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# Nickel-Catalyzed Reductive Defunctionalization of Esters in the absence of an External Reductant: Activation of C-O Bonds

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The nickel-catalyzed reductive cleavage of esters in the absence of an external reductant, which involves the cleavage of an inert acyl C-O bond in O-alkyl esters is reported. Various groups, such as Ncontaining heterocycles, esters, amides, and even arene rings can function as a directing group.

Organic synthesis involves the breaking of an existing bond and the formation of a new one to convert simple, small compounds into complex and large targeted molecules by C-C bond and C-heteroatom bond formation.<sup>1</sup> Thus, C-C bond and C-heteroatom bond formation has long been a subject of interest in the field of organic synthesis. In sharp contrast, much less attention has been given to the defunctionalization of organic molecules, except for the decarbonylation of aldehydes, a reaction that is widely used in the synthesis of natural products.<sup>2</sup> In recent years, defunctionalization reactions have attracted more attention since they are related to the preparation of useful compounds from readily available and sustainable organic resources, such as biomass and naturally occurring carboxylic acids.<sup>3</sup> A key challenge in defunctionalization reactions involves the activation of relatively strong and unreactive chemical bonds, such as C-C,<sup>4</sup> C-O,  $^{\rm 5}$  and C-N bonds.  $^{\rm 6}$  Reductive defunctionalization is an example of such a reaction. The majority of reductive defunctionalization reactions reported thus far have involved the use of an external hydrogen source, such as H<sub>2</sub> or a hydrosilane. For example, the defunctionalization of anisole derivatives, which is recognized as a model reaction in the degradation of lignin, leading to the formation of arenes was achieved using H<sub>2</sub> and hydrosilane as reducing agents.<sup>7</sup> The reductive defunctionalization of aniline derivative,<sup>8</sup> ketones,<sup>9</sup> acid fluorides,<sup>10</sup> thioethers,<sup>11</sup> amides,<sup>12</sup> CN,<sup>13</sup> and nitro<sup>14</sup> derivatives have also been studied. In most cases, a hydrogen source is required for the success of such reactions.

Cross-coupling reactions of esters involving the cleavage of C-O bonds have been extensively studied.<sup>5i-1</sup> However, aryl esters (-C(O)-OAr) were generally used as the starting ester because an aryloxy group is a good leaving group, compared with an alkoxy group in O-alkyl esters (-C(O)-OR). Nevertheless, there are only two examples of the reductive removal of ester groups (Figure 1). The first report, which was reported by our group, involved the ruthenium-catalyzed reductive cleavage of O-pyridylmethyl esters using ammonium formate as a hydride source.<sup>15</sup> Rueping recently reported on the removal of ester groups from O-phenyl esters with hydrosilanes in the presence of a nickel catalyst.<sup>12b</sup> However, in these studies, the addition of an external reducing agent was required for achieving a successful reaction. Herein, we wish to report on the nickelcatalyzed reductive cleavage of esters in the absence of an external reductant. The reaction involves the cleavage of an inert acyl C-O bond in an O-alkyl ester.<sup>16</sup> The presence of a N(sp<sup>2</sup>)- or O(sp<sup>2</sup>)-directing group accelerates the reaction. It is noteworthy that an arene ring also can be employed as a directing group.17





Figure 1. Transition-metal-catalyzed reductive removal of an ester group

Our study began by optimizing the conditions for the reaction of ethyl benzoate with an oxazolyl group at the ortho position, as in **1a** (Table S1). Among NHC ligands examined, free IMes were found to be the most effective. Finally, the following conditions were determined as a standard reaction conditions: **1a** (0.2 mmol), Ni(cod)<sub>2</sub> (0.02 mmol), IMes (0.02 mmol) in toluene (0.5 mL) at 180 °C for 14 h.

We next examined the effect of an alkoxy group in O-alkyl esters (Table 1). All esters with primary alkoxy groups and secondary alkoxy groups gave the desired product **2** in good yields. However, the reaction of an ester with tertiary alkoxy group **1e** gave the desired product but in low yield.

