# SELENIUM ASSISTED CARBONYLATION OF ALKYL ARYL KETONES WITH CARBON MONOXIDE

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Abstract—Selenium assisted carbonylation of alkyl aryl ketones with carbon monoxide leading to formation of 1,3-dicarbonyl compounds as C-carbonylated products is described. o-Hydroxyacetophenone (7a) and its derivatives (7b, 7c, and 7d) have been converted to the corresponding 4-hydroxycoumarins (8a, 8b, 8c and 8d) in moderate to quantitative yields by treatment with an equivalent of selenium and carbon monoxide with concomitant formation of hydrogen selenide (9) (Eq. (8)). It was further revealed that oxidation of *in situ* formed hydrogen selenide to selenium with an appropriate oxidizing agent such as nitrobenzene permitted catalytic use of selenium for the carbonylation of 7. Possible rationalizations for the formation of 4-hydroxycoumarins are suggested.

### **INTRODUCTION**

Recently, the use of carbon monoxide as a reducing agent or a source of carbon in organic synthesis has become a subject of considerable importance.<sup>1</sup> A large number of works<sup>10-c,2</sup> concerning transition metal catalyzed reactions has shown that carbon monoxide is particularly useful for carbonylation of various organic compounds.

Compared with transition metal catalyzed carbonylations, there have been few reports of carbonylations with carbon monoxide in which non-transition metals act as catalysts. Known examples of non-transition metal catalysis are concentrated in the following three types of reactions: (1) alkaline base-catalyzed O-carbonylation of alcohols to formates and Ncarbonylation of alcohols to formatides;<sup>3</sup> (2) acidcatalyzed C-carbonylation of olefins or alcohols to carboxylic acids (Koch reaction);<sup>1,4</sup> (3) free radical initiated copolymerization of olefins and carbon monoxide to polyketones.<sup>5</sup> We previously found that selenium, a non-transition element, effectively catalyzed the carbonylation of various amines with carbon monoxide and oxygen to give urea derivatives quantitatively (Eq. (1)).<sup>6</sup>

Several experimental findings<sup>†</sup> on the carbonylation suggested that the reaction process involved formation of amine salts (2) of selenocarbamic acid by a nucleophilic attack of amines at the carbon of carbonyl selenide (1), generated in situ from carbon monoxide and selenium under basic conditions (Eq. (2)). Amine salts 2 were converted to the corresponding ureas following nucleophilic attack of another amine molecule. From further investigations on the reaction, it has been shown that carbamates 38 or unsymmetrical ureas 4<sup>6</sup> can be synthesized in good yields by treatment of selenocarbamate amine salts 2 with alcohols or other amines (Eq. (3)). In addition, it was revealed that functionalized amines such as diamines, ethanol amines, and thioethanol amines were also catalytically carbonylated with carbon monoxide to yield cyclic ureas (5: X = NH), carbamates (5: X = O), and



<sup>†</sup> The following observations are compatible with the reaction path in Eq. (2): (1) amine salt of selenocarbamic acid (2: R = piperidyl) was isolated from the reaction system;<sup>6</sup> (2) reaction of amines with isolated carbonyl selenide<sup>7</sup> gave the salts 2.<sup>14</sup>

thiocarbamates (5: X = S), respectively (Eq. (4)).<sup>9</sup> We next focused on the application of this reaction using carbon monoxide and selenium to carbonylation of other nucleophiles such as alcohols and thiols. The reaction of aliphatic alkoxides with carbon monoxide



and oxygen in the presence of catalytic amounts of selenium gave carbonates in high yields under atmospheric pressure (Eq. (5)).<sup>10</sup> Similarly dithiocarbonates were obtained from thiols (Eq. (6)).<sup>11</sup> Successful isolation of monoselenocarbonate (6) by alkylation of an intermediate, formed in the reaction shown in Eq. (5), with an alkyl halide (Eq. (7)) led us to postulate the reaction path depicted in Scheme 1.

