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Synthesis of malonic esters by the catalytic addition of methyl formate to α,β-unsaturated esters

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Abstract

Addition of methyl formate to α,β-unsaturated methyl esters was catalyzed by $Ru_3(CO)_{12}$ to form substituted dimethyl malonates concurrent with small amounts of succinates. A reaction mechanism is proposed which includes an α-methoxycarbonylalkyl complex as the major key intermediate.

Keywords: Methyl formate; Ruthenium; Substituted malonate; α,β-Unsaturated methyl esters

1. Introduction

The catalytic carbonylation of olefins has been recognized as one of the most synthetically important reactions and extensive studies have therefore been done in order to design catalytic systems which achieve high activity and selectivity [1–3]. Nevertheless carbonylation of certain substrates has ended in unsatisfactory results. One such example is the catalytic carbonylation of acrylic acid or acrylates at the α-position to give malonic acid derivatives. Recently Brunet et al. reported the first regioselective catalytic carbonylation of potassium or calcium acrylate to give methylmalonate [4], but the catalytic carbonylation of acrylic acid esters was claimed to be unsuccessful.

On the other hand, the catalytic addition of methyl formate to olefins is quite attractive because methyl formate is an inexpensive raw material and easy to handle, and the reaction provides a synthetically equivalent route to the hydroesterification of olefins with CO and MeOH [5–9]. However, investigation of this reaction has so far been limited to those of unfunctionalized olefins such as ethylene and cyclohexene. Therefore it is interesting to investigate whether the addition of methyl formate to α,β-unsaturated esters is applicable as a synthetic method for substituted malonates which can hardly be obtained by the conventional hydroesterification with CO and MeOH. These backgrounds as well as our continuous interest in catalytic carbonylation reactions [10–13] have prompted us to study the catalytic addition of methyl formate to α,β-unsaturated esters. We wish here to describe the results of this reaction catalyzed by $Ru_3(CO)_{12}$.

2. Results and discussion

Several ruthenium and rhodium complexes have been reported as active catalysts for the addi-

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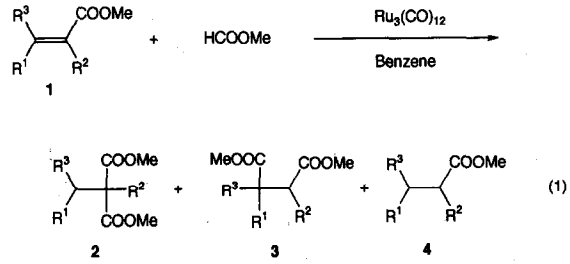
Table 1
Effects of catalysts for the addition of methyl formate to **1a** [a]

Run no.	Catalyst	Conversion (%) [b]	Yield (%) [b]	
			2a	**3a**
1	$Ru_3(CO)_{12}$	100	60	13
2	$Ru(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$	100	53	13
3	$RuCl_2(PPh_3)_3$	0	0	0
4	$RuH_2(PPh_3)_4$	0	0	0
5	$RhCl(PPh_3)_3$	20	0	0
6	$[RhCl(CO)_2]_2$	16	0	0
7	$Rh_4(CO)_{12}$	30	0	0
8	$Co_2(CO)_8$	0	0	0
9	$Fe_3(CO)_{12}$	n.d.	0	0
10	$Fe_2Cp_2(C)_4$	16	0	0

[a] Reaction conditions: methyl formate (84 mmol), **1a** (12 mmol), catalyst (0.45 mmol as metal atom), benzene (5 ml), CO (20 $kg \cdot cm^{-2}$ at room temp.), react. temp. (170 °C), react. time (20 h).
[b] Determined by GLC and based on the amount of **1a** charged.

tion of formates to olefins [5–9]. Therefore we started to employ those complexes as catalysts for the addition of methyl formate to methyl acrylate (**1a**). The results with various metal complex catalysts at 170°C under an initial CO pressure of 20 $kg \cdot cm^{-2}$ are summarized in Table 1. Among them, $Ru_3(CO)_{12}$ afforded the highest yield of dimethyl methylmalonate (**2a**, 60%) accompanied by formation of a minor amount of dimethyl succinate (**3a**, 13%) (Eq. 1).



