1444 Short Articles

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Carbonylation of Organic Halides with Carbon Monoxide Mediated by Samarium Diiodide. Improvement and Mechanistic Investigations

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Under an atmospheric pressure of carbon monoxide, photoinduced reductive carbonylation of organic halides (RX) with samarium diiodide (SmI_2) occurs to afford the corresponding unsymmetrical ketones ($RC(O)CH_2R$) in good yields. Mechanistic insight into this carbonylation, especially the pathway for the generation of an acylsamarium species ($RC(O)SmI_2$) as a key intermediate, is also investigated in detail.

Transition-metal-catalyzed carbonylation of organic halides with carbon monoxide via oxidative addition of the organic halides to the transition-metal catalysts is a synthetically useful process in organic synthesis. In contrast, examples of reductive carbonylation of organic halides involving electron-transfer process are rare. Recently, we have developed a novel reductive carbonylation reaction of organic halides (RX) with carbon monoxide (50 atm) mediated by samarium diiodide (SmI_2), which occurs upon visible-light irradiation, affording the corresponding unsymmetrical ketones ($RC(O)CH_2R$) in good yields.[1] Further detailed study on this carbonylation has led to an interesting finding that this SmI_2-induced reductive carbonylation of haloalkanes does proceed under an atmospheric pressure of CO upon visible-light irradiation (Eq. 1). Moreover, atmospheric carbonylation is advantageous to get insight into the present carbonylation pathway. In this paper, we wish to report the atmospheric carbonylation of organic halides with SmI_2 upon visible-light irradiation and its detailed mechanistic aspects.
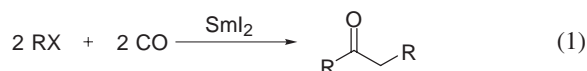
$$2\,RX \;+\; 2\,CO \xrightarrow{\;SmI_2\;} \underset{R}{\overset{O}{\diagdown}}R \qquad (1)$$

Table 1. Atmospheric Carbonylation of Organic Halides[a]

$$2\,R\text{–}X \;+\; \underset{1\ \text{atm}}{2\,CO} \xrightarrow{\;SmI_2\text{-}h\nu\;} \underset{R}{\overset{O}{\diagdown}}R$$

Entry	R–X	Yield/%
1	$^{n}C_{12}H_{25}Cl$	45
2	$^{n}C_{12}H_{25}Br$	50
3	$^{n}C_{12}H_{25}I$	58
4	$^{c}C_6H_{11}I$	85
5	$CH_2{=}CH(CH_2)_4Br$	68

a) R–X (0.5 mmol), SmI_2 (2 mmol), Sm (2 mmol), THF (15 mL), CO (1 atm), r.t., 6 h, $h\nu$: Xe lamp (500 W), Pyrex.

Results and Discussion

We initially investigated the influence of the visible-light irradiation on this reductive carbonylation under an atmosphere of carbon monoxide. When the reaction of 1-iodododecane (0.5 mmol) with CO (1 atm) was carried out using a SmI_2/Sm (2 mmol/2 mmol)[2] mixed system upon irradiation with a xenon lamp through Pyrex, reductive carbonylation took place with a 58% yield of dodecyl tridecyl ketone, which consisted of two dodecyl and two CO units (Eq. 2 and Entry 3 in Table 1). In contrast, no reductive carbonylation took place at all in the dark. A deep blue-colored solution of SmI_2 in THF has an absorption maximum in the visible region ($\lambda_{max} = 565$ and $617\,nm$), which is assigned to a $4f^6 \rightarrow 4f^55d^1$ transition. In a previous paper, we reported that irradiation at wavelengths between 500 and 700 nm is effective for the excitation of SmI_2, which dramatically enhances its reducing ability compared to SmI_2 in the ground state.[3]

