Chinese Chemical Letters Vol. 15, No. 10, pp 1245-1248, 2004
http://www.imm.ac.cn/journal/ccl.html

Photopromoted Methoxycarbonylation of Olefins Under Ambient Conditions in DMF

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Abstract: Photopromoted methoxycarbonylation of olefins with carbon monoxide can be carried out under ambient conditions with non-precious transition metal complexes (such as cobalt complexes) catalysts in DMF. The isotope experiments show that DMF is decomposed under irradiation and is conveniently used as a carbon monoxide source for the reaction.

Keywords: Photopromoted methoxycarbonylation, carbon monoxide, DMF, isotope experiment.

It is well known that the carbonylation of olefins is an essential reaction to synthesize valuable acid derivatives, which usually requires high temperatures (150-200°C) and high pressure (10-20 MPa) or precious metal complex catalysts (such as Ru, Rh, Ir)[1]. There are many advantages, however, for photopromoted methoxycarbonylations: room temperatures, atmospheric pressure and non-precious metal catalyst[2,3].

Our research shows that both acetone and DMF are good solvent for photopromoted methoxycarbonylation of olefins with CO under ambient conditions. From our previous work[3,4], CH_3OH/CH_3COCH_3 is a good solvent system for methoxycarbonylation to most cobalt complexes, and the addition of acetone can improve the activity of the reaction. We report herein a new method that photopromoted methoxycarbonylation of olefins with CO under ambient conditions can be catalyzed by complexes of non-precious metals, for example cobalt, $Co(OAc)_2$, $CoCl_2$, CoSalen, $Co(en)_3Cl_2$ using DMF in place of acetone as solvent. It was found that DMF can be decomposed under irradiation and used as a carbon monoxide source for the reaction.

Experimental

Carbon monoxide (99.9%, Dalian Guangming Institute); methanol, DMF (AP, Dalian merro Stock Chemical Reagent and Glass Apparatus Co.); *n*-decane (AP, Beijing PHENTEX Chemicals Co., Ltd.); cobalt acetate, cobalt chloride (AP, Shenyang Chemical Reagent Co.); $H^{13}CON(CH_3)_2$ (N,N-Dimethylformamide-carbonyl-^{13}C, 99

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atom% ^{13}C, Aldrich Chem. Co.); 1-octene (97%, Hong Kong Farco Chemical Supplies), cyclohexene (Military Medicine Academy of Sciences Material Supplies).

A typical reaction procedure was as follows: A quartz test tube containing a solution of olefin (100 mmol/L), catalyst (5 mmol/L) in CH_3OH-DMF (V/V=5:1, 6 mL) was irradiated for 20 hours with a high-pressure mercury lamp of 400W (Philips & Yaming Corp.) at room temperature under carbon monoxide at atmospheric pressure. The products were detected by GC retention time and GC-MS.

Results and Discussion

The reactions of cyclohexene and 1-octene with CO are as follows, and the results are shown in **Table 1**.

It can be seen that catalytic activities are of great difference according to the different ligands of cobalt salt. $Co(OAc)_2$ is the best catalyst of the four catalysts used for both cyclohexene and 1-octene. The products formed from 1-octene also involve $CH_3(CH_2)_7CO_2CH_3$, $CH_3(CH_2)_5CH(CH_3)CO_2CH_3$ as well as $CH_3(CH_2)_4CH(C_2H_5)CO_2CH_3$ and $CH_3(CH_2)_3CH(n\text{-}Pr)CO_2CH_3$, which can be explained as the results of double bond shifts during methoxycarbonylation[1,4]. 2-Octene has been detected in the reactions. The proportions of different esters formed from methoxycarbonylation of 1-octene are shown in **Table 2**. It can be seen that the proportions of C and D are relatively small. For the catalysts $Co(en)_3Cl_2$ and CoSalen, only a small amount of C is detectable, D is not detected. The ratio of A/B is between 1.2 to 1.5.

Scheme 1

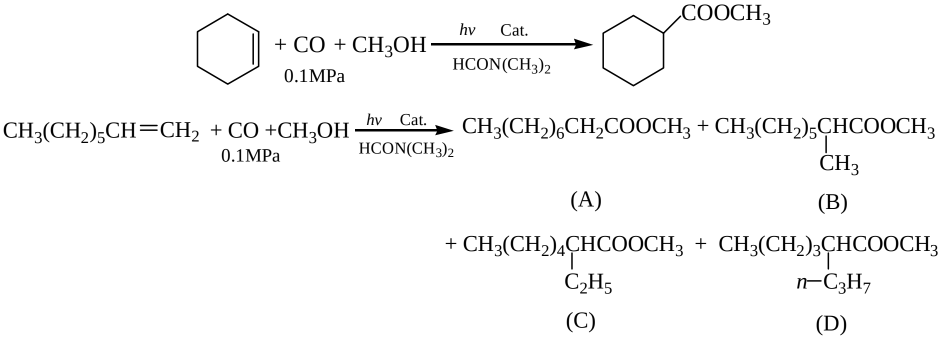


Table 1 Results of photopromoted methoxycarbonylation of olefins with CO in CH_3OH/DMF

Catalysts	Cyclohexene	1-Octene		
	Yields of ester(%)	Conversion (%)	Yields of ester(%)[a]	Selectivity(%)
$Co(OAc)_2$	37	76	62	80
$CoCl_2$	25	62	44	71
$Co(en)_3Cl_2$	15	48	38	79
CoSalen	12	49	34	69

a: total yields of all kinds of esters, Selectivity=Yields/Conversion.

