Carbonylation of Acidic Hydrocarbons with Selenium and Carbon Monoxide. A Novel Method for Synthesis of Selenol Esters

Hajime Maeda,[†] Shin-ichi Fujiwara,*[,‡] Tsutomu Shin-Ike,[‡]
Nobuaki Kambe,[†] and Noboru Sonoda*[,†]

Department of Applied Chemistry
Faculty of Engineering, Osaka University
Suita, Osaka 565, Japan
Department of Chemistry, Osaka Dental University
Hirakata, Osaka 573, Japan

Received May 20, 1996

Synthesis of esters *via* carbonylation with carbon monoxide is one of the principal transformations in organic chemistry.[1] These processes are roughly classified into two categories: (i) transition-metal-catalyzed carbonylation as represented by the Reppe reaction[2] and (ii) acid-catalyzed carbonylation (Koch reaction).[3] As for the synthesis of thiol and selenol esters using carbon monoxide, transition-metal-catalyzed carbonylation of disulfides,[4] sulfides,[4a,5] thiols,[4a,6] and diselenides[4c,7] has already been developed. It is also known that thiol esters can be formed by trapping of *in situ* generated acyllithiums with disulfides, CS_2, or sulfur.[8] Here we disclose a new methodology for carbonylation of acidic hydrocarbons with selenium and carbon monoxide, leading to the formation of selenol esters.

Organolithium compounds are known to react with selenium to give lithium selenolates.[9] Indeed, when (9-methylfluorenyl)lithium generated from **1a** and BuLi was allowed to react with selenium at 20 °C, the corresponding selenide **3a** was obtained in 93% yield after quenching with MeI (Scheme 1). However, we found that, when CO was introduced at 20 °C into a THF solution of selenolate **2a**, a stoichiometric amount of CO was absorbed within 90 min. Addition of MeI followed by usual workup gave carbonylated product **4a** in 93% yield (run 1 in Table 1).

The representative results of carbonylation of fluorenes **1** are listed in Table 1. Addition of HMPA accelerated CO absorption (run 2), and carbonylation proceeded even at −23 °C (run 3). Fluorenes having a butyl or cyclohexyl group afforded the corresponding selenol esters **4b** and **4c** in high yields (runs 4 and 5). