Multigram scale cobalt catalyzed photochemical methoxycarbonylation of alkenes

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Abstract

Photocarbonylation of alkenes was successfully carried out on a multigram scale (5–10 g) on a number of alkenes. Optimum conditions (temperature, solvent, concentration, UV source and filters) were established; it was shown that the rate of reaction depends on the concentration of the cobalt catalyst. The cobalt catalyst was stable only under a narrow range of conditions and any deviation from them either reduced the rate of photocarbonylation, or caused the cobalt to precipitate and stop the reaction. It was shown that the rate and selectivity of photocarbonylation reaction depend on a degree of substitution of alkenes. Mono and disubstituted alkenes gave the corresponding methyl esters in good yields (69–85%), while trisubstituted alkenes either did not react at all, or gave complex mixtures of products. Selectivity can be achieved in carbonylation of dienes if conversion is kept low. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Photochemical carbonylation; Alkenes; Carbon monoxide; Cobalt; β-Pinene

1. Introduction

Insertion of carbon monoxide into organic molecules is at the present time one of the most important uses of transition metals in organic synthesis. A wide variety of functional groups (esters, lactones, lactols, aldehydes, ketones, enones, carboxylic acids, alcohols, etc.) may be prepared using this method [1–5]. A number of modifications and variations with respect to the catalyst and conditions were reported [6–8]. In this work, photocarbonylation reaction was optimized on β-pinene **1** as a model compound and applied to a number of alkene substrates. Multigram scale optimum conditions were established and, in the process, it was observed that cobalt catalyzed photocarbonylation was highly sensitive to steric hindrance.

2. Strategy

Cobalt-catalyzed thermal carbonylation reactions are usually conducted under high pressure of carbon monoxide and at high temperature. Isomerization of alkenes and loss of volatile cobalt catalyst are common problems. Use of rather expensive rhodium and palladium catalysts allows the reaction to be run under milder conditions and in better yields [1–5]. Mirbach's

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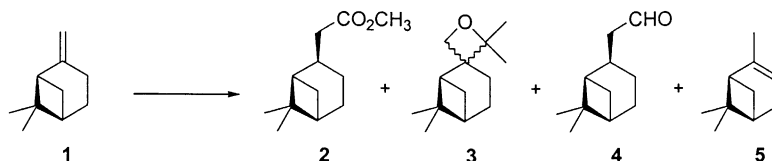
Scheme 1. Methoxycarbonylation of β-pinene.

group applied UV irradiation to promote cobalt catalyzed hydroformylation of alkenes with synthesis gas at a pressure of 80 atmospheres and a temperature of 80°C [9,10]. However, to conduct a photochemical reaction at high temperature and under high pressure is difficult and cost prohibitive for practical applications. Other groups reported cobalt-catalyzed carbonylation of aryl halides to give aryl carboxylates in the presence of a phase transfer catalyst [11–16]. Photocarbonylation with a cobalt salt as a catalyst precursor can be conducted at room temperature and under atmospheric pressure of carbon monoxide [17–19]. Thus, cobalt-catalyzed photocarbonylation combines the best features of both processes (inexpensive catalyst and mild conditions). Furthermore, since absorption of light is not temperature dependent, photocarbonylation can be carried out at a low temperature.
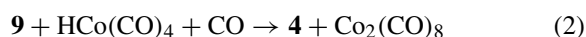
Although the mild reaction conditions reduced competing side reactions and formation of isomers, some competing photochemical reactions did interfere. The photocarbonylation of β-pinene **1** was chosen (Scheme 1) as a model for the investigation of the reaction rate, yield and selectivity on the following criteria. β-Pinene underwent carbonylation at a reasonable rate to provide a single ester **2** as a methoxycarbonylation product. As a product of competing Paterno–Büchi reaction oxetane **3** was formed [20,21]. In small amounts, a carbonylation product aldehyde **4** was produced. Cobalt catalyzed carbonylation of alkenes is often accompanied by isomerization. β-Pinene **1**, in the presence of a suitable catalyst, readily isomerizes to a more stable α-pinene **5**. Thus, β-pinene was a suitable representative substrate for a photocarbonylation reaction accompanied with side reactions.

