$ (8)	none	toluene	85
18[e]	$Pd(PPh_3)_2Cl_2$ (5)	none	toluene	37
19[f]	$Pd(PPh_3)_2Cl_2$ (5)	none	toluene	<5
20[g]	$Pd(PPh_3)_2Cl_2$ (5)	none	toluene	<5
21[h]	$Pd(PPh_3)_2Cl_2$ (5)	none	toluene	<5

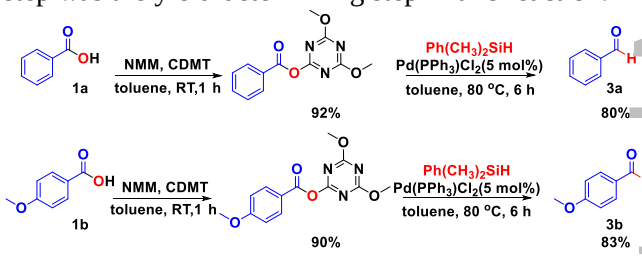
[a]Reactions were conducted on 0.3 mmol **1a** and 1 mL solvent at 80 °C using 0.45 mmol of hydrosilane in the presence of 5 mol% catalysis, for 6 h.
[b]Yield was determined by using GC.
[c]At 70 °C. [d]At 90 °C.
[e]Using 0.45 mmol Et_3SiH as the reductant.
[f]Using 0.45 mmol Ph_2CH_3SiH as the reductant.
[g]Using 0.45 mmol Ph_3SiH as the reductant.
[h]Using 0.45 mmol Ph_2SiH_2 as the reductant.
NMM= 4-Methylmorpholine.
dba= dibenzylideneacetone



[a]Reactions were conducted on 0.3 mmol **1** and 1 mL toluene at 80 °C using 0.45 mmol of $Ph(CH_3)_2SiH$ in the presence of 5 mol% of $Pd(PPh_3)_2Cl_2$, for 6 h.
[b]GC yield was given because a product with a low boiling point was considerably lost during the isolation process.
Scheme 2. Scope of carboxylic acids in the one-pot synthesis of aldehydes[a]

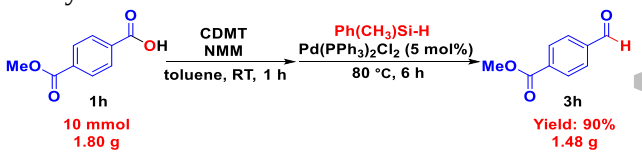
Under optimized reaction conditions, we explored the functional-group tolerance of carboxylic acids in the case of 5 mol% $Pd(PPh_3)_2Cl_2$ and $Ph(CH_3)_2SiH$ (1.5 equiv) in toluene at 80 °C for 6 h (**Scheme 2**). Benzoic acid **1a** was employed as a substrate and resulted in the highest yield (**3a**, 85%). To investigate electronic factors, $Ph(CH_3)_2SiH$ (**2a**) was used as a reducing reagent. Several carboxylic acids with electron-donating groups in *para*-positions reacted with **2a** to provide corresponding aldehydes in good yields (**3b-3f**). Electron-withdrawing substrates containing trifluoromethyl, aldehyde, ester, and cyano groups were well tolerated in this protocol and provided the desired products in 64%, 96%, 88%, and 75% yields respectively (**3g-3j**). In addition, steric hindrance on the carboxylic acid (**3d**) was also tolerated. The halide substituents F (**1k**), Cl (**1l**), and Br (**1m**) were tolerated in this reaction and afforded the desired products in medium yield. In addition, alkenyl (**1n**) and heteroaromatic acid (**1o**) demonstrated good reactivity and provided the corresponding products in 81% and 61% yields (**3n, 3o**). Other carboxylic acids including primary/secondary/tertiary alkyl acids (**1p-1t**) were all well tolerated and obtained excellent yields.

To explore the yield-determining step, the phenyl and *p*-methoxyphenyl triazine esters were isolated and purified. These triazine esters were reacted with hydrosilanes directly (**Scheme 3**). Considering the yield of aldehydes, the subsequent silane reduction step was the yield-determining step in this reaction.



