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Journal of Molecular Catalysis A: Chemical 137 (1999) 253–262

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

$Ru_3(CO)_{12}$/1,10-phenanthroline-catalyzed hydroformylation of styrene and acrylic esters

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Received 24 October 1997; accepted 21 February 1998

Abstract

The $Ru_3(CO)_{12}$/1,10-phenanthroline-catalyzed hydroformylation of styrene under 100 atm of syngas ($CO:H_2 = 1:1$) at 120°C in DMF gives the corresponding branched and linear aldehydes in 58 and 22% yields, respectively. With the use of quinuclidine as a ligand in place of 1,10-phenanthroline in *N,N*-dimethylacetamide, the corresponding branched and linear oxo-alcohols were obtained in 53 and 28% yields, respectively. Hydroformylation of methyl acrylate by a catalyst system of $Ru_3(CO)_{12}$/1,10-phenanthroline to afford 4-methoxy-4-methyl-δ-valerolactone **1** in 31% yield, while the catalyst system of $Ru_3(CO)_{12}/PPh_3$ yields the open-chain aldehyde, dimethyl 2-formyl-2-methylglutarate (**3**), which is the precursor of lactone **1** in 18% yield. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Acrylic ester; Hydroformylation; Ruthenium; Styrene

1. Introduction

The oxo process is one of the most important processes in the chemical industry. Homogeneous cobalt- and rhodium-based catalysts are employed in this process. Recently, ruthenium complex-catalyzed hydroformylation has been extensively studied [1–39]. In our previous paper, we reported the hydroformylation of α-olefins using a novel, versatile and highly efficient catalyst system, $Ru_3(CO)_{12}$/1,10-phenanthroline in amide solvents [39]. For example, propylene was hydroformylated under 80 atm of syngas ($CO:H_2 = 1:1$) at 130°C in *N,N*-dimethylacetamide to give C_4-aldehydes in high yield (93%) with high linearity (*n*-selectivity = 95%). In the case of hydroformylation of 1-octene at 120°C, the corresponding C_9-aldehydes were obtained in moderate yield (55%) with high linearity (*n*-selectivity = 95%). We now report the hydroformylation of functionalized alkenes such as styrene and acrylic esters catalyzed by $Ru_3(CO)_{12}$/1,10-phenanthroline.

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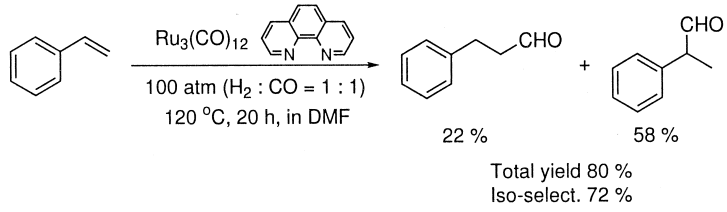
PII: S1381-1169(98)00078-8

2. Results and discussion

2.1. Hydroformylation of styrene

Styrene was hydroformylated under 100 atm of syngas ($CO:H_2 = 1:1$) at 120°C in the presence of a catalytic amount of $Ru_3(CO)_{12}$ and 1,10-phenanthroline in DMF to give the corresponding aldehydes in total 80% yield with *iso*-selectivity of 72%.



(1)

This reaction proceeded efficiently in the presence of 1,10-phenanthroline ligand in amide solvents as observed in the hydroformylation of propylene [39]. In toluene, hydrogenation of styrene to ethylbenzene considerably proceeded (Table 1, Run 2).

The effect of the reaction temperature on the hydroformylation of styrene is shown in Fig. 1. As the reaction temperature increased, total yield of aldehydes also increased, while the *iso*-selectivity (*iso*-selectivity % = 100 × 2-phenylpropanal/(2-phenylpropanal + 3-phenylpropanal) %) slightly decreased.

