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Ruthenium complex catalyzed hydrosilylation of esters: a facile transformation of esters to alkyl silyl acetals and aldehydes

Mamoru Igarashi, Ryo Mizuno and Takamasa Fuchikami*

Sagami Chemical Research Center, 4-4-1 Nishi-Ohnuma, Sagamihara, Kanagawa 229-0012, Japan

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Abstract—Hydrosilylation of esters takes place in the presence of ruthenium catalysts to afford the corresponding alkyl silyl acetals in moderate to good yields, which can be converted into aldehydes by hydrolysis. © 2001 Elsevier Science Ltd. All rights reserved.

The conversion of ester groups to the corresponding aldehyde derivatives is one of the most important transformations in organic syntheses, and for a long time diisobutylaluminum hydride (DIBALH) reduction has been a sole efficient method for this purpose.[1] However, DIBALH reagent is difficult to handle in both laboratorial and industrial scales, because of its flammable, pyrophoric, moisture-sensitive, irritant, and toxic nature. Many attempts toward this transformation have been done using hydrosilanes as reducing agents, however, ethers[2,3] or alcohols[4–6] have been obtained as main products. Ojima and Kumagai reported the Rh-catalyzed 1,2-addition of hydrosilanes to conjugated esters, in which 1,4-adducts were obtained as major products.[7] Recently, Buckwald and co-workers reported $Cp_2Ti(p\text{-}ClC_6H_4O)_2$–TBAF/alumina catalyzed reduction of lactones to lactols using polymethylhydrosiloxane (PMHS), where only five- and six-membered lactones gave satisfactory results.[8] In this paper, we wish to describe efficient and general catalytic processes for the conversion of esters to the corresponding alkyl silyl acetals and aldehydes.

Initially, we surveyed the active catalytic system in the reaction of ethyl 2-methylpropanoate with triethylsilane. We found that $Ru_3(CO)_{12}$ shows an effective catalytic activity, and $[RuCl_2(CO)_3]_2$ possesses a similar activity in the presence of diethylamine and ethyl iodide as co-catalysts. However, other transition-metal carbonyl complexes such as $Cr(CO)_6$, $W(CO)_6$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Co_2(CO)_8$ and $Rh_6(CO)_{16}$ show no or little catalytic activity either in the absence or presence of co-catalysts.

Optimized conditions are as follows: *Method A:* A mixture of ethyl 2-methylpropanoate (1.0 mmol), Et_3SiH (1.5 mmol), and $Ru_3(CO)_{12}$ (0.0033 mmol) in toluene (1.0 ml) was heated at 100°C for 16 h under an Ar atmosphere. GLC analysis of the reaction mixture showed the formation of 1-ethoxy-1-triethylsiloxy-2-methylpropane in 78% yield. *Method B:* A mixture of ethyl 2-methylpropanoate (1.0 mmol), Et_3SiH (1.5 mmol), and $[RuCl_2(CO)_3]_2$ (0.005 mmol), EtI (0.05 mmol), and Et_2NH (0.05 mmol) in toluene (1.0 ml) was heated at 100°C for 16 h under an Ar atmosphere. The GLC analysis of the reaction mixture showed the formation of 1-ethoxy-1-triethylsiloxy-2-methylpropane in 86% yield.

Representative results are summarized in Tables 1 and 2. Methyl, isopropyl, and phenyl esters afforded the satisfactory results (entries 1, 2, and 3 in Table 1, entries 1, 3, and 4 in Table 2). Sterically hindered esters such as *tert*-butyl ester (entry 4 in Table 1) or 2,2-dimethylpropionate (entry 2 in Table 2) gave moderate yields of the products. Cyclohexanecarboxylate, benzoate and phenylacetate also easily converted into the corresponding methyl silyl acetals (entries 5, 6, and 7 in Tables 1 and 2). In sharp contrast with the results reported by Buchwald et al.,[8] five-membered lactone gave lower yield of the product (entry 8 in Tables 1 and 2) in the present catalytic systems.

Instead of triethylsilane, both *tert*-butyldimethylsilane and phenyldimethylsilane can be applicable in the

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Keywords: ruthenium and compounds; catalysts; silicon and compounds; esters; acetals; aldehydes.

