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# Ruthenium Complex Catalyzed Benzylation of Arenes with Benzyl Formates; Decarbonylation and Decarboxylation of Alkyl Formates

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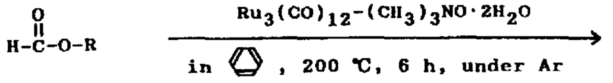
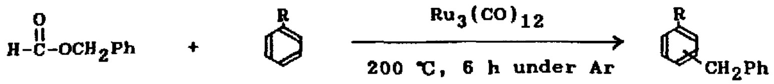
***Summary***: $Ru_3(CO)_{12}$-$(CH_3)_3NO \cdot 2H_2O$ showed high catalytic activity for the decarbonylation of alkyl formates to the corresponding alcohols at 150 - 200 °C under an argon atmosphere. Decarbonylation of $\beta$-phenetyl formate afforded $\beta$-phenetyl alcohol in 82 % yield. On the other hand, when decarbonylation of benzyl formate was performed in the absence of $(CH_3)_3NO \cdot 2H_2O$, benzylation of arenes, which were employed as a solvent, proceeded via catalytic decarboxylation of benzyl formate. For the reaction of toluene with benzyl formate, phenyltolylmethane (*o*-, *m*-, and *p*-mixture) was obtained in total 77 % yield.

Although formic acid and its derivatives, which are easily derived from carbon monoxide, are important as sources of functionalyzed $C_1$ units,$^{1)}$ there are relatively few reports of transition metal complex catalyzed reactions using them. Concerned with organic syntheses using alkyl formates, examples are limited to iridium(I) or rhodium(III) catalyzed isomerization of methyl formate to acetic acid,$^{2)}$ rhodium(I) catalyzed carbonylation of organic halides$^{3)}$ and palladium catalyzed carbonylation of olefins$^{4)}$ with alkyl formates as an alkoxylating reagent, ruthenium complex catalyzed addition of methyl formate to olefins.$^{5)}$ The simplest transformation of alkyl formates is decarbonylation and both heterogeneous$^{6)}$ and homogeneous$^{7)}$ transition metal catalyzed decarbonylations of alkyl formates were reported. However, the catalytic activities were rather low and high pressures are sometimes necessary for these reactions. In the course of our ruthenium complex catalysts,$^{8)}$ we found that low valent ruthenium complex showed high catalytic activity for the activation of formyl C-H bond,$^{9)}$ and in this paper, we firstly describe ruthenium complex catalyzed decarbonylation of alkyl formates to the corresponding alcohols (eq. 1) and secondly, benzylation of arenes with benzyl formate via catalytic decarboxylation of benzyl formate (eq. 2).



(1)



(2)

A typical reaction procedure was as follows; A mixture of alkyl formate (5.0 mmol), $Ru_3(CO)_{12}$ (0.10 mmol) and arene (4.0 ml) was placed in a 50 ml stainless steel autoclave equipped with a glass liner and a magnetic stirring bar (in decarbonylation reactions, $(CH_3)_3NO\cdot 2H_2O$ (0.50 mmol) was added as a cocatalyst). Reaction was carried out at 200 °C for 6 h under an argon atmosphere. All products were isolated by vacuum fractional distillation and satisfactory spectroscopic and analytical data for them were obtained.

Alkyl formates were smoothly decarbonylated by $Ru_3(CO)_{12}$-$(CH_3)_3NO\cdot 2H_2O$ system to give the corresponding alcohols in 50 - 82 % yields (Table 1). Even though reactivity of secondary alkyl formates was less than that of primary alkyl formates, secondary alkyl formates were also decarbonylated without an elimination reaction (Run 9).[7a] The present decarbonylation reaction proceeded even at 150 °C (Run 2), but at 120 °C, the catalytic activity was reduced drastically (Run 3). When $Ru(acac)_3$ was employed as a catalyst, decarbonylation of alkyl formate did not occur at all (Run 4). In the present reaction, the addition of $(CH_3)_3NO\cdot 2H_2O$ as a cocatalyst extremely enhanced both the conversion of alkyl formates and the selectivity of the corresponding alcohols (Runs 1, 5-10). The same phenomenon was observed in our previous study.[9c]

**Table 1. Ruthenium Complex Catalyzed Decarbonylation of Alkyl Formates[a]**

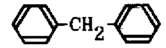
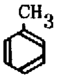
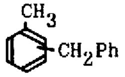
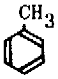
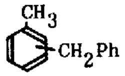
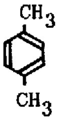
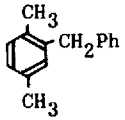
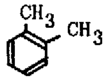
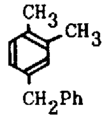
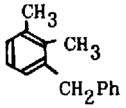
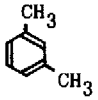
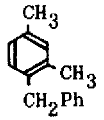
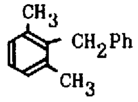
| Run | Alkyl Formate | Catalyst | Additive | Temp.(°C) | Conv.(%)[b,c] | Product(%)[c] | |
|---|---|---|---|---|---|---|---|
| 1 | $HCOOCH_2Ph$ | $Ru_3(CO)_{12}$ | $(CH_3)_3NO\cdot 2H_2O$ | 200 | 100 | $PhCH_2OH$ | 74 |
| 2 | $HCOOCH_2Ph$ | $Ru_3(CO)_{12}$ | $(CH_3)_3NO\cdot 2H_2O$ | 150 | 92 | $PhCH_2OH$ | 72 |
| 3 | $HCOOCH_2Ph$ | $Ru_3(CO)_{12}$ | $(CH_3)_3NO\cdot 2H_2O$ | 120 | 5 | - | 0 |
| 4[d] | $HCOOCH_2Ph$ | $Ru(acac)_3$ | $(CH_3)_3NO\cdot 2H_2O$ | 200 | 0 | - | 0 |
| 5 | $HCOOCH_2CH_2Ph$ | $Ru_3(CO)_{12}$ | $(CH_3)_3NO\cdot 2H_2O$ | 200 | 100 | $PhCH_2CH_2OH$ | 82 |
| 6 | $HCOOCH_2CH_2Ph$ | $Ru_3(CO)_{12}$ | - | 200 | 64 | $PhCH_2CH_2OH$ | 11 |
| 7 | HCOO-n-$C_6H_{13}$ | $Ru_3(CO)_{12}$ | $(CH_3)_3NO\cdot 2H_2O$ | 200 | 96 | n-$C_6H_{13}OH$ | 74 |
| 8 | HCOO-n-$C_6H_{13}$ | $Ru_3(CO)_{12}$ | - | 200 | 72 | n-$C_6H_{13}OH$ | 13 |
| 9 | HCOO  | $Ru_3(CO)_{12}$ | $(CH_3)_3NO\cdot 2H_2O$ | 200 | 62 |  | 50 |
| 10 | HCOO  | $Ru_3(CO)_{12}$ | - | 200 | 44 |  | 5 |