Scheme 3. Investigation of yield-determining step

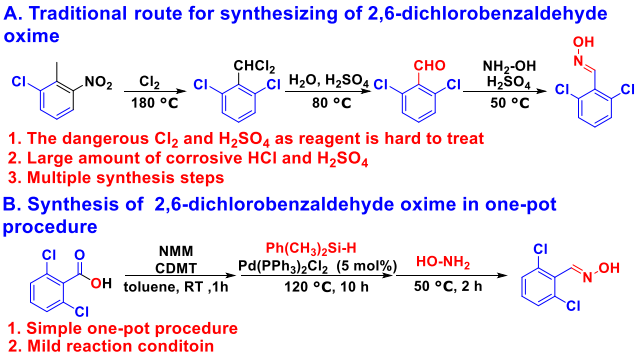
Fortunately, the present reaction is amenable to being scaled-up to a gram-scale using methyl 4-formylbenzoate and $Ph(CH_3)_2SiH$ as substrates, and 90% yield was achieved.



[a]Gram scale reaction (in 10 mmol), see the SI for details.
Scheme 4. Scale-up of the one-pot reaction[a]

To demonstrate the availability of this mild reduction method, we accomplished the synthesis of 2,6-dichlorobenzaldehyde oxime, an important pharmaceutical intermediate for the manufacture of diclofenac sodium and dichlobenil[21]. The traditional starting from 1-chloro-2-methyl-3-nitrobenzene

involves chlorination, hydrolysis, and deuteration[22]. Our method utilizes carboxylic acids as the starting material to obtain the target molecule with a one-pot procedure in 46% yield. This example emphasizes the potential synthetic utility of the method and this green and convenient method is suitable for industrial applications.



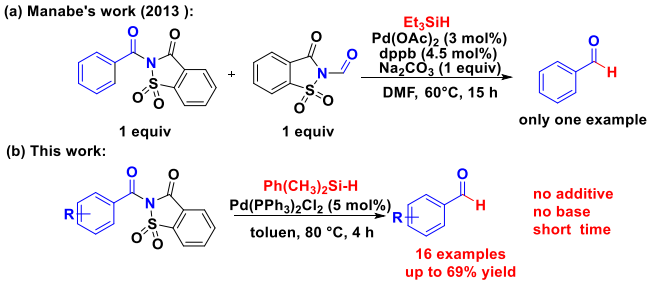
Scheme 5. Synthesis of 2,6-dichlorobenzaldehyde oxime

A step-wise reaction was then investigated by adding all components at one time. 4-(methoxycarbonyl)benzoic acid, as a representative example, was reacted with CDMT, NMM, $Ph(CH_3)_2SiH$ in the presence of Pd catalyst at 80 °C for 7 h in one-pot. The corresponding aldehydes were obtained in 89% yield (**Scheme 6**).

Scheme 6. One-pot procedure for synthesis of methyl 4-formylbenzoate

We then turned our attention to the reduction of the active amide. The electronic-destabilization of the N-C(O) bond in active amide enables a synthetically appealing catalytic reduction by C-N acyl cleavage[23]. In 2013, Manabe's group[24] reported the palladium-catalyzed reduction of *N*-benzoylsaccharin with Et_3SiH *via* Pd/dppb catalyzed in the presence of Na_2CO_3 (1 equiv) in DMF at 60 °C for 15 h to give benzaldehyde in 64% yield (**Scheme 7a**). It is regrettable that they only elucidated the mechanism by this reaction and only one example was reported.

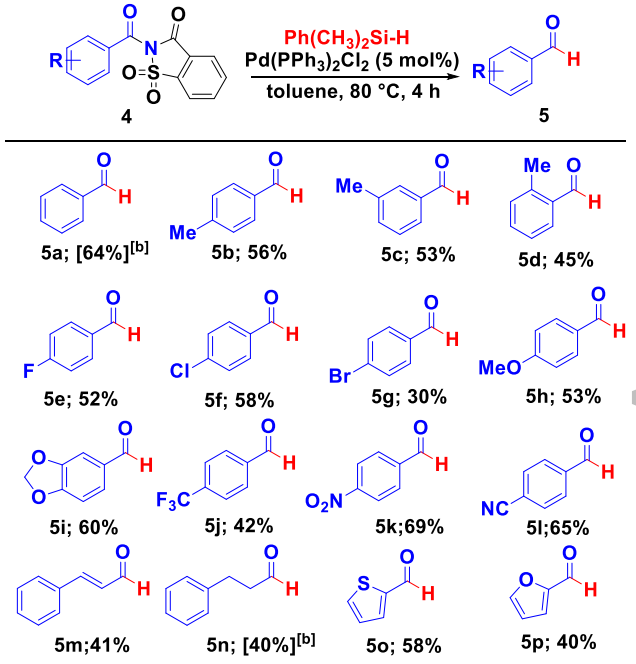
Inspired by Manabe's work, we considered that the easily prepared and stable *N*-acylsaccharins[25] can be harnessed as electrophile coupling partners with hydrosilanes in palladium-catalyzed reduction reactions (**Scheme 7b**).