The effect of CO pressure on the hydroformylation of styrene is summarized in Fig. 2. When P_{H_2} was kept at 50 atm, the *iso*-selectivity was gradually increased with the increase of CO pressure. However, further increase of CO pressure over 60 atm caused a rapid decrease of the total yield of aldehydes. This tendency is quite similar to that observed in the hydroformylation of α-olefins reported for the catalyst system of $Ru_3(CO)_{12}$/1,10-phenanthroline [39].

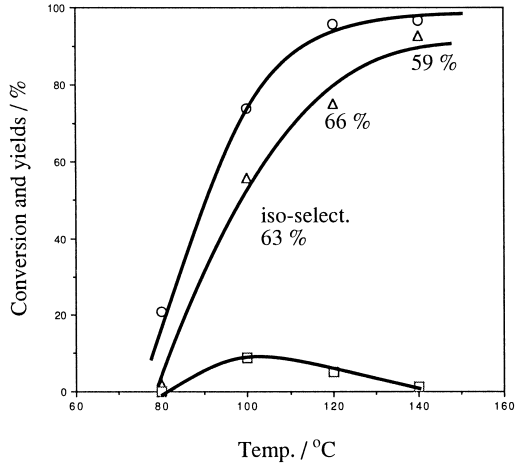
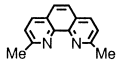
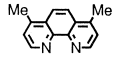
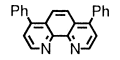
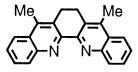
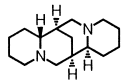
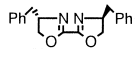


Fig. 1. Effect of temperature on hydroformylation of styrene. Reaction conditions; styrene 10 mmol, $Ru_3(CO)_{12}$ 0.10 mmol, 1, 10-phenanthroline 1.5 mmol, and DMAc 5.0 ml under H_2 50 atm, CO 50 atm for 20 h. Conversion of styrene (○), yield of phenylpropanals (△), yield of phenylpropanols (□).

Table 1
Ligand effect on ruthenium-catalyzed hydroformylation of styrene[a]

Run	Ligand	Conv.(%)	Aldehyde[b]		Alcohol[b]		Ethylbenzene[b]
			yield(%)	iso select.(%)	yield(%)	iso select.(%)	
1	——	99	35	54	18	45	49
2[c]	——	96	46	60	9	68	35
3		96	76	66	4	74	3
4[d]		98	80	72	7	61	8
5[d]		96	72	57	11	84	4
6		96	71	64	10	71	9
7		88	50	64	5	80	13
8		91	54	63	11	58	27
9[d]		96	70	50	14	63	13
10[d]		83	56	47	11	78	13
11		99	25	53	9	100	37
12[d]		94	66	45	8	54	17
13		99	39	66	41	70	4
14		85	4	45	81	66	3
15	NEt_3	91	49	62	26	64	3
16	$(DHQD)_2$ PHAL	100	32	64	7	100	25
17		82	45	73	6	70	12

[a] $Ru_3(CO)_{12}$ 0.10 mmol, styrene 10 mmol, DMAc (*N*,*N*-Dimethylacetamide) 5.0 ml, ligand (Ru/N = 1/10), CO 50 atm, H_2 50 atm, 120°C, 20 h. [b] GLC yields. [c] Solvent; toluene 5.0 ml. [d] Solvent; DMF 5.0 ml.

The effect of H_2 pressure is also examined (Fig. 3). When P_{CO} was kept at 50 atm, the selectivity of the aldehydes is not sensitive to H_2 pressure from 30 to 70 atm and almost constant, while total yield of aldehydes slightly increased.

