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The carbonylation of phenyl bromide and its derivatives under visible light irradiation

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Abstract

The carbonylation of phenyl bromide catalyzed by $Co(OAc)_2$ has been investigated with PhCOPh as a sensitizer under visible light in the presence of basic additive. With strong base CH₃ONa, PhCOOCH₃ is produced in 70% yield with 100% selectivity, the similar results are also obtained with a stronger base $(CH_3)_3CONa$. However, with another strong base NaOH, the yield of the ester is only 40%. On the other hand, with weak base NaOAc or $(n-C_4H_9)_3N$, phenyl bromide cannot be carbonylated. The results of carbonylation of the six substituted phenyl bromides suggest that the activities of o, m, p-BrC₆H₄CH₃ are similar to phenyl bromide, while the activities of o, m, p-BrC₆H₄Cl are higher with the high yields ($\geq 93\%$) of the corresponding chloro-esters. In addition, the relative position of bromine and chlorine or methyl on phenyl ring has little effect on the activity of the carbonylation. © 2011 Ying Ping Jia. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

Keywords: Carbonylation; Phenyl bromide; o, m, p-Bromotoluene; o, m, p-Bromochlorobenzene; Visible light

The carbonylation of aryl halides is an essential reaction to synthesize aryl carboxyl acids and their derivatives, which are valuable intermediates in the manufacture of pharmaceutical products and chemicals. However, the traditional carbonylation of the much less reactive aryl halides is difficult to carry out under mild conditions [1], and only a few systems allow such reactions. In contrast, the photopromoted carbonylation of aryl halides can be easily achieved [2–5]. Brunet *et al.* [2] reported the carbonylation of aryl halides with CO (1 atm) catalyzed by $Co_2(CO)_8$ at 65 °C under irradiation by means of a sunlamp (main emissions at 300, 315, 365, 405 and 435 nm) through a Pyrex flask. Kashimura *et al.* [3] described the polycarbonylation of polyhalogenated aromatics with CO (0.2 MPa) in the presence of a catalytic amount of $Co_2(CO)_8$ under the irradiation of a high-pressure mercury lamp by a Pyrex filter. Cash *et al.* [4] demonstrated the photochemical carbonylation of phenyl bromide with $Co((acac)_2)_2$ as catalyst under a low-pressure mercury lamp in a quartz glass reactor. In previous research [5], we have studied on the carbonylation of PhBr with CO (0.1 MPa) catalyzed by inexpensive stable less toxic $Co(OAc)_2$ under the irradiation of a high-pressure mercury lamp in a quartz glass reactor, PhCOOCH₃ was achieved with 91% yield by using CH₃ONa and PhCOCH₃ as additives in CH₃OH system. We noted that the photocarbonylation of aryl halides above mentioned occurred mostly under UV light irradiation and with Pyrex glass even quartz glass as reactor. Unsatisfactory, the UV light make the equipment aged easily due to its strong irradiation; meanwhile, it is dangerous to the operator's health. Furthermore,

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the high price of the special glass reactor limits the prospects for industrial application. In this paper, we report the first example of non-precious metal $Co(OAc)_2$ catalyzed carbonylation of PhBr and its derivatives with 0.1 MPa of CO in an ordinary glass reactor under visible light irradiation. In the study, irradiation was achieved with a 23 W household warm-white energy-saving lamp placed closely against the ordinary glass reactor, and CH₃ONa and PhCOPh were used as additives. We focused on the finding of the optimum reaction factors such as the concentration of additives CH₃ONa and PhCOPh.

1. Experimental

PhBr, *o*, *m*, *p*-BrC₆H₄CH₃, *o*, *m*, *p*-BrC₆H₄Cl (A.R., Shanghai Aladdin Reagent Co.); CO (99.9%, Dalian Guangming Institute); Co(OAc)₂, CH₃OH, PhCOPh, PhCOCH₃, NaOH, NaOAc, $(n-C_4H_9)_3N$, $n-C_{10}H_{22}$ (A.R., Beijing Chemical Engineering Co.); CH₃ONa, (CH₃)₃CONa (prepared in laboratory).

A typical experimental procedure was as follows: first, methanol solution of PhBr or its derivatives (20 mmol/L), catalyst (2 mmol/L) and additives was placed in an ordinary glass reactor with an interlayer, through which the circulating water from thermostat water bath was passed to keep constant temperature. Then, the reactions were carried out under 0.1 MPa of CO pressure with irradiation by a household warm-white energy-saving lamp (Philips type: Energy Saver 23 W, Chinese type: YPZ 220/23-3U. RD.D., Philips (China) Investment Co., Ltd.). Last, the products were analyzed by GC (Hitachi GC-3900) and GC–MS (HP 6890/5973) with $n-C_{10}H_{22}$ as the internal standard. The emission spectrum of the lamp, provided by Philips (China) Investment Co., Ltd., and reaction device are shown in Fig. 1.