From the studies of selenium catalyzed carbonylation described above, the use of a C-nucleophile instead of an N- or O-nucleophile would be of special interest since a novel C-carbonylation with carbon monoxide assisted by selenium might be expected. We examined the C-carbonylation using enolates of several ketones as the C-nucleophile and found that the reaction of o-hydroxyacetophenone (7a) with carbon



monoxide and selenium permitted a quantitative formation of 4-hydroxycoumarin (8a): the carbonyl group of 8a must have been derived from carbon monoxide through a C—C bond formation with the enolate (Eq. (8)).<sup>12</sup>

In this paper, we now provide full details of our investigation on the carbonylation of alkyl aryl ketones to 1,3-dicarbonyl compounds with carbon monoxide and selenium. Possible rationalizations for the formation of 4-hydroxycoumarins are also suggested.

# **RESULTS AND DISCUSSION**

Carbonylation of o-hydroxyacetophenones with carbon monoxide in the presence of stoichiometric amount of selenium

The carbonylation of o-hydroxyacetophenone (7a) to 4-hydroxycoumarin (8a) with carbon monoxide and an equimolar amount of selenium was examined varying bases and temperatures: the results are summarized in Table 1. The nature of the base has a marked effect on this reaction: strongly basic conjugated diaza compounds such as 1.5diazabicyclo[5.4.0]undec-5-ene (DBU) and 1.5diazabicyclo[4.3.0]non-5-ene (DBN) were most effective for the carbonylation of 7a (entries 6, 8, and 9 of Table 1), but the carbonylation did not take place in reactions using tertiary amines such as triethylamine, N-methylpyrrolidine, or 1,4-diazabicyclo[2.2.2]octane (DABCO) (entries 1, 2, and 3 of Table 1).

It has been reported that DBU is the base of choice in the carboxylation of active methylene compounds with carbon dioxide, where a  $CO_2$ -DBU complex (10)

Table 1. Selenium assisted carbonylation of o-hydroxyacetophenone (7a) with CO<sup>a</sup>

Entry	Base	(mmol)	Temp (°)	% Yield of <b>8a</b> <sup>b</sup>
1	Et <sub>3</sub> N	(40)	100	0
2	[]N−CH₃	(40)	100	0
3	DABCO <sup>c</sup>	(40)	100	0
4	DBU⁴	(40)	40	0
5	DBU	(40)	80	trace
6	DBU	(40)	100	26
7	DBU	(40)	120	4
8	DBU	(80)	100	100
9	DBN <sup>e</sup>	(80)	100	40

\*All reactions were run on 20 mmol of **7a** in 10 ml of tetrahydrofuran (THF) with 1 equiv of selenium and CO (30 kg cm<sup>-2</sup>: initial pressure at 25°) in the presence of base for 30 hr.

<sup>b</sup> Isolated yields.

° 1,4-Diazabicyclo[2.2.2]octane.

<sup>4</sup> 1,5-Diazabicyclo[5.4.0]undec-5-ene.

\* 1,5-Diazabicyclo[4.3.0]non-5-ene.

formed from carbon dioxide and DBU has been considered to be an active species for carboxylation.<sup>13</sup> Furthermore, we found that carbonyl sulfide (S=C=O) when blown into the N,Ndimethylformamide (DMF) solution of DBU at room temperature afforded white solids, which were thermally unstable and regenerated carbonyl sulfide on warming to 45°. These solids were assumed to be a SCO-DBU complex.<sup>14</sup>

In spite of our efforts confirming the SeCO-DBU complex, both attempted isolation from the present reaction system and spectroscopic detection of the complex were unsuccessful, probably because the complex would be much more susceptible to air and thermally unstable, compared with 10. It is not



 $\uparrow$  An alternative explanation, which does not involve the formation of SeCO, can be also offered in the present carbonylation: (1) reaction of nucleophile with CO gave rise to a CO-nucleophile addition product, which was rapidly trapped by selenium to afford Nu—C(O)—Se<sup>-</sup>, or (2) reaction of nucleophile with selenium occurred at first, followed by insertion of CO between nucleophile and selenium which gave Nu—C(O)—Se<sup>-</sup>. At present, we do not have enough evidence to rule out the possibility of the above explanation.