(1)

The activity observed with $Ru(\eta^6\text{-}C_6H_6)(\eta^4\text{-}1,3\text{-}C_6H_8)$ was comparable to that of $Ru_3(CO)_{12}$, whereas ruthenium phosphine complexes and other transition metal carbonyl complexes showed no activities for this reaction.

Effects of the reaction conditions tabulated in Table 2 indicate that a reaction temperature of 170°C and CO pressure of 20 $kg \cdot cm^{-2}$ are optimal with respect to the activity and selectivity for the formation of **2a**. Higher temperatures slightly decreased the selectivity. Appropriate CO pressure is essential for this reaction. Thus, lower pressures than 20 $kg \cdot cm^{-2}$ decreased both the yield and the selectivity of **2a**, whereas higher pressures lowered the reaction rate. As a solvent, THF, hexane, and ether can be used without substantial decrease in the yield of **2a**, but DMF and acetonitrile were not suitable for this reaction.

Watanabe et al. reported that the addition of $Me_3NO \cdot 2H_2O$ considerably enhanced the catalytic activity of $Ru_3(CO)_{12}$ for the reaction of cyclohexene with benzyl formate [5]. On the other hand, we previously revealed that iodides are effective additives for the $Ru_3(CO)_{12}$-catalyzed carbonylation of olefins [11]. In the present study, effects of several additives were examined by using **1a** as the substrate. However, $Me_3NO \cdot 2H_2O$, MeI, and PPh_3 seriously decreased the yield of **2a**, while Me_4NI lowered the selectivity of the reaction to **2a** with little change in the total yield of **2a** and **3a** (Table 3). Thus, $Ru_3(CO)_{12}$ catalyst without additives is preferable in the reactions of α,β-unsaturated esters and methyl formate.

The results of the catalytic addition of methyl formate to other α,β-unsaturated esters are sum-

Table 2
Effects of reaction conditions on the $Ru_3(CO)_{12}$-catalyzed addition of methyl formate to **1a** [a]

Run no.	Temp. (°C)	CO ($kg \cdot cm^{-2}$)	Conversion (%)[b]	Yield (%) [b]	
				2a	**3a**
1	160	20	60	38	6
2	170	20	100	60	13
3	180	20	100	58	18
4	190	20	100	58	17
5	200	20	100	54	17
6	170	0	62 [c]	<1	<1
7	170	10	100	38	15
8	170	15	100	43	14
9	170	20	100	60	13
10	170	25	88	57	12
11	170	30	73	45	9

[a] Reaction conditions: methyl formate (84 mmol), **1a** (12 mmol), $Ru_3(CO)_{12}$ (0.15 mmol), benzene (5 ml), react. time (20 h).
[b] Determined by GLC and based on the amount of **1a** charged.
[c] Methyl propionate 51%.

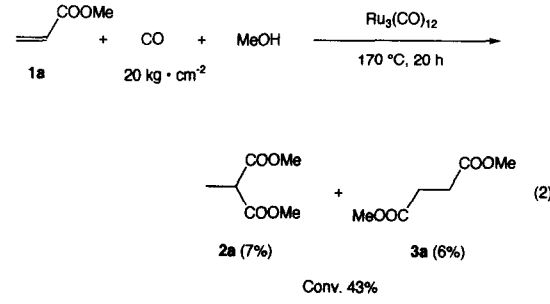
Table 3
Effects of additives [a]

Run no.	Additive	Conversion (%) [b]	Yield (%) [b]	
			2a	3a
1	none	100	60	13
2	$Me_3NO \cdot 2H_2O$	100	0	0
3	PPh_3	21	3	0
4	MeI	97	17	1
5	Me_4NI	97	52	26