* Corresponding author. Fax: +81-42-749-7631; e-mail: scrc1@sagami.or.jp

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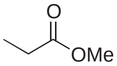
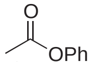
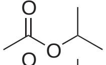
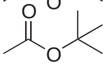
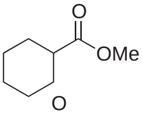
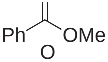
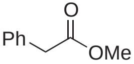
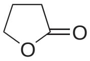
Table 1. Hydrosilylation of esters by triethylsilane using $Ru_3(CO)_{12}$ catalyst

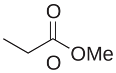
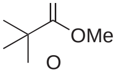
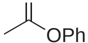
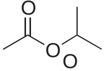
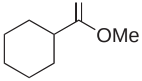
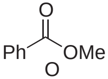
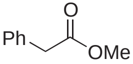
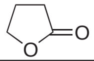
$$\text{Ester} \; + \underset{(1.5\text{eq})}{\text{Et}_3\text{SiH}} \xrightarrow[\substack{\text{PhMe} \\ 100°\text{C, 16 h}}]{\text{Ru}_3(\text{CO})_{12}\ ([\text{Ru}]=1\text{mol\%})} \text{Alkyl Silyl Acetal}$$

Entry	Ester	Conv. of Ester(%)[a]	Yield of Acetal(%)[a,b]
1		100	57
2		89	94
3		100	74
4		100	45
5		90	61
6		51	57[c]
7		81	84
8		93	36

a) Determined by GLC
b) Yields are conversion yields.
c) Determined by ^{1}H-NMR

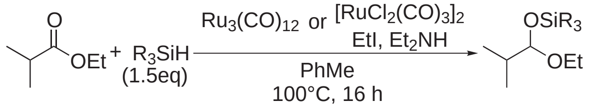
Table 2. Hydrosilylation of esters by triethylsilane using $[RuCl_2(CO)_3]_2$–EtI–Et_2NH catalyst

$$\text{Ester} \; + \underset{(1.5\text{eq})}{\text{Et}_3\text{SiH}} \xrightarrow[\substack{\text{PhMe} \\ 100°\text{C, 16 h}}]{\substack{[\text{RuCl}_2(\text{CO})_3]_2\ ([\text{Ru}]=1\text{mol\%}) \\ \text{EtI, Et}_2\text{NH(5mol\%)}}} \text{Alkyl Silyl Acetal}$$

Entry	Ester	Conv. of Ester(%)[a]	Yield of Acetal(%)[a,b]
1		100	57
2		42	66
3		79	98
4		100	91
5		95	97
6		73	63[c]
7		89	90
8		46	44

a) Determined by GLC
b) Yields are conversion yields.
c) Determined by ^{1}H-NMR.

Table 3. Hydrosilylation of ethyl 2-methylpropionate by hydrosilanes



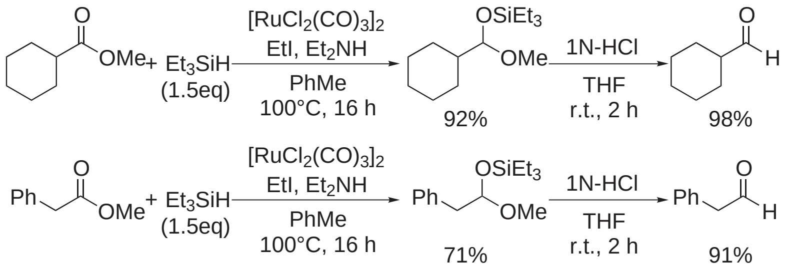
Entry	R_3SiH	Cat.	Conv. of ester (%)[a]	Yield of acetal (%)[a,b]
1	Et_3SiH	$Ru_3(CO)_{12}$	90	78
2	Et_3SiH	$[RuCl_2(CO)_3]_2$	100	86
3	$^tBuMe_2SiH$	$Ru_3(CO)_{12}$[c]	35	79
4	$^tBuMe_2SiH$	$[RuCl_2(CO)_3]_2$[c]	94	87
5	$PhMe_2SiH$	$Ru_3(CO)_{12}$[c]	54	87[d]
6	$PhMe_2SiH$	$[RuCl_2(CO)_3]_2$[c]	81	72[d]

[a] Determined by GLC.

[b] Yields are conversion yields.

[c] 5 mol% of [Ru] was used.

[d] Determined by ^1H NMR.



Scheme 1.

present reaction (in Table 3). One-step introduction of *tert*-butyldimethylsilyl group may be useful as the protecting group in organic synthesis.

Alkyl silyl acetals thus obtained can be easily converted into the corresponding aldehydes in excellent yields by the action of 1N HCl in tetrahydrofuran at room temperature (Scheme 1).

In summary, we have developed facile and efficient methods for the transformation of esters to aldehydes via alkyl silyl acetals, which are obtained by Ru complex-catalyzed hydrosilylation. Our method has the following advantages: All materials, starting hydrosilanes and formed alkyl silyl acetals, are stable enough toward air and moisture, and are easily handled without special care. The obtained alkyl silyl acetals can be converted into the corresponding aldehydes by acidic hydrolysis.

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