2. Results and discussion

The carbonylation reaction is described in Scheme 1. When $Co(OAc)_2$, CH_3ONa and PhCOPh are simultaneously added to the reaction system under visible light irradiation, PhBr can be carbonylated, particularly, the selectivity of the carbonylated product PhCOOCH₃ is 100%. The detailed results are presented in Table 1.

It is well known that a certain amount of heat energy produced during the irradiation leads to the increasing of the temperature of the reaction system, and as a result, to improve the reaction activity in general. However, the solubility of CO in CH₃OH decreases as the increasing of the temperature, which is disadvantage to the reaction. Above facts suggest that the optimum temperature is important to the reaction. Four experiments were carried out at 20, 30, 40 and 50 °C. The observed results as shown in Table 1 (entries 1–4) tell us the optimum temperature is 40 °C. But we should note that even at the optimum temperature, the reaction activity is still low. In order to improve the conversion, we



Fig. 1. (1) The emission spectrum of household warm-white energy-saving lamp and (2) schematic drawing of the reaction device.

Table 1 The carbonylation of phenyl bromide under visible light.

Entry	Temperature (°C)	Time (h)	Base	Base concentration (mmol/L)	PhCOPh (mmol/L)	Conversion (%)	Yield (%)
1	20	15	CH ₃ ONa	40	70	17	17
2	30	15	CH ₃ ONa	40	70	33	33
3	40	15	CH ₃ ONa	40	70	37	37
4	50	15	CH ₃ ONa	40	70	30	30
5	40	12	CH ₃ ONa	40	70	19	19
6	40	18	CH ₃ ONa	40	70	37	37
7	40	20	CH ₃ ONa	40	70	36	36
8	40	24	CH ₃ ONa	40	70	36	36
9	40	15	CH ₃ ONa	50	70	51	51
10	40	15	CH ₃ ONa	60	70	61	61
11	40	15	CH ₃ ONa	65	70	70	70
12	40	15	CH ₃ ONa	70	70	58	58
13	40	15	CH ₃ ONa	65	40	36	36
14	40	15	CH ₃ ONa	65	50	49	49
15	40	15	CH ₃ ONa	65	60	55	55
16	40	15	CH ₃ ONa	65	80	68	68
17	40	15	(CH ₃) ₃ CONa	65	70	72	72
18	40	15	NaOH	65	70	40	40
19	40	15	NaOH	100	70	40	40

PhBr 20 mmol/L, Co(OAc)₂ 2 mmol/L, n-C₁₀H₂₂ 5 mmol/L, CH₃OH 4.5 mL.

tested the effect of reaction time on the reaction (Table 1, entries 3, 5–8). It is found that the conversion has little change when reaction time is between 15 h and 24 h. One explanation is that the reaction may reach the equilibrium after 15 h under our experimental conditions.

We also investigated the effects of basic additives on the carbonylation of PhBr under visible light. The three basic additives such as CH₃ONa, NaOAc and $(n-C_4H_9)_3N$ were used as in our previous work [5]. To our surprise, only CH₃ONa was effective to the reaction, while there was no PhCOOCH₃ with NaOAc or $(n-C_4H_9)_3N$. The results indicate that strong basicity is necessary for the reaction under visible light, which are remarkably different from those under UV light. Furthermore, the conversion of PhBr and the yield of PhCOOCH₃ significantly depend on the concentration of CH₃ONa (Table 1, entries 3, 9–12). With an increase in the concentration of CH₃ONa, the conversion of PhBr and the yield of PhCOOCH₃ increase rapidly, the selectivity of 100% remaining unchanged. The best concentration of CH₃ONa is 65 mmol/L, and the conversion of PhBr can be reached to 70%. We further tested the effects of other two strong bases, i.e., (CH₃)₃CONa and NaOH, on the reaction (Table 1, entries 17–19). With (CH₃)₃CONa, the yield of PhCOOCH₃ was similar to that with CH₃ONa. However, with NaOH, the yield of PhCOOCH₃ was lower (40%). Meanwhile, considering the weaker basicity of NaOH compared to CH₃ONa, a high concentration of NaOH was added to the reaction system, there was no increasing of the yield. The reason why CH₃ONa and (CH₃)₃CONa have stronger influence on the reaction than NaOH is probably that a large amount of $-OCH_3$ provided by CH₃ONa and (CH₃)₃CONa [(CH₃)₃CONa + CH₃OH \rightarrow CH₃ONa + (CH₃)₃COH], is favorable to the formation of carboxylic methyl ester [6]. Especially, the existence of $-OCH_3$ under visible light is more important than that under UV light. One possible explanation is that except as base and nucleophile, -OCH₃ acts as an electron donor in the reaction under visible light. It has been reported [2] that the formation of charge transfer complexes between PhBr and cobalt compound might be possible under irradiation, and cobalt compound is a poor electron-donating species, thus the existence of electron donor -OCH₃ is advantage to the reaction.