[a] Reaction conditions: methyl formate (84 mmol), **1a** (12 mmol), $Ru_3(CO)_{12}$ (0.15 mmol), additive (1 mmol), benzene (5 ml), CO (20 kg·cm^{-2} at room temp.), react. temp. (170 °C), react. time (20 h).
[b] Determined by GLC and based on the amount of **1a** charged.

marized in Table 4. In all runs except for the reaction of methyl methacrylate, the substituted malonates were obtained as the major products, although in some cases more drastic reaction conditions than those for methyl acrylate were required to achieve the high conversion. Methyl methacrylate gave dimethyl methylsuccinate as the main product probably because of the steric hindrance at the α-carbon. In the case of methyl crotonate, dimethyl glutarate was produced as a side product by way of the C=C double bond migration to methyl 3-butenoate.

It has been known that $Ru_3(CO)_{12}$ is an effective catalyst for the decarbonylation of methyl formate to methanol [14] and $Ru_3(CO)_{12}$-based catalyst systems are active in the hydroesterification of olefins with CO and alcohols [11,15–17]. Therefore the decarbonylation of methyl formate may be involved in the present catalytic synthesis of alkylmalonates. Watanabe also suggested the participation of such decarbonylation in the catalytic reaction of alkyl formates with cyclohexene [5]. In order to obtain information about this point, the hydroesterification of **1a** with CO and methanol by $Ru_3(CO)_{12}$ was attempted (Eq. 2).

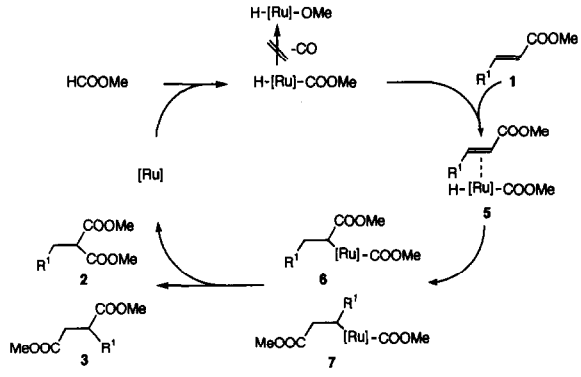


However, the yields of **2a** and **3a** from a reaction at 170°C under an initial CO pressure of 20 kg·cm^{-2} for 20 h were only 7% and 6%, respectively, which were much lower than in the catalytic addition of methyl formate to **1a** under the same conditions. This result indicates that the decarbonylation of methyl formate is not involved in the catalytic cycle of the present alkylmalonates synthesis. At present, we assume the catalysis proceeds via the oxidative addition of the formyl C–H bond to an active ruthenium species such as $Ru(CO)_4$, the insertion of the C=C bond of **1** into

Table 4
$Ru_3(CO)_{12}$-catalyzed addition of methyl formate to **1** [a]

Run	Substrate				Temp.	Time	Conversion	Yield (%) [b]		
	R^1	R^2	R^3		(°C)	(h)	(%) [b]	2	3	4
1	H	H	H	(**1a**)	170	20	100	60	13	n.d.
2 [c]	Me	H	H	(**1b**)	185	48	82	48	8	11
3	H	Me	H	(**1c**)	200	48	92	4	69	14
4	Ph	H	H	(**1d**)	200	48	59	32	4	18
5	CO_2Me	H	H	(**1e**)	170	20	98	74	–	12
6	H	H	CO_2Me	(**1f**)	170	20	90	68	–	10
7	CH_2CO_2Me	H	H	(**1g**)	185	48	100	68	3	25

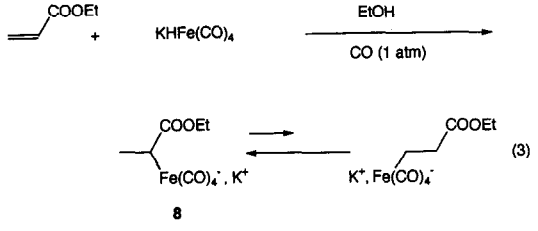
[a] Reaction conditions: methyl formate (84 mmol), **1** (12 mmol), $Ru_3(CO)_{12}$ (0.15 mmol), benzene (5 ml), CO (20 kg·cm^{-2} at room temperature).
[b] Determined by GLC and based on the amount of **1** charged.
[c] Dimethyl glutarate was formed in 8% yield.



