

Table 2. Photoinduced Carbonylation of Alkyl Chlorides with CO and SmI₂^a

entry	chloride	product	yield, %
1			89
2			63
3			61
4			68

^a RCl (0.5 mmol), CO (50 atm), SmI₂ (4 mmol), THF (20 mL), 50 °C, 9 h, *hν* > 400 nm (xenon lamp 500 W, filter).

reduction of alkyl chlorides with SmI₂, the copresence of carbon monoxide leads to a novel carbonylation involving alkyl radicals (or acylsamarium species) as key intermediates. Thus, we examined the photoinitiated reaction of alkyl chlorides with SmI₂ in the presence of carbon monoxide.^{11,12} When the reaction of 1-chlorododecane with SmI₂ was carried out under the pressure of carbon monoxide (50 atm) upon irradiation with a xenon lamp through a filter (*hν* > 400 nm),¹³ carbonylation of 1-chlorododecane took place successfully, giving 89% of dodecyl tridecyl ketone (**5**, R = *n*-C₁₂H₂₅), which incorporated two dodecyl and two carbon monoxide units (eq 3 and entry 1 in Table 2). On the other hand, no carbonylation took place in the dark.

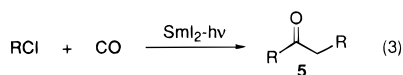
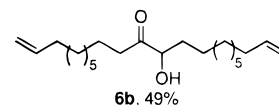


Table 2 represents the results of the photoinduced carbonylation of alkyl chlorides with CO and SmI₂. The carbonylation of alkyl chlorides bearing an olefinic unit proceeded successfully to give the corresponding asymmetrical ketones in good yields (entries 2 and 3). Similarly, secondary alkyl chlorides such as cyclohexyl chloride underwent photoinduced carbonylation to provide the products consisting of two alkyl and two carbon monoxide units (entry 4). With tertiary alkyl chlorides like 1-adamantyl chloride and aryl chlorides like β-naphthyl chloride, however, no carbonylation took place at all (only reduction to the corresponding hydrocarbons occurred).

Recently, Kagan et al. reported that the reaction of acyl chlorides with SmI₂ generated acylsamarium species, which underwent dimerization to give asymmetrical ketones in the presence of excess amounts of SmI₂.¹⁴ In fact, the reaction of

cyclohexanecarbonyl chloride with SmI₂ (8 equiv) at 38 °C for 0.5 h upon irradiation with visible light afforded cyclohexylmethyl ketone (**5d**) in 64% yield. Furthermore, the photoinduced carbonylation of 9-decyl chloride with SmI₂ and CO under controlled conditions gave rise to 49% of α-ketol (**6b**). It was also known that the controlled reaction of acyl



chlorides with SmI₂ afforded α-ketols.^{14e} Therefore, these results suggest that the photoinduced carbonylation with SmI₂ included the formation of acylsamarium species (as a key intermediate), which may dimerize to give asymmetrical ketones. As to the carbonylation step, the following two mechanistic pathways can be proposed: The first postulates the reaction of alkyl radical with CO to give acyl radical, which undergoes further reduction with excess SmI₂ to acylsamarium species. The second includes the reaction of alkylsamarium with CO.¹⁵ However, the second mechanistic pathway can be ruled out easily by the fact that the photoinduced reaction of an alkylsamarium (*n*-C₁₂H₂₅SmI₂) with CO (50 atm) at 40 °C did not afford the desired carbonylated product at all. In order to clarify the formation of acyl radicals in this carbonylation, several attempts to capture acyl radicals with olefins were performed, but no trace of addition products could be detected.¹⁷ In addition, in the carbonylation of 4-heptenyl chloride (entry 3 in Table 2), any product derived from 5-*exo* cyclization of the acyl radical was not detected. Moreover, the present carbonylation could proceed even under the atmospheric pressure of CO,¹⁸ while the radical carbonylation usually requires higher pressures of CO.¹⁰ However, these observations can be explained if the electron transfer from SmI₂ to acyl radicals is extremely fast.¹⁹ We are currently examining the application of this photoinduced new reduction system with SmI₂ to different classes of substrates, as well as clarifying the precise mechanism of this carbonylation.

