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The Ruthenium-Catalyzed Reductive Decarboxylation of Esters: Catalytic Reactions Involving the Cleavage of Acyl−Oxygen Bonds of Esters

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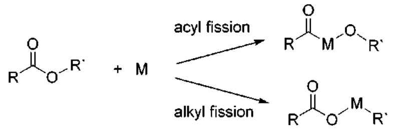
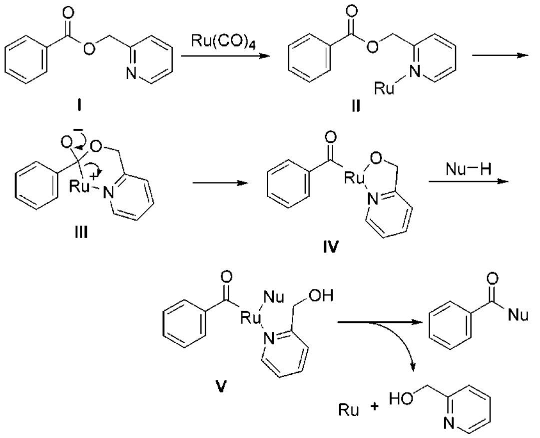
The cleavage of a carbon−oxygen bond promoted by transition metal complexes has become an important process in organic synthesis.[1,2] The majority of these reactions reported thus far involve the cleavage of an alkyl−O bond (alkyl fission) in esters (Scheme 1). A typical example is the Pd-catalyzed reactions of allyl acetates with nucleophiles, in which allyl−O bonds are cleaved.[3] The catalytic cleavage of benzyl−O or vinyl−O bonds is also well-known.[1] In contrast, the cleavage of an acyl−O bond (acyl fission) in esters, catalyzed by transition metal complexes, is very rare, and only a few stoichiometric reactions have been reported to date. Yamamoto reported on the stoichiometric reaction of phenyl acetate with $Ni(cod)_2$ in the presence of bipyridine. In this reaction, a methylnickel phenoxide complex is formed via the oxidative addition of the acetyl−O bond of phenyl acetate to the nickel complex followed by decarbonylation.[4] Other complexes, such as $Mo(N_2)_2(dppe)_2$,[5] $HRh(PPh_3)_4$,[6] and $Ru(CO)_2(PPh_3)_3$,[7] have also been found to promote the cleavage of acyl−O bonds of esters, with the ester carbonyl group being ultimately converted to a CO ligand, which is attached to the metal. It is noteworthy in this respect that a related acyl complex was isolated from the reaction of aryl acetate with a Rh(I) complex by Grotjahn.[8] Recently, Yamamoto and co-workers reported that electronicallyl activated esters, such as aryl trifluoroacetates, oxidatively add to Pd(0) under mild conditions to give the corresponding (aryloxo)(trifluoroacetyl)palladium complexes.[9] More recently, they also reported on the Pd-catalyzed reaction of aryl trifluoroacetates with arylboronic acids, leading to aryl trifluoromethyl ketones.[10] To our knowledge, this represents the first example of a catalytic reaction, which involves the cleavage of an acyl−O bond of an ester by transition metals.[11,12] As a result of recent studies in this laboratory,[13−15] we have discussed a new catalytic transformation of esters, which involves the cleavage of an acyl C−O bond in esters, and we report herein on the $Ru_3(CO)_{12}$-catalyzed reductive decarboxylation of esters. Ammonium formate was used as the reducing reagent.

