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Photopromoted Carbonylation of Alkyl Halides Under Ambient Conditions

Yan SUN[1,2], Jing Mei YIN[2,1]*, Da Bin GAO[2], Guang Yun ZHOU[2], Ying Ping JIA[2]

[1]Department of Chemistry & Technology, Dalian University of Technology, Dalian 116012
[2]Department of Chemistry and Chemical Engineering, Dalian University, Dalian 116622

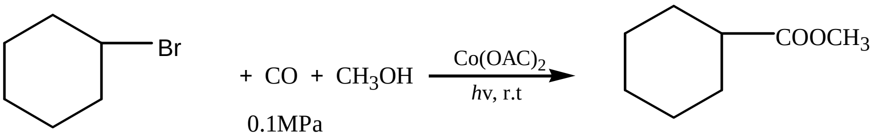
Abstract: Photopromoted carbonylation of alkyl halides with carbon monoxide can be carried out under ambient conditions with non-precious transition metal complexes (such as cobalt complexes) catalysts. Our preliminary work showed that alkyl halides can be transformed into alkene and alkane directly under irradiation, but the esters can not be transformed. It is assumed that the carbonylation of alkyl halides may be proceeded in two ways.

Keywords: Photopromoted carbonylation , alkyl halides , carbon monoxide.

The methoxycarbonylation of olefin is important and essential reaction to synthesize valuable esters, which requires high temperature (150-200^{0}C), high pressure (10-20 M Pa) and precious metal complex catalysts (such as Ru, Rh, Ir)[1,2]. In contrast with it, photopromoted carbonylations have many advantages: ambient conditions (room temperature and atmospheric pressure); non-precious metal catalyst[3,4] is required. So this reaction has attracted more and more attentions.

In previous papers [5,6], we have established that the methoxycarbonylation of olefins can be completed in the presence of ultraviolet light under mild conditions by using inexpensive metal complexes (such as $Co(OAc)_2$ and $Co(acac)_2$) as catalysts. Here we report the photopromoted carbonylation of alkyl halides.

The alkyl halides used as substrate in photopromoted carbonylation included alkyl bromide (RBr), alkyl iodide (RI) and active benzyl halide (such as benzyl chloride and benzyl bromide). In terms of bromocyclohexane and 1-bromododecane, the reactions are as follows:



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[*] E-mail: jingmeiyin@163.com

$$CH_3(CH_2)_{10}CH_2Br + \underset{0.1MPa}{CO} + CH_3OH \xrightarrow[h\nu\text{ ,r.t}]{Co(OAc)_2} CH_3(CH_2)_{10}CH_2COOCH_3 + CH_3(CH_2)_{10}CH_3 + CH_3(CH_2)_9CH{=}CH_2$$

It was found that these reactions did not proceed when either the catalyst or the light was absent.

Reagent

Carbon monoxide (99.9%, Dalian Guangming Institute); methanol , acetone (AP, Dalian merro Stock Chemical Reagent and Glass Apparatus Co.); sodium acetate, *n*-decane,; bromocyclohexane, 1-bromododecane (AP, Beijing PHENTEX Chemicals Co., Ltd.) cobalt acetate (AP, Shenyang Chemical Reagent Co.).

Procedure

A typical reaction procedure was as follows: A quartz test-tube, which contained solution (CH_3OH or CH_3OH-CH_3COCH_3) of substrate (100mmol/L) and $Co(OAc)_2$ (10mmol/L), was irradiated by 400W high pressure mercury lamp (GGY-400 , Philips and Yaming Corp.) at room temperature and under 0.1 MPa of CO pressure. NaOAc was used as additives. The products were analyzed by GC (Shimadzu GC-14B) and GC-MS (HP6890-5973).

Results and Discussion

The photocatalyzed carbonylation of bromocyclohexane is completed under ambient conditions to give the ester. It was reported[3] that acetone was used as photosensitizer in photopromoted carbonylation of olefin and the reaction can not be completed if acetone is absent (catalyst is $Co(acac)_2$). However, we found that the carbonylation of alkyl hallides can also be completed with the catalyst $Co(OAc)_2$ without acetone, though the selectivity is not so satisfactory. The results are shown in **Table 1.**

Table 1 The effect of catalyst and photosensitizer in photocatalyzed carbonylation of bromocyclohexane

run	$Co(OAc)_2$:NaOAc(mol:mol)	Conversion Of bromocyclohexane(%)	Yield of ester (%)
1	1:0	100	6[a]
2	1:30	100	28[a]
3	1:0	54	14[b]
4	1:30	38	30[b]

Bromo-cyclohexane: 100 mmol/L; $Co(OAc)_2$: 10 mmol/L; irradiation time 30 h ; a: CH_3OH is the sole solvent ; b: CH_3OH:CH_3COCH_3=3:1(v/v)

From **Table 1**, it can be seen that: [1] sodium acetate is a good additive with which the yield of ester is increased from 6% to 28% in CH_3OH and from 14% to 30% in

CH_3OH-CH_3COCH_3; [2] Comparing (2) and (4), it can be found that the conversion is high and the yield is similar -it means the selectivity of esters is low when acetone is absent. The addition of CH_3COCH_3 can improved the selectivity of esters.