 $\pm$  Similar observations were reported in the carboxylation<sup>13</sup> of 7a with carbon dioxide, where 3–4 molar equivalents of DBU to 7a were required. It may be assumed that DBU was consumed for both generation of dianion (11a) from 7a and formation of a SeCO–DBU complex. Furthermore, DBU may also react with hydrogen selenide (9) formed *in situ* to give a H<sub>2</sub>Se–DBU salt ([DBU · H]<sup>+</sup>[SeH]<sup>-</sup>).

§ Hydrogen selenide 9 was isolated from the present reaction system by acidification of the system with conc. sulfuric acid.<sup>15</sup> understood why DBU is effective in the present carbonylation while other tertiary amines are not. However, it is assumed from analogy with the carboxylation with carbon dioxide in the presence of DBU that DBU would react with carbonyl selenide 1, a key intermediate in the present carbonylation, to form a DBU-SeCO complex, which might act as an active SeCO-transfer species.<sup>†</sup>

The molar ratio of DBU/7a is also important, and the reaction proceeded smoothly when four molar equivalents of DBU to substrate 7a were employed (entry 8 of Table 1).<sup>‡</sup> The best reaction temperature for the carbonylation was 100° (entries 4–7 of Table 1). The present carbonylation also proceeded in benzene, dioxane, or DMF as the solvent, although the yields were slightly lower. The best reaction conditions leading to the quantitative formation of 4-hydroxy-coumarin (8a) were as follows: a stirred mixture of 7a (20 mmol), selenium (20 mmol), carbon monoxide (30 kg cm<sup>-2</sup>: initial pressure at 25°), DBU (80 mmol), and THF (10 ml) in a stainless steel autoclave were heated at 100° for 30 hr to give 8a (100%) with concomitant formation of hydrogen selenide (9).§

Similar reaction occurred under the same reaction conditions with 5-methyl-2-hydroxyacetophenone (7b) and 4-methoxy-2-hydroxyacetophenone (7c) to give 6methyl-4-hydroxycoumarin (8b) and 7-methoxy-4hydroxycoumarin (8c), respectively, in about 40% yields (entries 2 and 4 in Table 2). In order to increase the yields of 8b and 8c, greater excesses of base were required (entries 3 and 5 in Table 2). When this reaction was applied to o-hydroxypropiophenone (7d), whose enolate (11d) possessed a secondary carbanion at the reaction site, the expected 3-methyl-4-hydroxycoumarin (8d) was not formed in the reaction at 100° for 30 hr in spite of appreciable uptake of carbon monoxide (entry 6 in Table 2). However, a 42% yield of 8d was obtained with a slightly elevated temperature (at 130°) (entry 7 in Table 2).

# $Catalytic carbonylation of o-hydroxy acet ophenone with \\ carbon monoxide$

In the study of carbonylation of ohydroxyacetophenones (7) using a stoichiometric amount of selenium, it was revealed that hydrogen selenide (9) was formed in an equimolar amount with the carbonylated products. If the hydrogen selenide 9 formed *in situ* could be oxidized to selenium by an appropriate oxidizing agent, it would be expected that the carbonylation could proceed with a catalytic amount of selenium (Scheme 2).

Various types of oxidizing agents including pquinone, manganese dioxide, and molecular oxygen were examined for this purpose in vain. Finally, however, the carbonylation of 7a with carbon monoxide was found to proceed catalytically in the presence of nitrobenzene as the oxidizing agent. For instance the reaction of 10 mmol of 7a with 0.2 equivalent of selenium and carbon monoxide (30 kg cm<sup>-2</sup> at 25°) in the presence of DBU (40 mmol) and nitrobenzene (5 mmol) in THF (5 ml) at 90° for 2 days afforded 6.8 mmol of carbonylated product 8a in which the turnover number of selenium catalyst was about 3.5. Nitrobenzene was reduced concomitantly to aniline during the reaction.<sup>16</sup> The proposed catalytic cycle is given in Scheme 3.

Table 2. Selenium assisted carbonylation of substituted acetophenones with carbon monoxide\*

Entry	Substrate	DBU (mmol)	THF (ml)	Temp (°)	Product	Yield <sup>b</sup> (%)
1	Осн <sup>3</sup> сн <sub>3</sub>	7 <b>a</b> 20	5	100		100
2	сн 3 Осн 3 сн 3 с	7 <b>b</b> 20	5	100 C	он <b>вь</b>	35
3		40	15	100	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	77
4 C	сн <sub>з</sub> о Осн з с	7e 20	5	100 Ci	H <sub>3</sub> 0 OC 0 8c	28
5		40	15	100		36
6		rd 20	5	100	OH CH <sub>3</sub> 8d	0
7		20	5	130		42

<sup>a</sup> Reactions were run on 5 mmol of substrate in tetrahydrofuran with 1.0 equiv of selenium and carbon monoxide (30 kg cm<sup>-2</sup> at 25°) in the presence of DBU for 30 hr. <sup>b</sup> Isolated yields.

# A plausible reaction path

The exact course of the carbonylation of 7 with carbon monoxide and selenium has not been elucidated yet. The two plausible reaction paths are illustrated in Scheme 4. The first possibility is that the reaction involves selenocarboxylic acid 12a, formed by nucleophilic attack of the enolate site of 11a to the carbon atom of 1, followed by intramolecular cyclization with elimination of hydrogen selenide to give 8a (Path A: Ccarbonylation). The second possibility is that the phenolate site of 11a attacks 1 to form selenocarbonate 13a (Path B: O-carbonylation). The trapping of an intermediate anion by alkylation would be desirable. It has already been described that carbonylation of 7d to





#### Scheme 4.

8d did not proceed at 100° for 30 hr in spite of appreciable absorption of CO. Here, the resulting reaction mixture was a homogeneous yellow solution, and metallic selenium had disappeared. On exposure to air, the yellow solution gradually changed to a dark brown solution with deposition of metallic selenium. When the brown solution was worked up in the usual way, no carbonylated product was obtained: starting 7d was recovered in almost quantitative yield. These observations suggested that the yellow solution might introduced into the yellow solution, 12d or 13d would decompose to 11d, metallic selenium, and CO. As shown above, it seems difficult to trap the carbonylated intermediate from the carbonylation of 7d.

Relevant interesting observations were reported for the carboxylation of 7a using carbon dioxide and DBU.<sup>13</sup> Carboxylation of 7a with carbon dioxide gave the carboxylic acid 17 in 85% yield at room temperature. When this reaction was carried out for a prolonged time or at elevated temperatures, 8a was



include a transient carbonylated intermediate, which gave the starting compounds 7d and metallic selenium on exposure to air. A slight excess of allyl bromide relative to 7d was added dropwise to the yellow solution to yield 3-allyl-3-methyl-2,4-chromandione 16(44% yield based on 7d) with concomitant formation of diallyl selenide, however, the desired alkylated intermediate (14d or 15d) was not obtained at all. This experimental result would suggest the following (see Scheme 5). (1) Carbonylation of 7d might occur even at 100° to form intermediate 12d or 13d. The cyclization of 12d or 13d proceeded at 130° to give 8d (Table 2, entry 7). (2) Treatment of the yellow solution with allyl bromide might afford Se-allylated intermediate 14d or 15d, which might easily cyclize at room temperature to give 8d, since RSe<sup>-</sup> is a much better leaving group than  $Se^{2-}$ . Formation of 16 might be due to further alkylation of thus formed 8d. (3) When air was

formed instead of 17 (Eq. (9)). These observations suggest that the C-carbonylation path seems to be more plausible for the present carbonylation of 7 with CO and selenium.