Scheme 7. The reduction of *N*-acylsaccharins

Next, we optimized the reaction conditions. After several experiments for extensive optimization (see SI for optimization details), we identified conditions to achieve the reduction of *N*-acylsaccharins. The aldehyde products were obtained in the highest yield with 5 mol% $Pd(PPh_3)Cl_2$ catalyst, $Ph(CH_3)_2SiH$ (1.5 equiv) in toluene at 80 °C for 4 h. Other Pd(**II**) precatalysts, ligands, solvents, and hydrosilanes were screened (see SI) and provided aldehydes in lower yields. As shown in the SI, $Ph(CH_3)_2SiH$ obtains a better yield than other hydrosilanes. Additionally, the reaction using toluene as a solvent had a higher yield than THF, CH_3CN, DMF, and DMSO.

The high reactivity of the developed reaction system was emphasized in this transformation, as electron-neutral (**5a, 5b, 5c, 5d, 5e, 5f, 5g**), electron-rich (**5h** and **5i**) and electron-deficient (**5j, 5k, 5l**) substrates were all tolerated (**Scheme 8**). In an effort to synthesize alkenyl, heteroaryl, and alkyl substituents (**5m, 5n, 5o, 5p**), the target molecules were obtained in 40-58% yield. *N*-acylsaccharins will be developed as new intermediate reducing carboxylic acids to generate a variety of aldehydes.

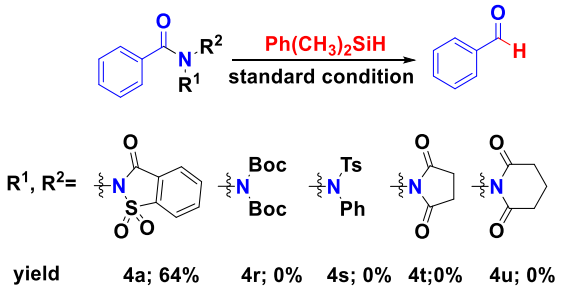


[a] Reactions were conducted on a 0.3 mmol **4** and 1 mL toluene at 80 °C using 0.45 mmol of $Ph(CH_3)_2SiH$ in the presence of 5 mol% of $Pd(PPh_3)_2Cl_2$, for 4 h.

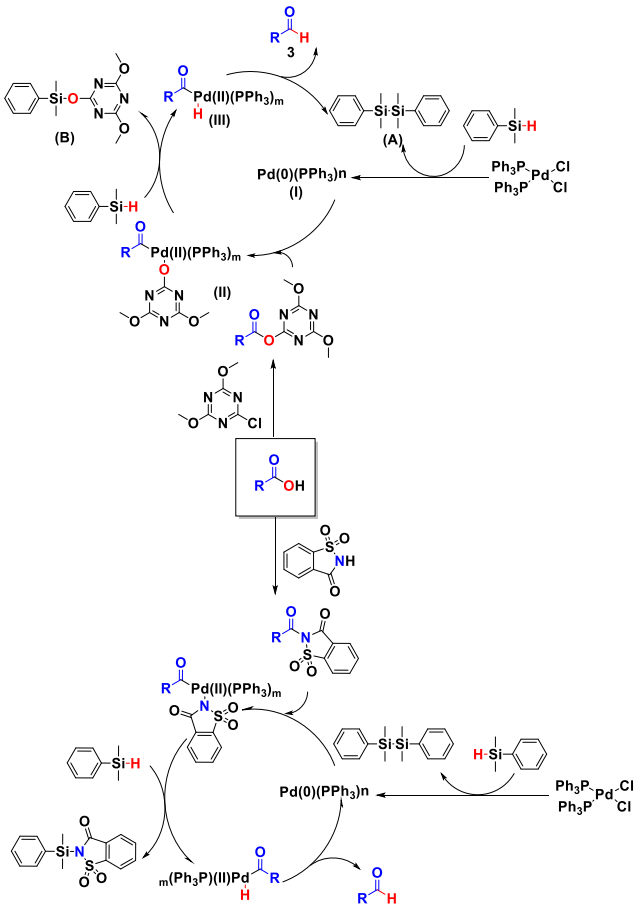
[b] GC yield was given because a product with a low boiling point was considerably lost during the isolation process.