[a] Alkyl formate (5.0 mmol), $Ru_3(CO)_{12}$ (0.10 mmol), $(CH_3)_3NO\cdot 2H_2O$ (0.50 mmol) and benzene (4.0 ml) for 6 h under an argon atmosphere. [b] Conversion of alkyl formate. [c] Determined by GLC. [d] $Ru(acac)_3$ (0.30 mmol) was used.

Only when decarbonylation of benzyl formate was examined in the absence of $(CH_3)_3NO\cdot 2H_2O$, quite different reaction occurred; i.e., benzylation of arenes via catalytic decarboxylation of benzyl formate. For the reaction of benzene with benzyl formate, diphenylmethane was obtained in 22 % yield (Run 11 in Table 2).

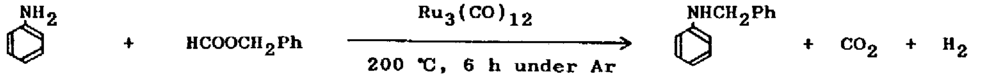
Results are summarized in Table 2. In the presence of a catalytic amount of ruthenium complex, benzylation of arenes with benzyl formate smoothly proceeded to give the products in 22 - 77 %. Toluene and xylenes were more reactive than benzene and the reaction of toluene with benzyl formate afforded a 42 : 9 : 49 (*o* : *m* : *p*) mixture of phenyltolylmethane in total 77 % yield together with the formation of $CO_2$ (2.36 mmol) (Run 13).

**Table 2. Ruthenium Complex Catalyzed Benzylation of Arenes with Benzyl Formate[a]**

| Run | Arene | Ru complex | Products(%)[b] | |
|---|---|---|---|---|
| 11 |  | $Ru_3(CO)_{12}$ |  | (22) |
| 12 |  | $Ru_3(CO)_{12}$ | <br>(*o*:*m*:*p* = 42:9:49)[d] | 68(53) |
| 13[c] |  | $RuCl_3 \cdot nH_2O$ | <br>(*o*:*m*:*p* = 40:8:52)[d] | 77 |
| 14 |  | $Ru_3(CO)_{12}$ |  | (51) |
| 15 |  | $Ru_3(CO)_{12}$ |  <br>(64 36)[d] | (48) |
| 16 |  | $Ru_3(CO)_{12}$ |  <br>(80 20)[d] | (59) |

[a] $HCOOCH_2Ph$ (5.0 mmol), $Ru_3(CO)_{12}$ (0.10 mmol), arene (4.0 ml) at 200 °C for 6 h under an argon atmosphere. [b] Determined by GLC and figures in the parentheses were isolated yields. [c] $RuCl_3 \cdot nH_2O$ (0.30 mmol) was used. [d] Determined by $^{13}C$-NMR.

*p*-Xylene also reacted with benzyl formate to give only one benzylated product (Run 14). On the other hand, *o*-, and *m*-xylene gave two isomers, respectively (Runs 15 and 16). In the reaction of *m*-xylene with benzyl formate, 2- and 4-position of *m*-xylene were benzylated but 5-position, which was meta position from both methyl substituent of *m*-xylene, was not benzylated at all (Run 16). These results suggest that the present benzylation reaction would proceed via electrophilic aromatic substitution mechanism.[10] In order to investigate the effect of substituent group on arenes, aniline was employed in the reaction. However, the reaction of aniline with benzyl formate gave only N-bezylaniline in 95 % yield (eq. 3).[11] Furthermore, when benzyl alcohol instead of benzyl formate was treated with toluene



(3)

under the same reaction conditions, the yield of phenyltolylmethane was drastically reduced to 23 %. At this stage, we speculated that in the present benzylation reaction, ruthenium catalyzed decarboxylation of benzyl formate firstly occurred and subsequently, generated benzyl cation or benzyl radical[12)] reacted with arenes to give the products. Among the ruthenium complexes, $Ru_3(CO)_{12}$ and $RuCl_3 \cdot nH_2O$ showed high catalytic activity (Runs 12 and 13) but Ru(COD)(COT), $Ru(acac)_3$ and Ru metal (250 mesh) showed no catalytic activity. Further mechanistic study and applications of the present reaction are now in progress.

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12) Although radical scavenger such as 2,6-di-*t*-butylphenol did not affect the reaction, the possibility of a tightly "caged" radical could not be eliminated completely.

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