Letter

Ruthenium-catalyzed Esterification of Olefin with Methyl Formate

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(Received June 16, 1987; accepted October 14, 1987)

Introduction

Methyl formate can be synthesized quite easily by (1) methanol dehydrogenation over Cu-based oxide catalysts, (2) methanol carbonylation using base catalyst at high pressure of CO, and (3) dimerization of formaldehyde on metal oxide [1]. Considerable attention, therefore, has been paid to methyl formate as an intermediate compound in chemical synthesis. Methyl formate has been used for acetic acid synthesis by isomerization, for which reaction a rhodium complex has been found to be effective as a catalyst [2].

An interesting feature is the C-H bond activation of the formyl group of formate esters by organometallic complexes. Felkin *et al.* [3] reported decarbonylation of ethyl formate by a dinitrogen complex of Fe to yield the corresponding carbonyl complex and ethanol. Tatsumi *et al.* [4] reported that the reactions of formate esters with dinitrogen molybdenum complex yield decarbonylation products and molybdenum carbonyl complex. In both cases, it was believed that the reaction proceeded via the cleavage of the formyl C-H bond. On the basis of these findings, we attempted a reaction of methyl formate activated by metal complex with olefin to produce ester, and found that the reaction took place using the ruthenium dihydride complex catalyst, RuH_2 (PPh₃)₄, I, (Scheme 1). We will discuss here this novel synthetic reaction which has not previously been reported.

$$\begin{array}{c} \text{HCOOCH}_3 + \text{RCH} = \text{CH}_2 \xrightarrow{I} \text{RCH}_2 \text{CH}_2 \text{COOCH}_3 + \text{RCHCOOCH}_3 \\ \text{R} = \text{H}, \text{CH}_3, \text{C}_2 \text{H}_5 \end{array} \xrightarrow{I} \text{CH}_3 \end{array}$$

Scheme 1.

Experimental

Dihydrido(tetrakistriphenylphosphine)ruthenium(II) complex, I, was prepared according to the literature reported elsewhere [5]. To a solution

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of $\operatorname{RuCl}_2(\operatorname{PPh}_3)_3$ and PPh_3 in ethanol was added NaBH_4 under Ar atmosphere to give a yellow powder.

Commercially available reactants and solvents were used for reaction after purification by standard methods, except ethylene, propylene and 1butene.

The reaction was carried out in a 50 ml titanium-coated stainless steel autoclave. In a typical experiment, methyl formate (13 mmol) in solvent (7 ml) was allowed to react with olefin (40 mmol) in the presence of I under stirring at an elevated temperature. The products were isolated and identified by the usual methods (GC-MS, IR, NMR). Quantitative analysis was carried out by GC (PEG 20M on Celite and Porapak T), using the internal standard method.

Results

A catalyst screening was made first by using many kinds of transition metal complexes, in order to discover an effective catalyst for the title reaction. As a result, $\operatorname{RuH}_2(\operatorname{PPh}_3)_4$, I, was found to be a unique effective catalyst among the complexes tested, although the reaction conditions used may not have been adequate for catalyst screening. Other catalysts, for example RuH-(CO)(PPh₃)₃, showed some activity but gave very poor results, mainly catalyzing the decomposition of methyl formate.

The reaction conditions and the results for esterification of olefins by methyl formate using complex I are summarized in Table 1. Inspection of Table 1 reveals that when ethylene was allowed to react with methyl formate at elevated temperature in the presence of I, methyl propionate was formed, the amount corresponding to more than five times of the amount of catalyst (run 2). This result and the fact that no esterification occurred in the absence of catalyst, imply that the reaction is catalytic. The yield of product, however, did not improve even when the reaction time was longer (runs 5 and 6). This suggests that the catalyst was either decomposed or transformed to metal or other complex at the beginning of the reaction.

Replacing ethylene by propylene or 1-butene leads to low yields of the corresponding ester. Though two isomers (iso- and normal-) of product can be formed, the normal isomer is predominant in both cases (runs 5 - 11). 1-Hexene does not react (run 12). The yield of methyl propionate was dependent on the solvent used (runs 1, 2, 3). This might be due to the solubility of ethylene; the solubilities of ethylene in benzene, methanol and THF at 25 °C under 1 atm of ethylene are 1.4, 0.8 and 1.3×10^{-4} mol cm⁻³ solvent, respectively.

In the IR analysis of the Ru complex used for the reaction, a strong band was observed at 1896 cm⁻¹. The same band also appeared when methyl formate alone was allowed to react with I at 120 °C. Methanol, hydrogen and trace amounts of CO₂ and methane were also formed in this reaction. Similar results were reported by Keister and Gentle [6].

Since $\operatorname{Ru}(\operatorname{CO})_3(\operatorname{PPh}_3)_2$, III, has a CO stretching band at 1895 cm⁻¹ [7], Ru complex I seems to be converted to III by the reaction with methyl

TABLE 1

Esterification of olefins with methyl formate using $RuH_2(PPh_3)_4$ catalyst

	n:iso	1	I	-	I	92:8	93:7	82:18	85:15	100:0	95:5	92:8	-	
Yield of ester	Product/I	2.4	5.4	0.4	no reaction	0.8	1.1	0.8	1.0	0.2	0.3	0.1	no reaction	
Time	Time (h)		23	15	20	1	16	37	15	37	15	60	24	
Temp.	Temp. (°C)		06	06	25	06	06	06	06	100	100	100	160	
Solvent		benzene	THF	methanol	THF	benzene	benzene	THF	methanol	benzene	THF	methanol	THF	
Methyl formate	1	128	128	128	123	157	128	126	128	66	128	103	2	A CONTRACT AND A CONTRACTACT AND A CONTRACTACT AND A CONTRACTACT AND A
Olefin ^a		ethylene	ethylene	ethylene	ethylene	propylene	propylene	propylene	propylene	1-butene	1-butene	1-butene	1-butene	
Run		1	5	e S	4	5 2	9	7	80	6	10	11	12	

^aThe pressures of ethylene, propylene and 1-butene at standard reaction conditions were 40, 40 and 15 kg cm⁻², respectively.

formate through pathway 1 in Scheme 2 when olefin is absent from the reaction system. This reaction might be the deactivation process, because carbonyl complexes were found to be inactive for the title reaction from the catalyst screening. Complex II was assumed as the most plausible intermediate by analogy with the intermediate in the reaction of $trans-Mo(N_2)$ -(PPh₂CH₂CH₂PPh₂) with formate [4]. When olefin is present in the reaction system, it may react with complex II and then ester may form via pathway 2.



Scheme 2.

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