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Scheme 1. Screening of directing groups. Reaction conditions: ester (0.2 mmol),  $Ni(cod)_2$  (0.02 mmol), IMes (0.02 mmol) in toluene (0.5 mL) at 180 °C for 14 h. Yields shown are isolated yields, unless otherwise noted. <sup>a</sup>GC yield. <sup>b</sup>NMR yield. <sup>c</sup>ICy·HCI (0.04 mmol) and NaO'Bu (0.04 mmol) were used instead of IMes.



 $\begin{array}{l} \textbf{Scheme 2. Substrate scope. Reaction conditions: ester (0.2 mmol), Ni(cod)_2 (0.02 mmol), IMes (0.02 mmol) in toluene (0.5 mL) for 14 h at 180 °C. Yields shown are isolated yields, unless otherwise noted. <math display="inline">^a\text{GC}$  yield  $^b\text{ICy-HCI}$  (0.04 mmol) and NaOtBu (0.04 mmol) were used instead of IMes.  $^cN,N$ -Diethylbenzamide was obtained in 12% NMR yield.  $^d$ Napthalene was also obtained in 17% GC yield.

We next turned our attention to evaluating the effect of directing groups (Scheme 1). The reaction was applied to aromatic esters with an *N*-heteroaromatic ring, as in **3**, **4**, and **5**. Curiously, we found that amide and ester groups also function as directing groups. Secondary and tertiary amide groups, as in **6** and **7** can be used as directing groups. When using diisopropyl phthalate (**8**), isopropyl benzoate was obtained in 38% yield.

We next examined the scope of the reaction with respect to substrates. An oxazoyl group served as a good directing group, as in **9** and **10**. In the case of a substrate with two ester groups, as in **10c**, reductive cleavage of an ester group decoursed only at the ortho-position of an oxazolyl group and the other ester group at the meta-position remained intact. Various functional groups, such as  $CF_3$ , ester, amide, NMe<sub>2</sub>, and OMe were tolerated. However, the reaction of a substrate containing a 4pyridyl group **11** gave no desired product and 91% of the starting material was recovered. An amido group also promoted the reductive defunctionalization, as in **12**, **13** and **14**. The reaction was also applicable to  $\pi$ -extended aromatic esters, **15** and **16** and the indole derivative **17**.



Scheme 3. Substrate scope. Reaction conditions: ester (0.2 mmol),  $Ni(cod)_2$  (0.02 mmol), ICy·HCI (0.04 mmol), NaO'Bu (0.05 mmol) in toluene (0.5 mL) for 14 h at 180 °C. Yields shown are isolated yields. <sup>a</sup>GC yield <sup>b</sup>NaO'Bu (0.06 mmol) was used.

It is noteworthy that an arene ring also functions as a directing group. While ethyl [1,1'-biphenyl]-4-carboxylate (**18**) gave biphenyl only in 13% yield, the reaction of ethyl [1,1'-biphenyl]-2-carboxylate (**19a**) gave the biphenyl in 52% yield, indicating that a phenyl group at the ortho-position would coordinate to Ni, which would then accelerates the reaction.<sup>17</sup> It was found that an electron-withdrawing group on the phenyl ring facilitates the reaction, as in **19d**. A naphthalene ring, as in **21** and **22** and heteroaromaric rings, as in **24** and **25** were also found to function as a directing group. An alkene also serves as a directing group, as in **27**.

Mechanistic studies were conducted in an attempt to gain insights into the reaction mechanism (Scheme 4). The reaction of **1f** gave **2** in 92% yield along with 5-nonanone in quantitative yield, suggesting that the  $H_{\alpha}$  atom is transferred to the orthoposition (Scheme 4a). In fact, in the reaction of **1a-d**<sub>5</sub>, a deuterium atom was transferred to the ortho-position, although some deuterium loss was observed (Scheme 4b). A crossover experiment using **1a-d**<sub>5</sub> and **10e** was conducted (Scheme 4c). Curiously, deuterium atoms were scrambled, **Journal Name** 