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Supporting Information Available: Experimental details and ¹H NMR spectra (8 pages). See any current masthead page for ordering and Internet access instructions.

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(15) The third hypothesis suggests that the alkyl radical reacts with samarium carbonyl species¹⁶ to give acylsamarium species directly. Thus, we attempted to detect samarium carbonyl species with IR spectrometer: After the reaction of SmI₂ with CO (50 atm) upon visible light irradiation (in the absence of substrates), CO was purged and immediately IR spectra of the resulting solution was measured. However, no absorbance assigned to samarium carbonyl species was detected.

(16) For a carbonyl complex of samarium, see: Kolobova, N. E.; Suleimanov, G. Z.; Kazimirchuk, E. I.; Khandozhko, V. N.; Mekhdiev, R. Yu.; Lokshin, B. V.; Ezernitskaya, M. G.; Beletskaya, I. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1985**, 2833.

(17) The tin radical-mediated carbonylation of alkyl iodides with CO in the copresence of excess styrene proceeds *via* the capture of acyl radicals with styrene: Ryu, I.; Kusano, K.; Yamazaki, H.; Sonoda, N. *J. Org. Chem.* **1991**, *56*, 5003.

(18) The photoinduced reaction of 1-dodecyl chloride (0.5 mmol) with SmI₂ (4 mmol) and CO (1 atm) in THF (20 mL) at 50 °C for 6 h provided 39% of dodecyl tridecyl ketone and 52% of *n*-dodecane.

(19) The rate constants for the reaction of primary alkyl radicals with SmI₂ in THF/HMPA are reported to be 5 × 10⁵ to 7 × 10⁶ M⁻¹ s⁻¹ (Hasegawa, E.; Curran, D. P. *Tetrahedron Lett.* **1993**, *34*, 1717). While the rate constant for the decarbonylation of PhCH₂CO[•] is known to be 1.08 × 10⁷ s⁻¹ (41 °C), the reaction of phenylacetyl chloride with SmI₂ did not give any decarbonylated product.^{14b} This suggests that the reduction of acyl radicals by SmI₂ is much faster than that of primary alkyl radicals.

N. Synlett **1995**, 1249. (e) Ryu, I.; Muraoka, H.; Kambe, N.; Komatsu, M.; Sonoda, N. *J. Org. Chem.* **1996**, *61*, 6396. (f) Ryu, I.; Sonoda, N.; Curran, D. P. *Chem. Rev.* **1996**, *96*, 177. (g) Ryu, I.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1050 and references cited therein.

(11) For the reactions of divalent organosamarium complexes with CO, see: (a) Evans, W. J.; Grate, J. W.; Hughes, L. A.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 3728. (b) Evans, W. J.; Grate, J. W.; Hughes, L. A.; Drummond, D. K.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 1722. (c) Evans, W. J. *Polyhedron* **1987**, *6*, 803. (d) Evans, W. J.; Drummond, D. K. *J. Am. Chem. Soc.* **1988**, *110*, 2772. (e) Evans, W. J.; Drummond, D. K.; Chamberlain, L. R.; Doedens, R. J.; Bott, S. G.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 4983.

(12) Collin, J.; Kagan, H. B. *Tetrahedron Lett.* **1988**, *29*, 6097.

(13) The photoinduced carbonylation was conducted by using a stainless steel autoclave bearing glass windows. For the detailed experimental procedure, see the Supporting Information.

(14) (a) Girard, P.; Couffignal, R.; Kagan, H. B. *Tetrahedron Lett.* **1981**, *22*, 3959. (b) Soupe, J.; Namy, J. L.; Kagan, H. B. *Tetrahedron Lett.* **1984**, *25*, 2869. (c) Sasaki, M.; Collin, J.; Kagan, H. B. *Tetrahedron Lett.* **1988**, *29*, 6105. (d) Collin, J.; Dallemer, F.; Namy, J. L.; Kagan, H. B. *Tetrahedron Lett.* **1989**, *30*, 7407. (e) Collin, J.; Namy, J. L.; Dallemer, F.; Kagan, H. B. *J. Org. Chem.* **1991**, *56*, 3118. (f) Namy, J. L.; Colomb, M.; Kagan, H. B. *Tetrahedron Lett.* **1994**, *35*, 1723.