In contrast with CH_3OH/DMF system, the yield of methoxycarbonylation of cyclohexene in CH_3OH/CH_3COCH_3 (V/V=3:1) is 63%, when the concentration of catalyst $Co(OAc)_2$ is 10 mmol/L (the other conditions are as the same as those when using DMF as solvent). The yield and conversion of methoxycarbonylation of 1-octene are 51% and 87%, respectively, with the proportion of A, B, C and D of 33%, 29%, 20%, 18% and ratio of A/B of 1.1. It can be seen that the selectivity of methoxycarbonylation of 1-octene is better in CH_3OH/DMF than that in CH_3OH/CH_3COCH_3. And the rate of double bond shifts during methoxycarbonylation in CH_3OH/DMF is slower than that in CH_3OH/CH_3COCH_3.

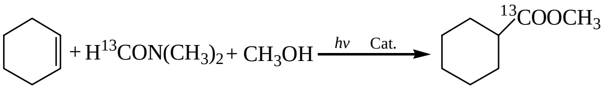
Table 2 The proportion of different esters from methoxycarbonylation of 1-octene

Catalysts	A (%)	B(%)	C(%)	D (%)	A/B
$Co(OAc)_2$	53	42	3	2	1.3
$CoCl_2$	55	36	7	2	1.5
$Co(en)_3Cl_2$	53	42	5	0	1.3
CoSalen	53	44	3	0	1.2

b: the structure of A、B、C、D are shown in **Scheme 1**.

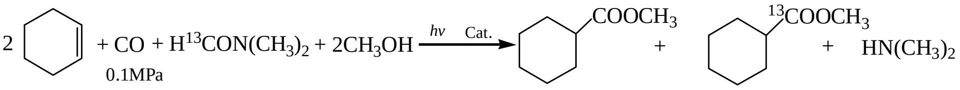
In the experiment of control when carbon monoxide is absent, the solution of CH_3OH, DMF, $Co(OAc)_2$ and cyclohexene under N_2 is irradiated. The ester from cyclohexene did formed with the yield as high as 25%. In order to figure out what is the carbon monoxide source, $H^{13}CON(CH_3)_2$ is used in the place of $HCON(CH_3)_2$. The solution of CH_3OH: $H^{13}CON(CH_3)_2$ (V/V = 5:1，0.3 mL), $Co(OAc)_2$ and cyclohexene is irradiated under N_2 with other conditions the same as above. The GC-MS analysis of products showed that major product was cyclo-$C_6H_{11}{}^{13}COOCH_3$ (M=143) (**Scheme 2**). So it was confirmed that DMF was the source of CO. The MS analysis of cyclo-$C_6H_{11}{}^{13}COOCH_3$ is shown in **Table 3**.

Scheme 2



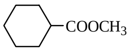
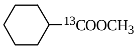
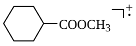
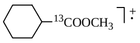
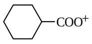
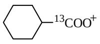
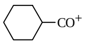
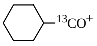
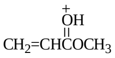
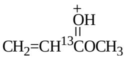
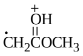
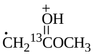
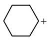
It would be interesting to find out what would happened when both CO and DMF are present. The above reaction was carried out under CO (**Scheme 3**). The GC-MS analysis of the products showed that two products of cyclo-$C_6H_{11}{}^{13}COOCH_3$ (M=143) and cyclo-$C_6H_{11}COOCH_3$ (M=142) were obtained (**Table 3**).

Scheme 3



In addition, when the pure DMF (3 mL) was irradiated exactly in the same conditions, it was showed that DMF decomposed into $HN(CH_3)_2$ and CO.

Table 3 MS analysis of cyclo-$C_6H_{11}COOCH_3$ and cyclo-$C_6H_{11}{}^{13}COOCH_3$

			
Fragment peaks	*m/z*	Fragment peaks	*m/z*
	142		143
	127		128
	111		112
$C_6H_{10}CO^{+\cdot}$	110	$C_6H_{10}{}^{13}CO^{+\cdot}$	111
$C_3H_6COOCH_3^{+}$	101	$C_3H_6{}^{13}COOCH_3^{+}$	102
 $CH_2{=}CH\overset{\overset{+}{OH}}{\overset{\parallel}{C}}OCH_3$	87	 $CH_2{=}CH^{13}\overset{\overset{+}{OH}}{\overset{\parallel}{C}}OCH_3$	88
 $\dot{C}H_2\overset{\overset{+}{OH}}{\overset{\parallel}{C}}OCH_3$	74	 $\dot{C}H_2{}^{13}\overset{\overset{+}{OH}}{\overset{\parallel}{C}}OCH_3$	75
	83		83
$C_4H_7^{+}$	55	$C_4H_7^{+}$	55

Acknowledgment

We are indebted to the National Natural Science Foundation of China (No. 20242004, 20372012) and Foundations of Key Laboratory of Photochemistry, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences for the generous financial support.

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Received 25 August, 2003