Although the mechanism of cobalt-catalyzed carbonylation has been a subject of numerous studies, it is still not well understood. Photosensitized reduction of cobalt salts, in the presence of triplet-excited

ketones, under CO atmosphere in methanol or THF gives an equilibrium mixture of $HCo(CO)_4$ and $Co(CO)_4^-$, which have been identified as 'pre-catalysts' (Scheme 2). It was shown that the presence of a ketone, most conveniently acetone, is necessary for the reaction to proceed [17]. Described pre-catalysts exist in equilibrium with a number of other cobalt species. The nature of cobalt species present and the position of the equilibrium depend on the light source and filters [22]. Further, irradiation leads to loss of a carbon monoxide ligand to give a coordinately unsaturated $HCo(CO)_3$ and $Co(CO)_3^-$. Since, $HCo(CO)_4$ loses a carbon monoxide ligand
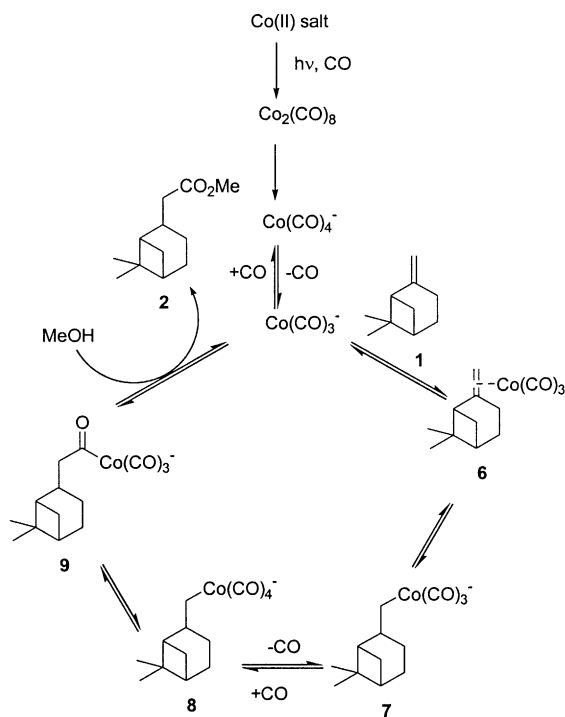
Scheme 2. Mechanism of photocarbonylation of β-pinene.

upon irradiation at 310 nm to give $HCo(CO)_3$ [23], it is unlikely that acetone sensitization is necessary for this step. Thus, the actual carbonylation catalyst is either $HCo(CO)_3$, $Co(CO)_3^-$, or both. These cobalt species were also proposed as a catalyst in thermal carbonylation reaction processes [2,4,5,24–26]. The methoxycarbonylation product appeared after a short (15–30 min) induction period. Formation of a π-complex **6** was identified as the rate determining step [27]. Esters are formed via alkylcobalt carbonyl and acylcobalt carbonyl intermediates **7–9**. UV irradiation was necessary for the photocarbonylation reaction and formation of carbonylation products stopped, if UV irradiation was discontinued and resumed, if irradiation was resumed [11–14,17,18]. Aldehydes are produced by the following process.

$$Co(CO)_4{}^- + MeOH \rightleftharpoons HCo(CO)_4 + MeO^- \qquad (1)$$

$$\mathbf{9} + HCo(CO)_4 + CO \rightarrow \mathbf{4} + Co_2(CO)_8 \qquad (2)$$

Alternative mechanisms for the photocarbonylation were proposed with supporting evidence [13,28,29]. It is likely that different mechanisms operate under different conditions and also that more than one mechanism operates at the same time.

3. Experimental

The ^1H and ^{13}C NMR spectra were taken on a Bruker model WH-400 NMR spectrometer in deuteriochloroform solutions, GC/MS were recorded on a Hewlett-Packard 5988. The percentage yields of the products that were not isolated were determined by GC (Hewlett-Packard 5890) gas chromatograph employing 15 m × 0.21 mm fused silica column coated with cross-linked SE 54 and equipped with flame ionization detector, using dodecane as an internal standard. Concentration of the solvent under reduced pressure (water aspirator) refers to solvent removal on a Büchi rotary evaporator at 15 mmHg.

Decomposition of the catalyst was indicated by disappearance of the pink color of the solution and formation of metal powder on the walls of the UV irradiator. Based on the literature data about the decomposition of cobalt catalyst, it was assumed that the precipitate was elemental cobalt [30].