$$2\,C_{12}H_{25}I \;+\; \underset{1\ \text{atm}}{2\,CO} \xrightarrow[\substack{h\nu \\ \text{dark}}]{SmI_2/Sm} \underset{C_{12}H_{25}}{\overset{O}{\diagup}}\hspace{-2pt}\underset{}{\diagdown}C_{12}H_{25} \quad \begin{matrix}58\% \\ -\end{matrix} \qquad (2)$$
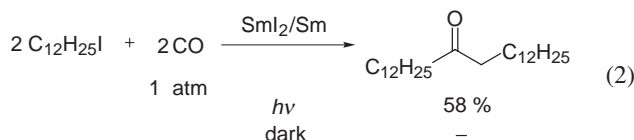
Table 1 summarizes the results of the photoinduced carbonylation of several organic halides with SmI_2/Sm under an atmosphere of CO. Primary alkyl halides, such as chloro-, bromo-, and iodododecanes (Entries 1–3), produced the corresponding unsymmetrical ketones in moderate yields. Similarly, cyclohexyl iodide as a secondary alkyl iodide underwent atmospheric carbonylation to afford an unsymmetrical ketone in
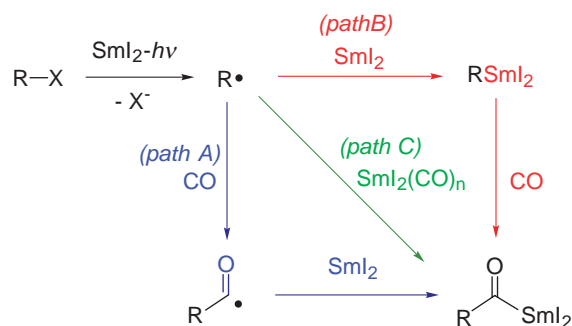
Scheme 1. Possible pathways for the formation of acylsamarium species.
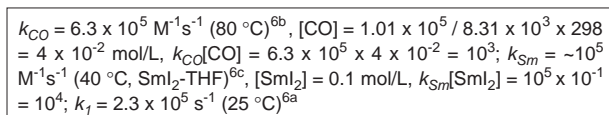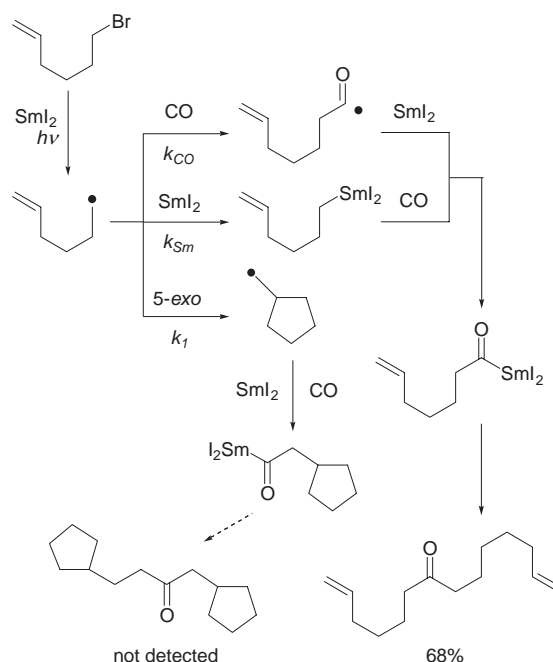
good yield (Entry 4).

The present photoinduced carbonylation may involve the formation of acylsamarium species ($RC(O)SmI_2$) as a key intermediate from haloalkane (RX), CO, and SmI_2. Kagan et al. previously reported that the reduction of an acyl chloride, ($RC(O)Cl$), by an excess amount of SmI_2 gave the corresponding unsymmetrical ketones ($RC(O)CH_2R$) and suggested that a possible reaction pathway might involve the dimerization of an acylsamarium species and then further reduction with SmI_2 (Eq. 3).[4]

$$2 \, \underset{R}{\overset{O}{\|}}_{Cl} + \underset{4 \, molar \, amounts}{SmI_2} \xrightarrow{THF} \underset{R}{\overset{O}{\|}}R \quad (3)$$
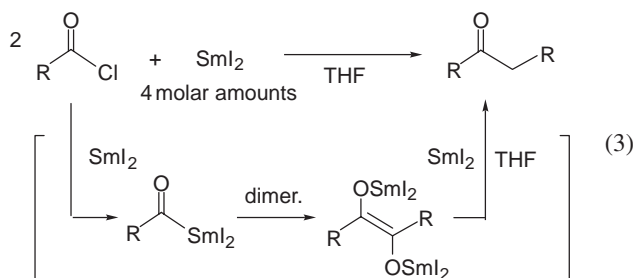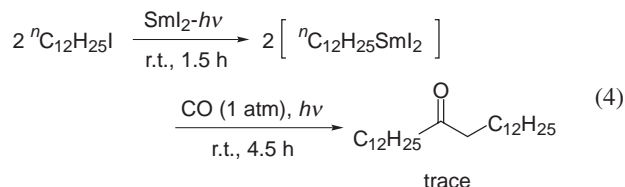
In this paper, the mechanistic study is focused on the carbonylation step to generate the acylsamarium species from haloalkanes and CO in the presence of low-valent samarium reagent (SmI_2/Sm). Scheme 1 shows some possible reaction pathways for the formation of the acylsamarium species ($RC(O)SmI_2$).