In summary, it has been shown that the carbonylation of o-hydroxyacetophenones (7) with carbon monoxide and selenium can lead to high yield formation of 4hydroxycoumarins (8) as C-carbonylated products. In addition, the catalytic reaction of 7 has been achieved by oxidation of hydrogen selenide formed in situ from elemental selenium and nitrobenzene.

## **EXPERIMENTAL**

General method. The instruments used were as follows: <sup>1</sup>H-NMR, Hitachi R-24B; IR, Shimadzu IR-400; MS, Hitachi RMU-6A; melting points, Yanagimoto micro melting point apparatus.





Tetrahydrofuran (THF), dioxane, and benzene used were dried over sodium wire and/or lithium aluminum hydride, and distilled before use. N,N-Dimethyl formamide (DMF) was purified by distillation. Metallic selenium (99.99%) from Nakarai Chem. Co. and carbon monoxide (99.999%) from Seitetsu Chem. Co. were used as purchased. Tertiary amines (1,5 - diazabicyclo[5.4.0]undec - 5 - ene (DBU), triethylamine, 1,4-diazabicyclo[2,2,2]octane (DABCO), and 1.5diazabicyclo[4.3.0]non-5-ene (DBN)), aryl alkyl ketones (o-2hydroxyacetophenone, o-hydroxypropiophenone, 2-hydroxy-4hydroxy-5-methylacetophenone, and methoxyacetophenone), and other reagents (nitrobenzene, pquinone, manganese dioxide, molecular oxygen, and allyl bromide) were all purchased from commercial sources, and purified by distillation or recrystallization.

# Synthesis of 4-hydroxycoumarin (8a): carbonylation of ohydroxyacetophenone (7a) using stoichiometric amount of selenium

In a 50 ml stainless steel autoclave were placed ohydroxyacetophenone (1.36 g, 10 mmol), selenium (0.79 g, 10 mmol), DBU (6.08 g, 40 mmol), THF (5 ml), and a magnetic stirring bar. The apparatus was flushed several times with carbon monoxide and charged with carbon monoxide at 30 kg cm<sup>-2</sup>. The mixture was heated with stirring at 100° for 30 hr. After the reaction was complete, carbon monoxide was purged and air was blown into the resulting solution to oxidize hydrogen sclenide to sclenium and water. Water (10 ml) was added to the mixture, which was then neutralized with aqueous hydrochloric acid (35%). The depositing sclenium was filtered off and the filtrate was poured into 50 ml of water. The product was extracted with diethyl ether (100 ml  $\times$  3), dried over anhydrous magnesium sulfate, concentrated on a rotary evaporator and recrystallized from benzene-ethyl acetate (1:1) solvent, affording 1.62 g(100%) of **8a** : m.p. 206.7-207.2° (lit.<sup>17</sup> 206°); IR (KBr) 3600-2000 (OH), 1680 (C=O, conj), 1605 cm<sup>-1</sup> (C=C); <sup>1</sup>H-NMR (d<sub>6</sub>-DMSO)  $\delta$  5.60 (s, 1H), 7.20-7.86 (m, 4H); MS 162 (M<sup>+</sup>).

# Carbonylation of 2-hydroxy-5-methylacetophenone (7b) into 4hydroxy-6-methylcoumarin (8b)

A mixture of 7b (0.75 g, 5 mmol), selenium (0.40 g, 5 mmol), DBU (6.08 g, 40 mmol) and THF (15 ml) was stirred at 100° for 30 hr under 30 kg cm<sup>-2</sup> of carbon monoxide (initial pressure at 25°). The resulting mixture was worked up in the same manner as described in the synthesis of 8a to yield 0.68 g (77%) of 8b: m.p. 255-257° (recrystallized from MeOH, lit.<sup>18</sup> 258°); IR (KBr) 3600-2200 (OH), 1680 (C=O, conj), 1600 cm<sup>-1</sup> (C=C); <sup>1</sup>H-NMR (d<sub>6</sub>-DMSO)  $\delta$  2.40 (s, 3H), 5.60 (s, 1H), 7.10-7.60 (m, 3H); MS 176 (M<sup>+</sup>).