In a typical experiment, a quartz irradiator equipped with a medium pressure mercury lamp (Hanovia 450 W UV lamp, Vycor filter) was placed in a water bath. A recirculating chiller was used to cool the UV lamp and maintain the reaction temperature at 14°C. A solution of β-pinene **1** (4.7 ml, 0.03 mol, 0.1 M) and bisacetonylcobalt(II) [Co(acac)₂] (0.77 g, 0.003 mol, 0.01 M) in methanol/acetone mixture (3:1 by volume, 300 ml) was placed in the Hanovia type irradiator for irradiation under slow purging of CO at 14°C. When monitoring the progress of reaction by GC, a small portion of solution was withdrawn from the irradiator, passed through a short column of Florisil to remove the catalyst, and injected into GC. After 24 h, the irradiation was discontinued and the reaction mixture was filtered through a short column of Florisil (3 cm × 6 cm). The column was eluted with ether (50 ml). Eluents were combined and evaporated to a small volume. The residue was chromatographed on a silica–gel column (3 cm × 12 cm) using hexanes:dichloromethane:diethyl ether (9:3:1) as eluent. Eluents were evaporated. Yield of the methyl ester **2** was 4.06 g (69%).

3.1. Identification of the products

Products **2**, **4**, **13** and **15** were characterized and reported before [17]. Compounds **5** and **11** were identified, by means of GC, by coinjection with authentic samples of α-pinene and methyl cyclohexanecarboxylate, respectively. [3] Spectral data for oxetane **3**: ^1H NMR (400 MHz, CDCl₃) δ: 0.59 (s, 3H), 1.12 (s, 3H), 1.24 (s, 3H), 1.37 (s, 3H), 1.50–1.95 (m, 6H), 2.06 (m, 1H), 2.59 (m, 1H), 4.22 (dd, 1H), 4.32 (d, 1H). ^{13}C NMR (100 MHz, CDCl₃) δ: 22.02, 22.75, 24.55, 24.79, 25.87, 26.25, 27.10, 39.00, 39.91, 47.12, 48.32, 81.15, 90.43.

4. Results and discussion

4.1. Effect of light sources and filters

Multigram scale reactions were conducted using variety of filters (Pyrex, Corex, Vycor or Quartz)

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[3] Obtained from Aldrich Chemical Company, 14,752-4 α-pinene and 19,742-4 methyl cyclohexanecarboxylate.

Table 1
Effect of light sources and filters on photocarbonylation of β-pinene[a]

Entry	Filter	[β-Pinene] (M)	[Co(acac)$_2$] (M)	2 (%)	3 (%)	4 (%)	5 (%)	Recovered 1 (%)	Rate[b] (mmol/h)
1	Quartz	0.10	0.010	14.4	5.8	4.3	3.4	54.2	0.94
2	Quartz	0.05	0.005	11.1	4.1	5.5	12.5	43.1	0.42
3	Vycor	0.10	0.010	17.8	4.4	3.6	0.8	67.4	1.07
4	Corex	0.10	0.010	20.4	4.8	4.5	1.8	52.3	1.24
5	Corex	0.20	0.020	3.9	0.4	0.7	0.5	72.6	0.46
6	Pyrex	0.10	0.010	1.2	0	0	0	93.5	0.06
7	Pyrex	0.05	0.005	18.8	3.9	5.6	1.3	16.0	0.61
8	Pyrex	0.05	0.0025	10.8	2.8	11.4	1.0	21.4	0.56
9	Pyrex[c]	0.025	0.0025	9.0	1.8	11.0	1.4	32.4	0.17

[a] Irradiation time 6 h, 450 W UV lamp, temperature 14°C, solvent methanol/acetone (3:1, 300 ml).

[b] In mmol (methyl ester 2 + aldehyde 4)/h.

[c] A 200 W medium pressure mercury UV lamp was used instead of 450 W.

(Table 1). An ideal filter would allow UV radiation to produce Co(CO)$_3^-$ from Co(CO)$_4^-$ at a high rate while not dissociating additional ligands (causing cobalt to precipitate). Furthermore, a filter with too low cut-off may activate the alkene and thus promote undesired side reactions. The Quartz filter, which the lowest cut-off of the filters examined, was not satisfactory. Reaction rate was high, however cobalt catalyst underwent decomposition even at high concentrations and low temperatures. Furthermore, yields of the desired products were low while oxetane 3 and α-pinene 5 were formed in large amounts. It was suspected that β-pinene 1 was activated by the short wave UV radiation, since it gave numerous byproducts when irradiated in the absence of a cobalt catalyst. Corex and Vycor filters have shown to be the most useful and after optimum concentration was determined, good reaction rates and product yields were obtained. Vycor filter appeared to be more suitable of the two. When Corex filter was used some cobalt precipitate was observed and the material balance was not as good as when using Vycor filter. Reaction rates using Pyrex filter (one with the greatest cut-off) were low and an increase in concentration of cobalt species sharply decreased the yield. In fact, carbonylation almost stopped when 0.01 M Co(acac)$_2$ was used as a catalyst precursor (Table 1, entry 6). When the concentration of Co(acac)$_2$ was reduced the carbonylation rate increased (entries 7 and 8). It is interesting that at lower concentrations of Co(acac)$_2$ (0.0025 M), the reaction rate was faster using 200 W Hanovia medium pressure mercury lamp (entry 9) compared to using 450 W lamp and 0.01 M Co(acac)$_2$ (entry 6). Use of 100 W lamp was not attempted as this would result in impractically low rates.