Scheme 1. Two Modes of the Cleavage of C−O Bonds of Esters by Transition Metal Complexes



Scheme 2. Working Hypothesis



Our strategy is based on the methodology that heteroatom-directing groups promote the site-selective cleavage of unreactive bonds, as shown in Scheme 2. We have previously reported on catalytic reactions which involve the site-selective cleavage of C−H,[13] C−C,[14] and C−F[15] bonds by taking advantage of the coordination of the directing group to transition metals. These observations prompted us to examine the possibility that this approach might be used in the cleavage of C−O bonds in esters. The coordination of the pyridine nitrogen in ester **I** to ruthenium renders the metal more nucleophilic. The cleavage of a C−O bond takes place via a tetrahedral intermediate **III** to give an acyl ruthenium complex **IV**, which reacts with pronucleophiles to give a product and 2-pyridinemethanol, along with the regenerated ruthenium. 2-Pyridylmethyl 2-naphthalenecarboxylate (**1**) was chosen as the test substrate and $Ru_3(CO)_{12}$ as the catalyst. Among the wide variety of pronucleophiles examined, we found that ammonium formate, $HCOONH_4$, can be used as a nucleophile, resulting in a clean reduction reaction, but the expected aldehydes were not obtained. The reaction of **1** (0.2 mmol) and $HCOONH_4$ (0.6 mmol) in the presence of $Ru_3(CO)_{12}$ (0.01 mmol) in toluene (0.6 mL) at 160 °C for 40 h gave naphthalene (**2**) in 55% GC yield, along with 17% of unreacted **1**. The corresponding benzyl ester did not react with $HCOONH_4$, indicating that the presence of the nitrogen in the substrate is essential for the reaction to proceed. The ^1H NMR spectrum indicated that 2-pyridinemethanol is formed in a yield comparable to that of **2**. Of the solvent examined, dioxane is the solvent of choice, although the type of solvent had no significant effect on the yield of **2** (dioxane 95%, PrCN 71%, CH_3CONMe_2 84%, toluene 55%). The use of other

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(12) For recent papers on catalytic reaction involving the cleavage of C(O)−S bonds of esters, see: Liebeskind, L. S.; Srogl, J. *J. Am. Chem. Soc.* **2000**, *122*, 11260. Shimizu, T.; Seki, M. *Tetrahedron Lett.* **2001**, *42*, 429.

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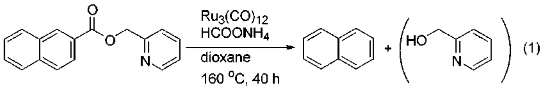
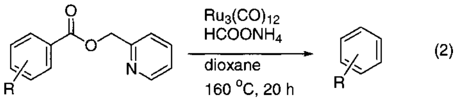
10.1021/ja0103501 CCC: $20.00

hydrogenation reagents, such as HCOONa, *i*-PrOH, and HSiMe$_2$-Ph, was not effective.



1 **2** 95%

A variety of functional groups can be tolerated in the reaction as shown in eq 2. Both electron-donating and -withdrawing groups did not appreciably affect the reaction. However, the reaction of a 4-nitro ester, such as **4f**, resulted in the reduction of the nitro group to give 2-pyridylmethyl 4-aminobenzoate in 27% yield with no nitrobenzene being obtained. Although an ester group (COOMe) at the 4-position on the phenyl ring was tolerated, the use of a cyano-substituted ester, such as **4k**, resulted in a low yield of benzonitrile **5k**.[16] Steric bulkiness around the carbonyl group, as in **4b**, led to a low conversion.



4 **5**

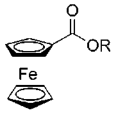
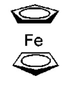
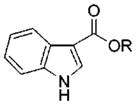
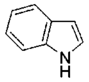
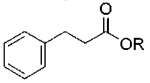
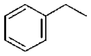
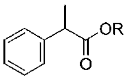
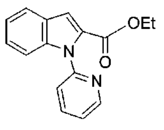
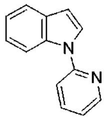
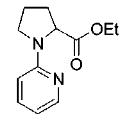
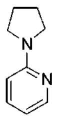
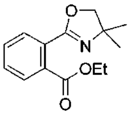
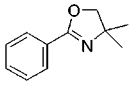
a: R = 2,5-Me$_2$ (100%) **b**: R = 2,4,6-Me$_3$ (4%)
c: R = 4-OMe (90%) **d**: R = 3,4,5-(OMe)$_3$ (88%)
e: R = 4-NMe$_2$ (95%) **f**: R = 4-NO$_2$ (0%)
g: R = 2-Cl-4-F (71%) **h**: R = 4-SO$_2$Me (79%)
i: R = 3,5-(CF$_3$)$_2$ (83%) **j**: R = 4-COOMe (78%)
k: R = 4-CN (23%)