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although no H/D exchange was observed in the recovered starting materials. To gain additional insights into the reaction mechanism, the reaction of **10e** with a deuterium labeled aldehyde was examined. The reaction gave the desired product albeit in low yield and 26% of the atoms introduced in the *ortho* position of the product were deuterium atoms (Scheme 4d). The reaction of **1a** with a boronic ester gave the coupling product in 29% yield (Scheme 4e).<sup>18</sup> This result indicates that the present reaction proceeds via a similar pathway to that of previously reported coupling reactions of esters.<sup>51</sup>

Ni(cod)<sub>2</sub> 10 mol% IMes 10 mol% toluene 0.5 mL Bu 180 °C. 14 h Ή, Вu 1f 0.2 mmol 2 92% (GC) >99% (GC) (b) Ni(cod)<sub>2</sub> 10 mol% IMes 10 mol% toluene 0.5 mL 180 °C. 14 h (89% D) >99% D 1a-d<sub>5</sub> 0.2 mmol 2-d 72% (GC) (C) 0 Me<sub>2</sub>N Ni(cod)<sub>2</sub> 0.04 mmol IMes 0.04 mmol OC<sub>2</sub>C toluene 1.0 mL OC<sub>2</sub>H 180 °C, 3 h >99% D Ĉ 1a-d5 0.2 mmol 10e 0.2 mmol Me<sub>2</sub>N 1a-d<sub>5</sub> 10e H/L H/D 54% D 46% (34% D) 17% 30% 2-d 60% (GC) (d) Me<sub>2</sub>N OC<sub>2</sub>H<sub>4</sub> C11H23 95% D 10e 0.5 mmo 0.5 mmol Me<sub>2</sub>N Ni(cod)<sub>2</sub> 10 mol% IMes 10 mol% toluene 1 mL 180 °C, 14 h H/ 4% (isolated by GPC) (26% D) (e) PhBnep 1.5 equiv Ni(cod)<sub>2</sub> 10 mol% IMes 10 mol% Na<sub>2</sub>CO<sub>3</sub> 2.0 equiv toluene 0.5 mL OC<sub>2</sub>H<sub>5</sub> 180 °C, 14 h 29% 29% (GC) 1a 0.2 mmol

A proposed reaction mechanism is shown in Scheme 5. The coordination of a nitrogen atom to Ni(0) follow by the oxidative addition of a C-O bond gives the complex  $B^{19}$  through  $A^{20}$  Decarbonylation in complex **B** affords the complex  $C^{21}$ , which undergoes  $\beta$ -hydride elimination to form complex **D** 

with the elimination of acetaldehyde.<sup>22</sup> Finally, reductive elimination gives **2** with the regeneration of the catalytic active Ni(0) species. In a crossover experiment (Scheme 4c), no H/D exchange between the starting materials was detected, suggesting that the cleavage of a C-O bond and/or decarbonylation is irreversible. The results obtained from a crossover experiment (Scheme 4c), in which deuterium atom scrambling was observed in the products and the result obtained from Scheme 4d suggest that the  $\theta$ -hydride elimination step is reversible. The results obtained from Scheme 4e indicate that an alkoxy intermediate **C** is a key intermediate.



Scheme 5. Proposed mechanism.

In conclusion, we report the nickel-catalyzed reductive removal of an ester group in the absence of an external reductant. This new reaction proceeds via a mechanism involving the oxidative addition of the inert C–O bond of an *O*-alkyl ester, which was achieved by the assistance of a directing group. In the course of our investigations of the substrate scope, we found that an aryl group also functioned as a directing group and new mechanistic aspects of the reaction were revealed. Studies aimed at expanding this new reactivity of nickel complexes to reactions without a directing group are ongoing in our laboratories.

#### **Conflicts of interest**

There are no conflicts to declare.

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Scheme 4. Mechanistic Studies.

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DG DG Ni/none 0 R Ö

activation of C(O)-OR (R = alkyl) bond no an external reductant DG =  $N(sp^2)$  and  $O(sp^2)$  atoms and arene ring!!

*† Electronic Supplementary Information (ESI) available*: Experimental details and Spectroscopic data. See DOI: 10.1039/x0xx00000x

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