#### Carbonylation of 2-hydroxy-4-methoxyacetophenone (7c) into 4-hydroxy-7-methoxycoumarin (8c)

Reaction of 7c (0.83 g, 5 mmol) and the following workups were performed as described above, resulting in the formation of 8c in 36% yield (0.35 g); m.p. 255–256° (recrystallized from MeOH, lit.<sup>19</sup> 256°); IR (KBr) 3600–2000 (OH), 1685 (C=O), 1600 cm<sup>-1</sup> (C=C); <sup>1</sup>H-NMR (d<sub>6</sub>-DMSO)  $\delta$  3.81 (s, 3H), 5.35 (s, 1H), 6.70–7.70 (m, 3H); MS 192 (M<sup>+</sup>).

#### Carbonylation of o-hydroxypropiophenone (7d) into 4-hydroxy-3-methylcoumarin (8d)

A mixture of 7d (0.75 g, 5 mmol), selenium (5 mmol), DBU (20 mol), and THF (5 ml) was stirred at 130° for 30 hr under carbon monoxide (30 kg cm<sup>-2</sup>; initial pressure at 25°). The crude product obtained in the same manner as described in the

synthesis of **8a** was subjected to column chromatography on silica gel (n-hexane-MeOH) to afford 0.74 g (42%) of **8d**; m.p. 228-230° (lit.<sup>20</sup> 230-231°); IR (KBr) 3500-2000 (OH), 1675 (C=O, conj), 1615 cm<sup>-1</sup> (C=C); <sup>1</sup>H-NMR (d<sub>6</sub>-DMSO)  $\delta$  2.00 (s, 3H), 6.55-7.95 (m, 4H); MS 176 (M<sup>+</sup>).

### Catalytic carbonylation of 4-hydroxycoumarin (8a)

A mixture of 7a (1.36 g, 10 mmol), selenium (0.16 g, 2 mmol), DBU (6.08 g, 40 mmol), nitrobenzene (5 mmol), and THF (5 ml) was heated with stirring under a pressure of carbon monoxide (30 kg cm<sup>-2</sup>: initial pressure at 25°) at 90° for 30 hr. The resulting mixture was worked up in the same manner as described in the synthesis of 8a using a stoichiometric amount of selenium, and 1.10 g of 8a was obtained (6.8 mmol, 68%).

An attempt for the trapping of the intermediate. In a 50 ml stainless steel autoclave with a glass insert were placed ohydroxypropiophenone (1.50 g, 10 mmol), selenium (0.79 g, 10 mmol), DBU (6.08 ml, 40 mmol), and THF (5 ml). The mixture was stirred at 90° for 24 hr under the pressure of carbon monoxide (30 kg cm<sup>-2</sup>: initial pressure at 25°). The final pressure after cooling to 25° was 23 kg cm<sup>-2</sup>. After releasing the pressure, the glass insert was taken out, into which allyl bromide (0.95 ml, 11 mmol) was added at 0° under nitrogen. The mixture was stirred at room temp for an additional 10 hr. Extraction of the product with diethyl ether (100 ml  $\times$  3), followed by column chromatography on silica gel (n-hexane-Et<sub>2</sub>O) gave 3 - allyl - 3 - methyl - 2,4 - chromandione (16) (44% yield): m.p. 62.0° (lit.21 65-65.5°); IR (NaCl) 1780 (C=O),  $1700 (C=0), 1620 \text{ cm}^{-1} (C=C); ^{1}\text{H-NMR} (CDCl_{3}) \delta 1.55 (s, 1.55)$ 3H), 2.65 (d, 2H), 4.80-5.95 (m, 3H), 6.95-7.90 (m, 4H); MS 216 (M<sup>+</sup>).

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