It was anticipated that aldehydes, which are formed via reduction of esters by HCOONH$_4$, would be produced initially and then undergo decarbonylation to give arenes under the reaction conditions used here. To examine this possibility, some controlled experiments were performed. The reaction of 2-naphthalenecarbaldehyde (**3**) under the reaction conditions identical to those in eq 2 gave naphthalene in 23% GC yield, along with a 7% yield of 2-naphthalenemethanol (GC yield was determined as silyl ether) and a 61% yield of 2-methylnaphthalene, with the latter two products being obtained by reduction of **3** by HCOONH$_4$. Treatment of a mixture of **3** and 2-pyridylmethyl 3,4,5-trimethoxybenzoate (**4d**) with HCOONH$_4$ under identical conditions gave a 91% recovered yield of **4d** and 2-naphthalenemethanol (45% GC yield). The expected 1,2,3-trimethoxybenzene (**5d**) was obtained in trace amounts, and naphthalene and 2-methylnaphthalene were not detected by GC. These results show that the present reductive decarboxylation does not involve an aldehyde intermediate.

The reaction is not limited to a benzene ring system, but it is applicable to heteroaromatic as well as aliphatic systems, as shown in Table 1. The reaction of ferrocenecarboxylic ester **6** gave ferrocene (**7**) in 56% yield, along with 28% of unreacted **6** (entry 1). The reaction of **8** under the same conditions as those described in eq 2 gave indole (**9**) in 23% yield. However, changing solvent to toluene increased the product yield to 70% (entry 2). It was found that aliphatic esters **10** and **12** give ethylbenzene efficiently, and that styrene, which could have been formed by β-hydride elimination, was not present in the reaction mixture (entries 3 and 4). The reaction was not limited to esters, in which a 2-pyridylmethyl group is attached as the directing group at the alcohol moiety in the substrates (entries 5−7). These results show the apparent potential utility of this transformation in terms of its applications to organic synthesis.

We propose that the reaction proceeds via a mechanism which is similar to that shown in Scheme 1. The reason why the decarbonylation step from **IV** is unexpectedly fast is unclear at present.[17]

Table 1. The Ru$_3$(CO)$_{12}$-Catalyzed Reaction of Esters with HCOONH$_4$[a]

entry	ester	product[b]
1	 **6**	 **7** 56%
2[c]	 **8**	 **9** 70%
3	 **10**	 **11** 76%
4	 **12**	**11** 78%
5[c]	 **13**	 **14** 81%
6[c]	 **15**	 **16** 100%
7[c]	 **17**	 **18** 97%

[a] Reaction conditions: ester (0.2 mmol), HCOONH$_4$ (0.6 mmol), Ru$_3$(CO)$_{12}$ (0.01 mmol), dioxane (0.6 mL) at 160 °C for 20 h. R = 2-pyridinylmethyl. [b] GC yield. [c] Toluene was used as a solvent.

The present reaction demonstrates a new and rare example of a catalytic reaction that involves the cleavage of acyl C−O bonds in esters. As it impacts organic synthesis, the present reaction represents a new type of reductive decarboxylation in which esters can be converted to hydrocarbons,[18] similar to decarbonylation of aldehydes, a reaction which is frequently employed in organic synthesis.[19] In addition, a wide variety of functional groups can be tolerated in the reaction. Further investigation of the catalytic conversion of esters into carbonyl compounds using pronucleophiles is currently under way.

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) The reaction of a cyano group by HCOONH$_4$ would have taken place through the reaction. In fact, we found that the reaction of 2-naphthalenecarbnitrile under identical reaction conditions gives 2-methylnaphthalene in 27% yield and unidentified products.

(17) When the reaction was carried out even at 1 atm of CO, no reaction took place.

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