Time dependence of the hydroformylation of styrene is shown in Fig. 4. Laine reported that in the early stage of the hydroformylation of 1-pentene catalyzed by $Ru_3(CO)_{12}$ or $H_4Ru_4(CO)_{12}$ under water–gas shift reaction conditions, *n*-selectivity was very high (> 97%), then the *n*-selectivity

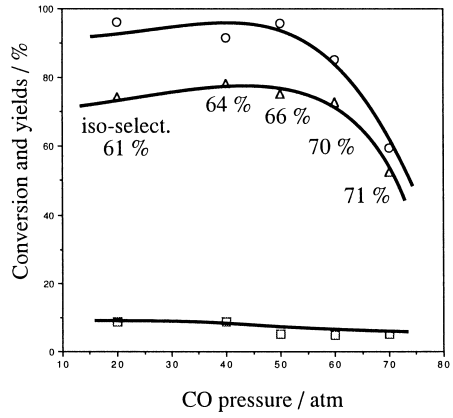


Fig. 2. Effect of CO pressure on hydroformylation of styrene. Reaction conditions; styrene 10 mmol, $Ru_3(CO)_{12}$ 0.10 mmol, 1, 10-phenanthroline 1.5 mmol, and DMAc 5.0 ml under H_2 50 atm, at 100°C for 20 h. Conversion of styrene (○), yield of phenylpropanals (△), yield of phenylpropanols (□).

decreased rapidly with the increase of olefin conversion [14]. In our catalyst system, this tendency of the decrease of the selectivity was not observed.

In the present hydroformylation reaction, the presence of nitrogen-ligands was essential. The effect of several nitrogen-ligands was examined and summarized in Table 1.

In the absence of nitrogen-ligands, a considerable amount of hydrogenated product, ethylbenzene, was obtained and the yield of aldehydes was quite low (Runs 1 and 2). When 1,10-phenanthroline was employed as a ligand (Run 3), hydrogenation of styrene was almost completely suppressed, and the reasonable yield of aldehydes was obtained. With aliphatic tertiary amines (Runs 13–15), further hydrogenation of the generated oxo-aldehydes to oxo-alcohols proceeded and, especially, with quinuclidine ligand, the oxo-alcohols were obtained as a main product (Run 14).

Time dependence of the hydroformylation of styrene catalyzed by $Ru_3(CO)_{12}$ with 10-fold amount

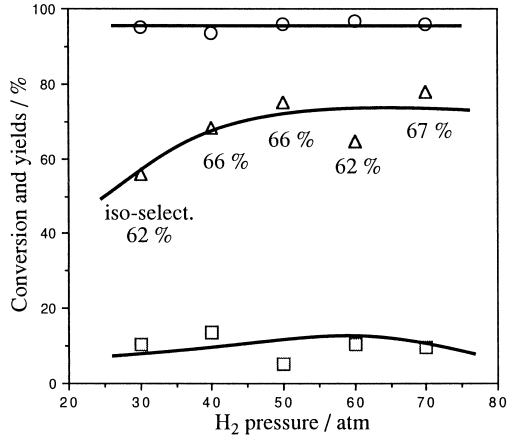


Fig. 3. Effect of H_2 pressure on hydroformylation of styrene. Reaction conditions; styrene 10 mmol, $Ru_3(CO)_{12}$ 0.10 mmol, 1, 10-phenanthroline 1.5 mmol, and DMAc 5.0 ml under CO 50 atm at 120°C for 20 h. Conversion of styrene (○), yield of phenylpropanals (△), yield of phenylpropanols (□).

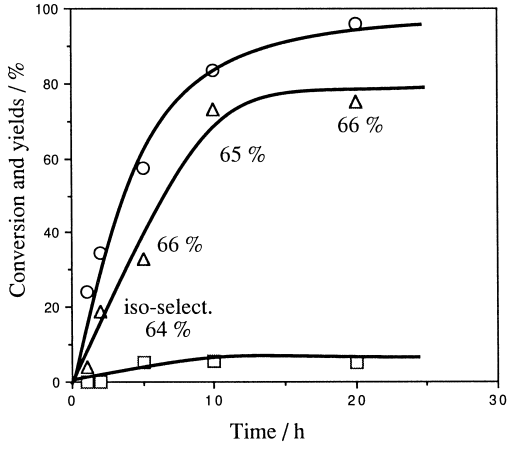


Fig. 4. Effect of reaction time on $Ru_3(CO)_{12}$ /1,10-phenanthroline-catalyzed hydroformylation of styrene. Reaction conditions; styrene 10 mmol, $Ru_3(CO)_{12}$ 0.10 mmol, 1, 10-phenanthroline 1.5 mmol, and DMAc 5.0 ml under H_2 50 atm, CO 50 atm at 120°C. Conversion of styrene (○), yield of phenylpropanals (△), yield of phenylpropanols (□).