Scheme 1. [Ru] = active ruthenium species. R^2 and R^3 in **1**, **2**, and **3** are omitted for clarity.

the Ru–H bond in complex **5** to give complexes **6** or **7**, and the reductive elimination of **2** or **3** from **6** or **7**, respectively (Scheme 1). The high CO pressure might be necessary in order to prevent the degradation of the methoxycarbonyl complex to the methoxo complex.

According to the mechanism, the insertion mode of **1** into the Ru–H bond should determine the selectivity between the products **2** and **3**. A related insertion reaction of acrylates into the Fe–H bond in $[HFe(CO)_4]^-$ has been studied repeatedly [18–21], and the α-alkoxycarbonylethyl complex **8** has been concluded to be the predominant product (Eq. 3).



This fact strongly suggests that the insertion of **1** into the Ru–H bond in **5** also gives the α-methoxycarbonylalkyl complex **6** as the major intermediate. The reductive elimination from **6** results in the predominant formation of **2**. It should be pointed out that the CO insertion into the metal–carbon bonds in α-alkoxycarbonylalkyl complexes is known to be often difficult due to the metal–carbon bond strengthening caused by the electron-withdrawing alkoxycarbonyl group [18]. This is probably the major reason why the conventional hydroesterification of α,β-unsaturated esters has failed to give substituted malonates. In contrast, CO insertion into the Ru–C bond in complex **6** is not necessary in the present catalytic addition of methyl formate, and this mechanistic difference from the hydroesterification has enabled the α-methoxycarbonylation of **1**.

In conclusion, malonic acid esters can be obtained as the major product by the catalytic addition of methyl formate to α,β-unsaturated esters, while the corresponding reaction is difficult to be achieved by the catalytic hydroesterification. The present study has shown that the catalytic addition of formates can be considered not only as a synthetically equivalent reaction to the hydroesterification but also as an alternative which overcomes some limitations of the hydroesterification.

3. Experimental

3.1. General

The organic reagents were commercially obtained and were used as received. The solvents were distilled from appropriate drying agents under N_2. Complexes, $Ru(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$ [22], $[RhCl(CO)_2]_2$ [23], $Rh_4(CO)_{12}$ [24], $Fe_2Cp_2(CO)_4$ [25], $Fe_3(CO)_{12}$ [26], $RuH_2(PPh_3)_4$ [27], $RuCl_2(PPh_3)_3$ [28], and $RhCl(PPh_3)_3$ [29] were prepared by literature methods. $Ru_3(CO)_{12}$ was a commercial product and was recrystallized before use. ^1H NMR spectra were obtained on a JEOL EX-270 spectrometer. IR spectra were recorded on a Shimadzu DR-8000 spectrophotometer. GLC analyses were performed on a Shimadzu GC-14A instrument equipped with a flame ionization detector by using a 25 m × 0.25 mm fused silica capillary column CBP 10.

3.2. Catalytic reactions of α,β-unsaturated esters with methyl formate

The following reaction procedure is representative. Methyl acrylate (12 mmol, 1.03 g), methyl formate (84 mmol, 5.04 g), $Ru_3(CO)_{12}$ (0.15 mmol, 96 mg), and benzene (5 ml) were charged in a 50 ml stainless steel autoclave. The autoclave was pressurized to 20 $kg \cdot cm^{-2}$ with CO at room temperature, and heated to 170°C in an oil bath with magnetic stirring for 20 h. After the reaction the autoclave was rapidly cooled to room temperature and the pressure was released. Decane was added to the reaction mixture as an internal standard, and the GLC analysis of the liquid phase indicated that dimethyl methylmalonate (**2a**) and dimethyl succinate (**3a**) were formed in 60% and 13%, respectively. The products were isolated from the reaction mixture by silica-gel column chromatography (hexane–ether) and bulb to bulb distillation, and were identified by ^1H NMR, IR, and GC/MS.