In the further experiments, we examined the influence of PhCOPh on the reaction. The result showed that no any reaction occurred in the absence of PhCOPh. The effects of PhCOPh are given in Table 1 (entries 11, 13–16). The optimum concentration of PhCOPh is 70 mmol/L and the yield of PhCOOCH₃ is 70% with 100% selectivity. Contrast to the present results, our previous work also showed that PhCOPh was beneficial to the carbonylation of PhBr under UV light, *i.e.*, the yield of PhCOOCH₃ was increased from 47% to 80% [5]. It is worthy to note that the selectivity of PhCOOCH₃ (80%) under UV light is lower than that (100%) under visible light. The reason is due to high energy of UV light, resulting in the formation of by-products such as benzene and anisole. Both results suggest that PhCOPh

Entry	Substrate	Product	Conversion (%)	Yield (%)	Selectivity (%)
1	o-BrC ₆ H ₄ Cl	o-ClC ₆ H ₄ COOCH ₃	94	93	99
2	m-BrC ₆ H ₄ Cl	m-ClC ₆ H ₄ COOCH ₃	98	97	99
3	p-BrC ₆ H ₄ Cl	p-ClC ₆ H ₄ COOCH ₃	95	94	99
4	o-BrC ₆ H ₄ CH ₃	o-CH ₃ C ₆ H ₄ COOCH ₃	70	70	100
5	m-BrC ₆ H ₄ CH ₃	m-CH ₃ C ₆ H ₄ COOCH ₃	72	72	100
6	p-BrC ₆ H ₄ CH ₃	p-CH ₃ C ₆ H ₄ COOCH ₃	71	71	100

Table 2 The carbonylation of some substituted phenyl bromides under visible light.

Substrate 20 mmol/L, the other conditions are the same as Table 1, entry 11.

plays different roles in different photochemical reaction. According to the literature [7], the roles of PhCOPh in the reaction under irradiation are as follows: (1) to abstract hydrogen from hydrogen donor; (2) to be employed as a sensitizer. Under UV light, the role of PhCOPh is mainly to inhibit the hydrodehalogenation of PhBr to form benzene *via* abstracting hydrogen. While under visible light, the role of PhCOPh is just assumed to be a sensitizer, since the hydrodehalogenation of PhBr does not occur at this condition. Interestingly, our earlier work showed that PhCOCH₃ was more effective than PhCOPh in terms of the yield and selectivity of PhCOOCH₃ under UV light. However, with PhCOCH₃ instead of PhCOPh under visible light, PhBr could not be carbonylated, which implied that PhCOCH₃ could not be used as a sensitizer under visible light. This result may be related to the triplet excited energy transfer of PhCOPh and PhCOCH₃ (PhCOPh: 69 kcal/mol, PhCOCH₃: 74 kcal/mol) [8]. Generally, substrates or related components can absorb photon is a premise to perform photoreaction. In the present reaction system, the catalyst absorbs photon to its excited state or charge transfer complex [2], of which the energy is similar to the energy level of PhCOPh at its triplet state. As a result, the energy transfer among Co(OAc)₂, PhCOPh and PhBr is occurred. However, the process cannot happen when PhCOCH₃ is used instead of PhCOPh.

In addition, the carbonylation of some substituted phenyl bromides was carried out under visible light, the results are listed in Table 2. In contrast with PhBr, *o*, *m*, *p*-BrC₆H₄Cl are very easily carbonylated and the corresponding chloro-esters are obtained in high yields (\geq 93%) accompanied by a small amount of bicarbonylated products (1%) (Table 2, entries 1–3). Moreover, the activities of *o*, *m*, *p*-BrC₆H₄Cl are similar to each other. On the other hand, *o*, *m*, *p*-BrC₆H₄CH₃ can also be carbonylated to give the corresponding methyl esters, and the activities of *o*, *m*, *p*-BrC₆H₄CH₃ are similar to PhBr. These results show that the effect of different substituents on the phenyl ring is different, *i.e.*, chlorine substituent can evidently improve the activity and methyl has no significant effect on the reaction, but the substituted position has little effect on the activity of the carbonylation.

In conclusion, the photopromoted carbonylation of PhBr and its derivatives catalyzed by $Co(OAc)_2$ proceeds smoothly in the presence of a strong base CH₃ONa or (CH₃)₃CONa and a sensitizer PhCOPh under visible light. Furthermore, the activities of *o*, *m*, *p*-BrC₆H₄CH₃ are similar to PhBr, but lower than those of *o*, *m*, *p*-BrC₆H₄Cl.

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