of quinuclidine is shown in Fig. 5, which clearly indicates that aldehydes formed in the early stage of the reaction were consecutively reduced into the corresponding alcohols.

2.2. High-pressure IR study

After the hydroformylation of styrene (Run 3 in Table 1), the IR spectrum of the reaction mixture was measured at room temperature under an argon atmosphere. This simple IR measurement, however, showed the existence of $[HRu_3(CO)_{11}]^-$ [40,41] (ν_{CO}: 2074 (vw), 2016 (vs), 1989 (s) and 1953 (m) cm^{-1}) as a sole complex, and no ruthenium carbonyl species containing 1,10-phenanthroline ligand can be observed. Therefore, in order to investigate the real active species under the

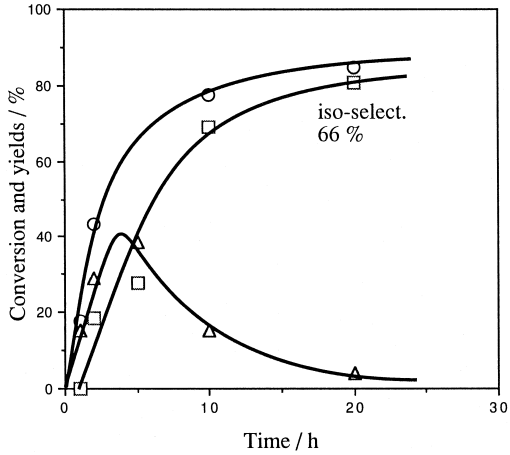


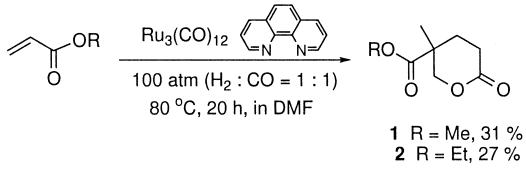
Fig. 5. Effect of reaction time on $Ru_3(CO)_{12}$ /quinuclidine-catalyzed hydroformylation of styrene. Reaction conditions; styrene 10 mmol, $Ru_3(CO)_{12}$ 0.10 mmol, quinuclidine 3.0 mmol, and DMAc 5.0 ml under H_2 50 atm, CO 50 atm at 120°C. Conversion of styrene (○), yield of phenylpropanals (△), yield of phenylpropanols (□).

hydroformylation conditions, the following high pressure IR study was carried out. Namely, IR spectrum of the mixture of $Ru_3(CO)_{12}$ and 1,10-phenanthroline in *N*-methylpyrrolidone in the absence of styrene was measured under 100 atm of syngas ($CO:H_2 = 1:1$) at 80–120°C. In contrast, a new strong and broad absorption band at 1967 cm^{-1} was observed besides the weak absorption bands (2016 (vw) and 1991 (vw) cm^{-1}) attributed to $[HRu_3(CO)_{11}]^-$, which indicates the formation of a new ruthenium carbonyl species together with a small amount of $[HRu_3(CO)_{11}]^-$. This absorption at 1967 cm^{-1} is characteristic and always observed at early stage in the 1,10-phenanthroline system, strongly suggesting the *pre*-coordination of 1,10-phenanthroline to ruthenium. While the temperature was held at 120°C for 2 h, additional new absorptions at 2013 (s) and 1988 (m) cm^{-1} appeared as well as those observed at 2016 (s), 1991 (m) and 1967 (m) cm^{-1}, which strongly suggests the formation of a ruthenium carbonyl species having a 1,10-phenanthroline ligand such as (1,10-phenanthroline)$Ru_3(CO)_9$ [42]. [1] No further change of the spectrum was observed at 150°C.