A microscale reaction was conducted on a 2.5 mmol of substrate in 5 ml solution of methanol-acetone in a Pyrex test tube and a 450 W Hanovia medium pressure UV lamp. The optimum concentration of Co(acac)$_2$ was found to be 5 mM [17,18]. Effects of light source and filter were also examined for different concentrations of cobalt catalyst and β-pinene with similar results.

4.2. Concentration effect

The reaction rate depended on the concentration of Co(acac)$_2$ but not on the β-pinene concentration (Table 2). At low concentrations of cobalt (0.001–0.050 M), the carbonylation reaction stopped after a short time and a large amount of precipitated metal powder was observed. It appears that UV irradiation stripped the catalyst of its CO ligands and caused it to precipitate as elemental cobalt. Therefore, the rate was low and the carbonylation eventually stopped because of the loss of the catalyst. At higher concentrations (0.02 M and above) cobalt species acted as a filter, reducing the intensity of UV radiation, and sharply decreasing the reaction rate. The reaction rate showed a maximum at 0.01 M concentration of Co(acac)$_2$, whereas, the change in concentration of β-pinene did not appear to have a significant effect on the reaction rate. At higher concentrations of β-pinene

Table 2
Effect of concentration on photocarbonylation of β-pinene[a]

Entry	β-Pinene (M)	Co(acac)$_2$ (M)	2 (%)	3 (%)	4 (%)	5 (%)	Recovered 1 (%)	Rate[b] (mmol/h)
1	0.10	0.005	15.7	6.1	5.4	2.8	42.5	0.53
2	0.10	0.010	24.4	5.4	5.5	2.2	45.2	0.75
3	0.10	0.020	5.2	3.2	0.8	1.3	81.7	0.15
4	0.20	0.010	11.9	5.6	2.6	0.9	66.5	0.72
5	0.50	0.010	4.4	3.3	0.9	0.9	88.7	0.66
6	1.00	0.010	0.9	3.4	0.4	0.9	98.2	0.45

[a] Irradiation time 12 h, Vycor filter (1.8 mm), temperature 14°C, solvent methanol/acetone (3:1, 300 ml).
[b] In mmol (methyl ester 2 + aldehyde 4)/h.

(more than 0.2 M), the rate of conversion became so low that, it was impractical to run reaction under such conditions. The optimum concentration for a microscale reaction was 50 mM of an alkene and 5 mM of Co catalyst [17]. The optimum concentration was related to the filter and light source used and for different combinations of filters and light sources the optimum concentration of cobalt catalyst was different.

4.3. Temperature effect: stability of the cobalt catalyst

In thermal carbonylation reactions, it was observed that the stability of a cobalt catalyst depended on its concentration-stability increased with increase in concentration of cobalt catalyst, temperature-stability decreased with temperature increase, and CO pressure-stability increased with increase in CO pressure [30]. Since the optimum concentration was already determined and the carbon monoxide pressure was not an adjustable parameter, the only variable was temperature. As with thermal reactions, the cobalt catalyst was unstable at higher temperatures. It was difficult to establish the exact temperature at which decomposition of cobalt catalyst began, but it was clear that, in a microscale reaction, at a temperature of 40°C, the reaction stopped due to decomposition of the catalyst. On a multigram scale, cobalt deposits were observed at even lower temperatures. This may be due to a different filter used (Vycor or Corex for multigram scale reaction, Pyrex for microscale reaction). At temperatures as low as 24°C some cobalt deposits were observed after prolonged reaction times. Stability of cobalt catalyst also depended on cobalt concentration. More concentrated solutions were more stable than less concentrated. However,

if concentration of cobalt catalyst became too high reaction rate sharply decreased (Table 1). Therefore, a balance had to be found between a concentration at which cobalt catalyst is stable, and at the same time, at which photocarbonylation proceeds at a reasonable rate.