At first, we presumed that an in situ generated an alkyl radical ($R\bullet$), reacted with CO to give an acyl radical species ($RC(O)\bullet$),[5] and the subsequent reduction of the acyl radical with SmI_2 formed the acylsamarium species (Path A). To elucidate whether atmospheric carbonylation includes the formation of acyl radical intermediates, we examined the photoinduced carbonylation of 5-hexenyl bromide with SmI_2 under an atmospheric pressure of CO. Scheme 2 summarizes the kinetic data related to this reaction system.[6] From Scheme 2, the rate for the 5-*exo* cyclization of 5-hexenyl radical is $k_1 = 2.3 \times 10^5 \, s^{-1}$ (25 °C). However, the rate for the reduction of 5-hexenyl radical and the rate for the carbonylation of 5-hexenyl radical can be estimated roughly to be $k_{Sm}[SmI_2] = \approx 10^4 \, s^{-1}$ and $k_{CO}[CO] = \approx 10^3 \, s^{-1}$, respectively. The kinetic data strongly suggest that the 5-*exo* cyclization of 5-hexenyl radical takes place preferentially and, in contrast, the direct carbonylation of 5-hexenyl radical is an unfavorable process at least under a CO atmosphere. Surprisingly, however, the expected cyclic carbonylated product was not obtained, and instead, an acyclic ketone was obtained in 68% yield. This result can not be explained by the free radical pathway (Path A in Scheme 1).
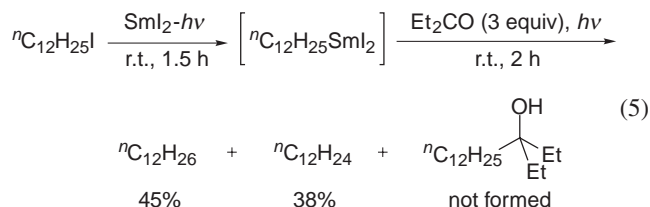
Since the free radical pathway (Path A) is not suitable for the formation of acylsamarium species, we next examined the organosamarium pathway, which consists of the reduction of haloalkanes (RX) with SmI_2 to generate an organosamarium species ($RSmI_2$), followed by the carbonylation of $RSmI_2$ with CO to give an acylsamarium species (Path B in Scheme 1). Dodecylsamarium diiodide was prepared by the reaction of 1-iodododecane (0.5 mmol) with SmI_2/Sm (2 mmol/2 mmol) at room temperature upon irradiation with xenon lamp through Pyrex for 1.5 h. Then, CO (1 atm) was introduced into the solution upon photoirradiation (rt, 4.5 h). However, the desired unsymmetrical ketone was not obtained (Eq. 4).

$k_{CO} = 6.3 \times 10^5 \, M^{-1}s^{-1}$ (80 °C)[6b], $[CO] = 1.01 \times 10^5 / 8.31 \times 10^3 \times 298$ $= 4 \times 10^{-2}$ mol/L, $k_{CO}[CO] = 6.3 \times 10^5 \times 4 \times 10^{-2} = 10^3$; $k_{Sm} = \sim 10^5$ $M^{-1}s^{-1}$ (40 °C, SmI_2-THF)[6c], $[SmI_2] = 0.1$ mol/L, $k_{Sm}[SmI_2] = 10^5 \times 10^{-1}$ $= 10^4$; $k_1 = 2.3 \times 10^5 \, s^{-1}$ (25 °C)[6a]

Scheme 2. Photoinduced atmospheric carbonylation of 5-hexenyl bromide with SmI_2.

$$2 \, {}^nC_{12}H_{25}I \xrightarrow[r.t., \, 1.5 \, h]{SmI_2\text{-}h\nu} 2 \left[{}^nC_{12}H_{25}SmI_2 \right]$$

$$\xrightarrow[r.t., \, 4.5 \, h]{CO \, (1 \, atm), \, h\nu} C_{12}H_{25}\overset{O}{\underset{\|}{C}}C_{12}H_{25} \quad (4)$$

trace

To determine if dodecylsamarium diiodide is formed in this reaction system,[7] we attempted to trap dodecylsamarium diiodide with excess amounts of diethyl ketones. However, the Grignard-type reaction did not occur, and instead dodecane and dodecene were obtained in 45 and 38% yields, respectively, as a result of reduction and disproportionation (Eq. 5). Furthermore, the same reaction was carried out between −15 to 5 °C, but the addition product was not detected.