In the presence of quinuclidine in place of 1,10-phenanthroline, similar changes in IR spectra were observed. At room temperature under 100 atm of syngas ($CO:H_2 = 1:1$), the absorptions at 2060 (s), 2015 (vs) and 1989 (s) cm^{-1} were observed. At 80°C, the only absorption at 2060 cm^{-1} disappeared, but the other two absorptions attributed to $[HRu_3(CO)_{11}]^-$ remained even at 120°C. However, new absorptions at 2013 (s) and 1991 (m) cm^{-1} appeared as well as those of $[HRu_3(CO)_{11}]^-$ during 1 h at 120°C. No additional change was observed between 120°C and 150°C. These new absorptions at 2013 (s) and 1991 (m) cm^{-1} can also be attributed to a quinuclidine-coordinated ruthenium carbonyl species. The results obtained in 1,10-phenanthroline and quinuclidine systems are very similar. Consequently, the coordination of the nitrogen-ligand to $Ru_3(CO)_{12}$ apparently occurred, and is essential in the present hydroformylation reaction. This is the reason why both the catalytic activity and product selectivity are highly affected by the nitrogen-ligands such as 1,10-phenanthroline and quinuclidine.

2.3. Hydroformylation of acrylic esters

Methyl acrylate and ethyl acrylate were hydroformylated under 100 atm of syngas ($CO:H_2 = 1:1$) at 80°C in the presence of a catalytic amount of $Ru_3(CO)_{12}$ and 1,10-phenanthroline in DMF to give 4-alkoxy-4-methyl-δ-valerolactone **1** and **2** in 31 and 27% yield, respectively.

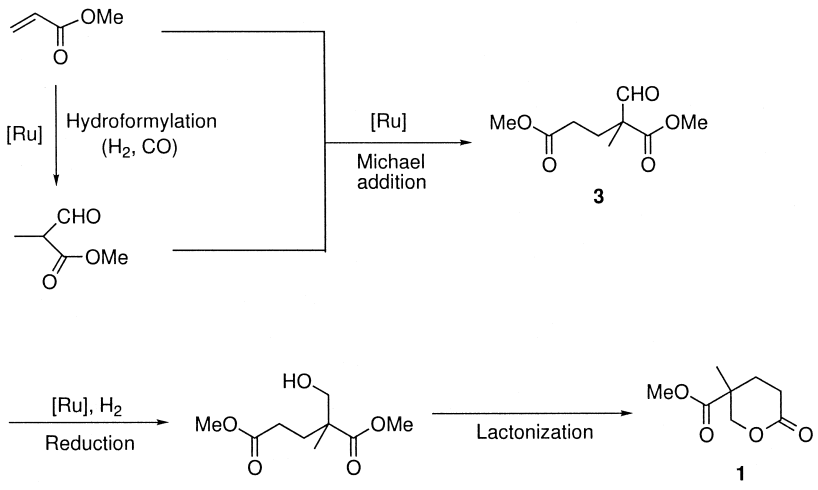


1 R = Me, 31 %
2 R = Et, 27 %

(2)

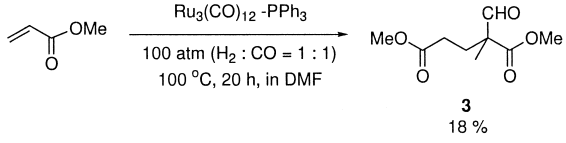
Simple hydrogenation of the substrates is a serious side reaction, and considerable amounts of methyl or ethyl propionate were obtained as a by-product. With the catalyst system of