Scheme 8. Scope of aldehydes in the reduction of *N*-acylsaccharins[a]

Furthermore, comparative experiments were carried out under the optimized reduction condition for a range of electronically and sterically different amides were carried out (**Scheme 9**). *N*-Boc (**4r**) and *N*-Ts (**4s**) were not suitable for this protocol. The reduction of twisted cyclic imides (**4t** and **4u**) was completely unreactive. The experimental data shows the unique activity of *N*-acylsaccharins (**4a**) in this transformation. An electron-withdrawing sulfonyl moiety and distortion of the amide bond might result in ground-state destabilization of *N*-acylsaccharins, which could explain its high reactivity in this reaction[20d, 26].



Scheme 9. Control reaction



Scheme 10. A plausible mechanism for the catalyst reaction

A plausible mechanism for the catalytic reaction is shown in **Scheme 10**. First, we employ active esters as a model to discuss the mechanism. Carboxylic acids and CDMT provide triazine esters. As shown in the scheme, Pd(**II**) is reduced to Pd(**0**), and intermediate **A** was detected by ^{1}H NMR. Then, the oxidative addition takes place at the C-O bond of the triazine ester to afford an acylpalladium (**II**) complex. Following transmetallation, complex (**III**) is generated under the reaction of hydrosilanes. Intermediate **B** was detected by ^{29}Si NMR measurements of the resulting reaction mixture (δ=1.13 ppm, without ^{1}H decoupling, s) Then, reductive elimination occurred to form aldehydes and regenerate the Pd(**0**) species. Next, the reduction of *N*-acylsaccharins to aldehydes proceeds through a similar mechanism as triazine ester.

In summary, we have developed a palladium-catalyzed approach for the reduction of triazine esters/*N*-acylsaccharins to aldehydes *via* C-O/C-N bond cleavage. This new approach offers an easy method and practical routine for the synthesis of aldehydes in the laboratory to avoid explosively flammable hydrogen as an H-source. Remarkably, the transformation was achieved under a simple catalyst system and a short reaction time. The high functional group tolerance allows the production of a variety of aldehydes in moderate to good yields. Notably primary, secondary, and tertiary alkyl carboxylic acids were also well tolerated. Overall, this reaction performed well at the gram scale, which indicates its potential applicability in batch processes.

Experimental Section

General Procedure for the synthesis of aldehydes by C-O bond cleavage

A sealed tube equipped with a stir bar was charged with 2-chloro-4,6-dimethoxy-1,3,5-triazine (CDMT) (0.3 mmol), carboxylic acids (0.3 mmol), and 4-methylmorpholine (0.3 mmol) stirring in toluene (1 mL) at room temperature for 1 h. After reaction completion monitored by TLC, the flask was charged with $Pd(PPh_3)_2Cl_2$ (5 mol%) and $Ph(CH_3)_2SiH$ (0.45 mmol). The mixture was stirred and heated at 80 °C for 6 h. After cooling to room temperature, the mixture was purified by silica gel column chromatography (petroleum ether or hexane/EtOAc = 50:1 or 20:1) to afford aldehydes and calculate the yields. Because some aldehydes have low boiling points, their reaction mixture was analyzed by GC directly and the yield was determined using cyclohexane, decane or dodecane as an internal standard.

General Procedure for the synthesis of aldehydes by C-N bond cleavage

A sealed tube equipped with a stir bar was charged with $Ph(CH_3)_2SiH$ (0.45 mmol), *N*-acylsaccharins (0.3 mmol., $Pd(PPh_3)_2Cl_2$ (5 mol%) and toluene (1 mL). The reaction mixture was placed in an oil bath and stirred for 4 h at 80 °C. After cooling to room temperature, the mixture was purified by silica gel column chromatography (petroleum ether or hexane/EtOAc = 50:1 or 20:1) to afford aldehydes and calculate the yields. Because some aldehydes have low boiling points, their reaction mixture was analyzed by GC directly and the yield was determined using cyclohexane, decane or dodecane as an internal standard.

Acknowledgments

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