References

[1] I. Wender and P. Pino, Organic Synthesis via Metal Carbonyls, Vol. 2, Wiley, New York, 1977.

[2] J. Falbe, New Synthesis with Carbon Monoxide, Springer Verlag, New York, 1980.

[3] I. Tkatchenko in G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 8, Pergamon Press, Elmsford, New York, 1982, p. 101.

[4] J.J. Brunet and E. Passelaigue, Organometallics, 9 (1990) 1711.

[5] T. Kondo, S. Yoshii, Y. Tsuji and Y. Watanabe, J. Mol. Catal., 50 (1989) 31.

[6] P. Isnard, B. Denise, R.P.A. Sneeden, J.M. Cognion and P. Durual, J. Organomet. Chem., 256 (1983) 135.

[7] W. Ueda, T. Yokoyama, Y. Morikawa, Y. Moro-oka and T. Ikawa, J. Mol. Catal., 44 (1988) 197.

[8] T.B. Marder, D.C. Roe and D. Milstein, Organometallics, 7 (1988) 1451.

[9] W. Keim and J. Becker, J. Mol. Catal., 54 (1989) 95.

[10] A. Fukuoka, Y. Koyasu, Y. Uchida and M. Hidai, J. Mol. Catal., 35 (1986) 29.

[11] Y. Koyasu, K. Chikanari, Y. Uchida and M. Hidai, J. Mol. Catal., 40 (1987) 243.

[12] Y. Ishii, M. Sato, H. Matsuzaka and M. Hidai, J. Mol. Catal., 54 (1989) L13.

[13] Y. Misumi, Y. Ishii and M. Hidai, J. Mol. Catal., 78 (1993) 1.

[14] G. Jenner, E.M. Nahmed and H. Leismann, J. Organomet. Chem., 387 (1990) 315.

[15] G. Jenner and G. Bitsi, J. Mol. Catal., 40 (1987) 71.

[16] A. Behr, U. Kanne and W. Kein, J. Mol. Catal., 35 (1986) 19.

[17] P. Isnard, B. Denise and R.P.A. Sneeden, J. Organomet. Chem., 240 (1982) 169.

[18] J.J. Brunet and E. Passelaigue, J. Organomet. Chem., 203 (1989) 203.

[19] H. Masada, M. Mizuno, S. Suga, Y. Watanabe and Y. Takegami, Bull. Chem. Soc. Jpn., 43 (1970) 3824.

[20] T. Mitsudo, Y. Watanabe, M. Yamashita and Y. Takegami, Chem. Lett., (1974) 1385.

[21] J.P. Collman, R.G. Finke, P.L. Matlock, R. Wahren, R.G. Komoto and J.I. Brauman, J. Am. Chem. Soc., 100 (1978) 1119.

[22] P. Pertici, G. Vitulli and M. Paci, J. Chem. Soc., Dalton Trans., (1980) 1961.

[23] J.A. McCleverty and G. Wilkinson, Inorg. Synth., 8 (1966) 211.

[24] S. Martinengo, G. Giordano and P. Chini, Inorg. Synth., 20 (1980) 209.

[25] R.B. King and F.G.A. Stone, Inorg. Synth., 7 (1963) 110.

[26] W. McFarlane and G. Wilkinson, Inorg. Synth., 8 (1966) 181.

[27] R. Young and G. Wilkinson, Inorg. Synth., 17 (1977) 75.

[28] P.S. Hallman, T.A. Stephenson and G. Wilkinson, Inorg. Synth., 12 (1970) 237.

[29] J.A. Osborn and G. Wilkinson, Inorg. Synth., 10 (1967) 67.