[1] The following experiment using Ru(cod)(cot)/1,10-phenanthroline catalyst in place of $Ru_3(CO)_{12}$/1,10-phenanthroline catalyst gave the additional important information about the catalytic intermediate. The result of the hydroformylation of styrene by Ru(cod)(cot)/1,10-phenanthroline catalyst (total yield of aldehydes, 56%; *iso*-selectivity, 71%) was similar to those by $Ru_3(CO)_{12}$/1,10-phenanthroline catalyst. In addition, IR spectra of the catalyst solutions derived from Ru(cod)(cot) and $Ru_3(CO)_{12}$ showed the same metal carbonyl stretching vibrations attributed to $[HRu_3(CO)_{11}]^-$. These results suggest that the common ruthenium carbonyl species containing 1,10-phenanthroline ligand is generated from either Ru(cod)(cot) or $Ru_3(CO)_{12}$, and after the reaction, it was recovered as a $[HRu_3(CO)_{11}]^-$. At this stage, the possibility that the highly active mononuclear ruthenium carbonyl species generated in a small amount works as a real active species can not be ruled out completely, although all the detected ruthenium carbonyl species by IR measurement were trinuclear.



Scheme 1.

$Ru_3(CO)_{12}/PPh_3$, hydroformylation of methyl acrylate at 100°C affords the open-chain aldehyde **3** in 18% yield.



(3)

In each case, simple hydroformylated products such as methyl-2-formylpropionate and methyl-1-formylpropionate were not obtained at all.

Tanaka et al. reported that hydroformylation of ethyl acrylate catalyzed by $PPN[HRu(CO)_4]$ gave the mixture of ethyl 2-formylpropionate, ethyl 2-(hydroxymethyl)propionate, 4-ethoxy-4-methyl-δ-valerolactone and diethyl 2-formyl-2-methylglutarate under 300 atm of syngas at 100°C [29]. In our system, even though the yields of **1**, **2**, and **3** were still low, a sole carbonylated product was obtained in each reaction by choosing the appropriate catalyst system ($Ru_3(CO)_{12}$/1,10-phenanthroline and $Ru_3(CO)_{12}/PPh_3$).

The possible mechanism of the formation of 4-methoxy-4-methyl-δ-valerolactone **1** from methyl acrylate under the hydroformylation conditions is illustrated in Scheme 1. First, methyl 2-formylpropionate was formed by the simple hydroformylation of methyl acrylate. The successive Michael addition between methyl acrylate and methyl 2-formylpropionate took place to give dimethyl 2-formyl-2-methylglutarate **3**. Further reduction of formyl functionality in **3** and the following lactonization yielded 4-methoxy-4-methyl-δ-valerolactone **1**.

3. Conclusion

The $Ru_3(CO)_{12}$/1,10-phenanthroline-catalyzed hydroformylation of styrene under 100 atm of syngas ($CO:H_2 = 1:1$) at 120°C in DMF gives the corresponding branched and linear aldehydes in 58 and 22% yields, respectively. With the use of quinuclidine as a ligand in place of 1,10-phenanthroline

in *N,N*-dimethylacetamide, the corresponding branched and linear oxo-alcohols were obtained in 53 and 28% yields, respectively.

The δ-valerolactones, **1** and **2**, were obtained in 31% and 27% yields, respectively, in the hydroformylation of acrylic esters by $Ru_3(CO)_{12}$/1,10-phenanthroline catalyst. With $Ru_3(CO)_{12}/PPh_3$ catalyst, the open-chain aldehyde **3**, which is the precursor of lactone **1**, was obtained in 18% yield.