$${}^nC_{12}H_{25}I \xrightarrow[r.t., \, 1.5 \, h]{SmI_2\text{-}h\nu} \left[{}^nC_{12}H_{25}SmI_2 \right] \xrightarrow[r.t., \, 2 \, h]{Et_2CO \, (3 \, equiv), \, h\nu}$$

$${}^nC_{12}H_{26} + {}^nC_{12}H_{24} + {}^nC_{12}H_{25}\overset{OH}{\underset{Et}{\overset{|}{C}}}Et \quad (5)$$

45%   38%   not formed

These results suggest that alkylsamarium diiodide is unstable under these conditions and, thus, decomposed before the reaction with the CO. Accordingly, the pathway through the generation of the alkylsamarium species (Path B) is unfavorable for this carbonylation reaction, because of the instability of alkylsamarium species as an intermediate.

Table 2.   SmI$_2$-Induced Reduction of 2-Octanone[a]

		Yield/%			
Entry	Reaction condition	2-Octanone	**1**	**2**	**3**
1	*hν*	15	72	7	6
2	dark	25	62	10	3
3	*hν* + CO	80	10	7	3

a) 2-Octanone (0.5 mmol), SmI$_2$ (2 mmol), Sm (2 mmol), THF (15 mL), CO (1 atm), *hν*: Xe lamp (500 W), Pyrex.

During the course of our study on this carbonylation reaction, we have found that the reducing ability of SmI$_2$ is greatly reduced in the presence of CO (Table 2). For example, when the photoinduced reduction of 2-octanone by SmI$_2$ was conducted at room temperature for 1 h in the absence of CO, 2-octanol (**1**) was obtained as the major product, along with small amounts of *vic*-diol (**2**), as a pinacol-type product, and ketone (**3**) as a pinacol rearrangement product (Entry 1). The same reaction without photoirradiation led to similar results as the case with photoirradiation (Entry 2). In the presence of CO, however, the photoinduced reaction of 2-octanone afforded the desired alcohol (**1**) in very poor yield, and instead, the starting material was mainly recovered (Entry 3). It is clear that the existence of CO decreases the reducing ability of SmI$_2$, most probably by the coordination of CO to samarium species.[8]

With these results in mind, a possible pathway for the formation of acylsamarium species (Path C in Scheme 1) is as follows: Dodecyl iodide undergoes single-electron transfer from SmI$_2$ to generate a dodecyl radical, which may be captured rapidly by the CO coordinated to the samarium species and simultaneously undergoes single electron reduction by SmI$_2$(CO)$_n$ generating acylsamarium species (Eq. 6).

$$(6)$$
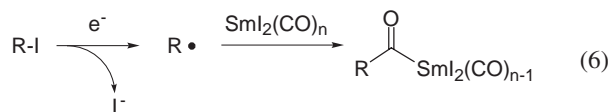
In conclusion, we have demonstrated the photoirradiated atmospheric carbonylation of organic halides with samarium diiodide. Further mechanistic studies of this carbonylation are now under investigation.

Experimental

Atmospheric Carbonylation. In a 20 mL three-necked glass flask (Pyrex) equipped with a dropping funnel, a cooler, and an inlet, were placed, under nitrogen, Sm powder (4 mmol, 0.601 g), 1,2-diiodoethane (2 mmol, 0.564 g), and THF (10 mL). The resulting mixture was stirred magnetically for 1.5 h to prepare a SmI$_2$/Sm reagent, and then, carbon monoxide was introduced into the vessel. Upon irradiation with a Xe lamp (500 W), the haloalkane (0.5 mmol) was added dropwise to the mixture over 1 h, and then, the reaction was continued for another 5 h. After the decomposition of the excess SmI$_2$/Sm with air, followed by 1 mol L^{-1} HCl, the product was extracted with ether. The extracts were dried (MgSO$_4$) and concentrated in vacuo. Purification of the product was performed by preparative HPLC or PTLC.

References

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2   By using only SmI$_2$ (i.e., in the absence of Sm metal), the reductive carbonylation of dodecyl iodide with CO occurred, but the yield of dodecyl tridecyl ketone was lower compared to the reaction using the SmI$_2$/Sm-mixed system. We already reported the combination of SmI$_2$ and Sm metal exhibited higher reducing power compared with SmI$_2$ or Sm metal itself. See: A. Ogawa, N. Takami, M. Sekiguchi, I. Ryu, N. Kambe, N. Sonoda, *J. Am. Chem. Soc.* **1992**, *114*, 8729.

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8   The existence of CO also decreases the reducing ability of SmI$_2$ in the reduction of 1-iodododecane. See: Ref. 1b.