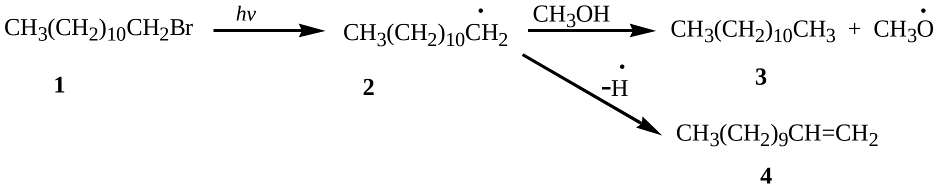
It is found that $CH_3(CH_2)_{10}CH_2COOCH_3$ and $CH_3(CH_2)_9CH(CH_3)COOCH_3$ in photopromoted carbonylation of 1-bromododecane, dodecene and dodecane were also obtained except the major products. The results are showed in **Table 2.**

Table 2 Photocatalyzed carbonylation of 1-bromododecane

run	$Co(OAc)_2$:NaOAc (mol:mol)	Conversion (%)	[c]yield (%)	$CH_3(CH_2)_9CH{=}CH_2$(%)	$CH_3(CH_2)_{10}CH_3$(%)
1	1:0	90	7	27	51[a]
2	1:30	95	11	0	78[a]
3	1:0	30	6	4	10[b]
4	1:30	60	20	0	28[b]

bromododecane: 100 mmol/L; $Co(OAc)_2$:10 mmol/L ; irradiation time 30 h; a:CH_3OH is sole solvent; b:CH_3OH:CH_3COCH_3=3:1(v/v); c: the yield of straight chain ester and isomeric esters

From **Table 2**, it can be seen that the yield can be increased with additive NaOAc, and the selectivity of esters become better when acetone is present. The results were similar to those of bromocyclohexane, the yield was slightly low due to long chain of 1-bromododecane. The reason of the formation of dodecane and dodecene probably is that alkyl halides converted into free radical after irradiation, which resulted the formation of alkane or alkene. This process can be showed as following[7]:



Based on the previous results[8], the carbonylation of olefins is easier than the carbonylation of alkyl halides. The carbonylation of alkyl halides may proceeded through two ways: (1) converted into esters directly; (2) alkyl halides be converted into alkene firstly and the later reacted with CO and methanol to produce esters.

In order to make clear the generation of alkene in the photopromoted carbonylation of alkyl halides, the solution of 1-bromododecane was irradiated on different conditions (carbon monoxide is not present). It is proved that acetone and sodium acetate is not favorable to the production of alkene. When the solution of 1-bromododecane in methanol was irradiated, the selectivity and yield of alkene is much better. The results are shown in **Table 3.**

For comparison, the process of carbonylation was as follows: solution of 1-bromododecane in methanol was irradiated for 5 hours; catalyst, CO and sodium acetate were added into reaction system to started the carbonylation. The result is listed in **Table 4.**

Table 3 Irradiation result of solution of 1-bromododecane for 5 hours

solvent	conversion (%)	$CH_3(CH_2)_9CH=CH_2$(%)	$CH_3(CH_2)_{10}CH_3$(%)
CH_3OH	51	31	20
CH_3COCH_3	6	2	4
CH_3OH:CH_3COCH_3=3:1(v/v)	6	2	4

Table 4 Comparison of two kinds of photocatalyzed carbonylation process

Time(h)	Conversion(%)	yield(%)	$CH_3(CH_2)_9CH=CH_2$(%)	$CH_3(CH_2)_{10}CH_3$(%)
10	70	14	0	30[a]
15	76	19	0	33[a]
10	10	0	3	4[b]
15	27	6	0	10[b]
20	33	12	0	18[b]
30	60	20	0	28[b]

a:The time include irradiation time (5 h) and the rest time is reaction time , acetone is absent ; b:CH_3OH:CH_3COCH_3=3:1(v/v), the reaction start directly without irradiation time; $Co(OAc)_2$: 10mmol/L; 1-bromododecane:100 mmol/L; $Co(OAc)_2$: NaOAc =1:30 (mol:mol);

From **Table 4**, it can be seen that the yield of phoropromoted carbonylation of alkyl halides can be increased if the alkyl halides were firstly transformed into olefins by irradiation.

It can be concluded that the photopromoted carbonylation of alkyl halides and carbon monoxide under ambient conditions may be proceeded through two ways. The exact mechanism is underway.

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