In general, reaction rate of a photochemical reaction depends on light source, filter, concentrations of reactants and sensitizer. It was not expected that the reaction rate would depend on temperature, as absorption of light is not temperature dependant. However, some dependence on temperature was observed. This observation indicates a thermal step in a photochemically driven reaction. Most likely, the rate of formation of catalyst Co(CO)$_3{}^-$ from pre-catalyst Co(CO)$_4{}^-$ increases with temperature. Once optimum conditions were determined, the reaction was conducted at different temperatures and the photocarbonylation rate become somewhat higher at higher temperatures (Table 3). Usually, microscale reactions were conducted at 16–18°C and multigram scale at 14°C.

4.4. Sensitizer effect

When using xanthone, benzophenone or acetophenone as sensitizers the rates of photocarbonylation were significantly lower compared to reactions in which acetone was a sensitizer. It was shown that a sensitizer is necessary for preparation of the precatalyst, Co(CO)$_4{}^-$ [17]. Whether it plays any role in the actual catalytic cycle (Schemes 2 and 3) is unclear.

4.5. Effect of solvent systems

Composition of the solvent mixture (methanol/acetone mixture) did not significantly influence the

Table 3
Effect of temperature on photocarbonylation of β-pinene[a]

Entry	T (°C)	2 (%)	3 (%)	4 (%)	5 (%)	Recovered 1 (%)	Rate[b] (mmol/h)
1	6	21.9	7.8	5.1	0.6	52.2	0.68
2	14	24.4	5.4	5.5	2.2	45.2	0.75
3	24	33.4	4.2	5.6	5.7	27.9	0.98

[a] Irradiation time 12 h, Vycor filter (1.8 mm), temperature 14°C, [β-pinene] = 0.10 M, [Co(acac)$_2$] = 0.010 M, solvent methanol/acetone (3:1, 300 ml).

[b] In mmol (methyl ester 2 + aldehyde 4)/h.

photocarbonylation reaction rate, where the concentration of methanol can vary in the range of 50–80% without a significant change in the rate or product yields. The 3:1 methanol/acetone mixture (by volume) was found to be the best. Alkenes are soluble in acetone and significantly less soluble in methanol. On the other hand, added salts (e.g. Co(acac)$_2$ or Co(OAc)$_2$) are more soluble in methanol than acetone.

The proposed reaction mechanism indicates that UV irradiation is necessary for the production of the pre-catalyst form Co(II) salt as well as for the production of the catalyst Co(CO)$_3^-$ from the pre-catalyst Co(CO)$_4^-$ (Scheme 2). In accordance with the postulated mechanism, it was observed that there was a 15–30 min induction time before the actual carbonylation reaction started. However, if the proposed mechanism were correct than, once the catalyst is formed, the reaction should propagate on its own since Co(CO)$_3^-$ is released at the end of a catalytic cycle. Therefore, carbonylation should continue without UV irradiation. That is not the case and the carbonylation stops as soon as UV irradiation is turned off and resumes, if it is turned back on. It is possible that the carbonylation proceeds as described in Scheme 2, but Co(CO)$_3^-$, formed by methanolysis of 9, captures a CO molecule to produce Co(CO)$_4^-$, rather than complexing an

alkene to give a π-complex 6. Such reaction is likely since Co(CO)$_3^-$ has high demand for ligands and will complex ligands as inert as N$_2$, Ar or Xe [31,32]. If that is the case, UV irradiation would be necessary to regenerate Co(CO)$_3^-$ from Co(CO)$_4^-$. Such catalytic cycle is better described by Scheme 3. Alternatively, it is possible that there is an additional photochemically driven step elsewhere in the reaction mechanism.
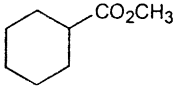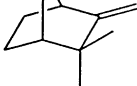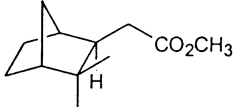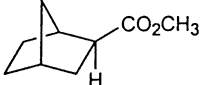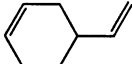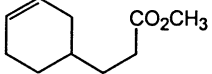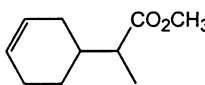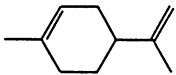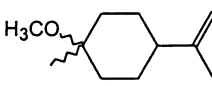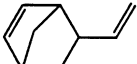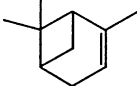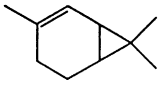
4.6. Carbonylation of other alkenes: effect of alkene structure