4. Experimental

4.1. General methods

The reagents employed in this study were commercial materials and were used without further purification except for methyl acrylate, triethylamine, pyridine and solvents, which were dried and distilled before use. The GLC analyses were performed on a Shimadzu GC-8A gas chromatograph with a glass column (2.8 mm i.d.× 3 m) packed with silicone OV-17 (2% Chromosorb W (AW DMCS), 60–80 mesh) and a Shimadzu GC-14A gas chromatograph with Shimadzu Capillary Column CBP20-S25-050. IR spectra were measured on a Shimadzu FTIR-8100 spectrometer. The ^{1}H-NMR spectra were recorded at 400 MHz. ^{13}C-NMR spectra were recorded at 100 MHz. Samples were analyzed in $CDCl_3$, and the chemical shift values are expressed relative to Me_4Si as an internal standard. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A mass spectrometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University.

4.2. Ruthenium-catalyzed hydroformylation of styrene

In a 50-ml stainless steel autoclave (Yuasa Giken; SUS 316) were placed $Ru_3(CO)_{12}$ (0.064 g, 0.10 mmol), 1,10-phenanthroline (0.27 g, 1.5 mmol), styrene (1.0 ml, 10 mmol) and solvent (5.0 ml). After CO (50 atm) and H_2 (50 atm) were introduced at 25°C, the mixture was heated to 120°C and held at this temperature for 20 h with stirring. GLC analyses showed that 2-phenylpropanal and 3-phenylpropanal were obtained in 58 and 22% yields, respectively.

4.3. Ruthenium-catalyzed hydroformylation of acrylic esters

*4.3.1. 4-Methoxy-4-methyl-δ-valerolactone (**1**)*

In a 50-ml stainless steel autoclave were placed $Ru_3(CO)_{12}$ (0.064 g, 0.10 mmol), 1,10-phenanthroline (0.24 g, 1.33 mmol), DMF (5.0 ml), and methyl acrylate (10 mmol). After CO (50 atm) and H_2 (50 atm) were introduced at 25°C, the mixture was magnetically stirred at 80°C for 20 h. Kugelrohr distillation of the reaction mixture under reduced pressure afforded 4-methoxy-4-methyl-δ-valerolactone **1** (31%).

Colorless liquid: bp 110–120°C (1.0 mmHg, Kugelrohr); IR (neat) 1732, 1739 (C=O) cm^{-1}; ^{1}H NMR (400 MHz) δ 1.30 (s, 3H), 1.76–1.84 (m, 1H), 2.38–2.45 (m, 1H), 2.58–2.63 (m, 1H), 3.76 (s, 3H), 4.08 (d, $J = 11.2$ Hz, 3H), 4.60 (dd, $J = 2.0$ and 11.2 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz) δ 21.6, 27.1, 28.8, 41.0, 52.3, 73.8, 170.3, 174.3. Exact mass calcd for $C_8H_{12}O_3$: 172.0736. Found: 172.0736.

*4.3.2. Dimethyl 2-formyl-2-methylglutarate (**3**)*

In a 50-ml stainless steel autoclave were placed $Ru_3(CO)_{12}$ (0.064 g, 0.10 mmol), PPh_3 (0.078 g, 0.30 mmol), DMF (5.0 ml), and methyl acrylate (10 mmol). After CO (50 atm) and H_2 (50 atm) were

introduced at 25°C, the mixture was magnetically stirred at 100°C for 20 h. Kugelrohr distillation under reduced pressure gave dimethyl 2-formyl-2-methylglutarate **3** (18%).

Colorless liquid: bp 110–120°C (1.0 mmHg, Kugelrohr); IR (neat) 1727, 1742 (C = O) cm^{-1}; ^{1}H NMR (400 MHz) δ 1.30 (s, 3H), 2.05–2.49 (m, 4H), 3.68 (s, 3H), 3.77 (s, 3H), 9.68 (s, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz) δ 17.1, 28.6, 29.5, 51.7, 52.6, 56.7, 172.1, 172.9, 198.5. Anal. Calcd for $C_9H_{14}O_4$: C, 53.46; H, 6.98. Found: C, 53.53; H, 7.23.

Acknowledgements

This work was supported in part by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Science and Culture. The authors thank Professor K. Komatsu and Dr. K. Kudo for taking a FT-IR spectrum under high pressure.

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