The photocarbonylation reaction showed high sensitivity toward steric hindrance. Monosubstituted double bonds reacted preferentially to disubstituted. Trisubstituted alkenes did not undergo photocarbonylation. Thus, cyclohexane 10, camphene 12 and norbornene 14 underwent methoxycarbonylation on a multigram scale to give the corresponding methyl esters in good yields (Table 4). Photocarbonylation of 4-vinylcyclohexene 16 gave a mixture of methyl esters 17 and 18. Since in this experiment emphasis was on selectivity, conversion was kept low. Extended reaction times lead to a non-specific carbonylation of the endocyclic double bond and a complex mixture of products. Therefore, a monosubstituted double bond underwent methoxycarbonylation in preference to the disubstituted double bond. Attempted carbonylation of structurally related limonene 19, provided methyl ether 20 as the only product. This ether is a result of addition of methanol to the endocyclic double bond [33]. Extended reaction times lead to a mixture of products. Geminaly disubstituted alkenes, such as β-pinene 1 and camphene 12, easily undergo methoxycarbonylation owing to less steric hindrance than a vicinaly disubstituted endocyclic double bond in 4-vinylcyclohexene 16.
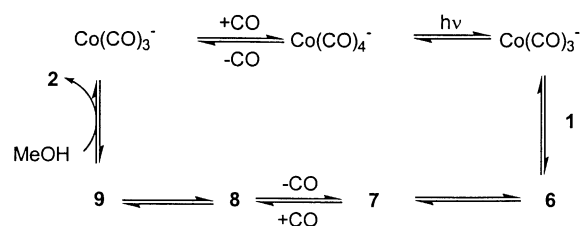
Scheme 3. Alternative mechanism of photocarbonylation of β-pinene.

Table 4
Photocarbonylation of alkenes[a]

Entry	Alkene	Product(s) (yield)
1	**10**	**11** (81%)[a]
2	**12**	**13** (74%)[a]
3	**14**	**15** (85%)[a]
4	**16**	**17** (15%)[b] **18** (14%)[b,c]
5	**19**	**20** (24%)[b]
6	**21**	Mixture of products
7	**22**	Mixture of products
8	**5**	No reaction
9	**23**	Mixture of products

[a] (a) Isolated yield; (b) GC yield; (c) 1:1 mixture of diastereoisomers.

The carbonylation of 5-vinyl-2-norbornene **21** also gave a complex mixture of products. This is in marked contrast to 4-vinylcyclohexene **16**, which undergoes carbonylation on the exocyclic double bond only, and gives the two corresponding esters as products. It is likely that the endocyclic bond in 5-vinyl-2-norbornene **21** is activated by the strain introduced by the presence of a methylene bridge. Carbonylation of 1-methylcyclohexene **22** gave a complex mixture of products. This is another example of a photochemical carbonylation not working on a trisubstituted olefin. α-Pinene **5** did not react under the usual carbonylation condition. In contrast to limonene **19**, α-pinene did not react with methanol to give methyl ether. Attempted carbonylation of Δ^3-Carene **23** gave a complex mixture of more than 10 different compounds according to GC analysis. Irradiation of Δ^3-Carene in methanol/acetone mixture under nitrogen instead of carbon monoxide and without $Co(acac)_2$ also gave a complex mixture of products of similar composition, according to GC analysis. Therefore, this alkene was activated by UV radiation and underwent competing photochemical reactions rather than carbonylation.

During the preparation of this manuscript, it was discovered that a part of the results and related studies were published by one (D.B.G.) of the authors in Chinese journals as short communications from his department without knowledge of the other coworkers. The publications contain scanty details and no experimental description [34,35]. We have demanded of the author to retract those publications.

5. Conclusions

Cobalt catalyzed photocarbonylation is suitable method for preparation of gram quantities of methyl esters under mild conditions. The reaction was limited to mono and disubstituted alkenes. The stability of cobalt catalyst is crucial for success of photocarbonylation. For given reaction scale and set of conditions (light source, filter, temperature), there is a narrow range of concentrations of cobalt catalyst at which the catalyst is stable and the reaction proceeds at a reasonable rate. The results indicate that with appropriate choice of light source, filter and concentration of cobalt catalyst one may be able to carry out the photocarbonylation reaction on a kilogram scale using suitable equipment (e.g. photochemical thin film reactor).

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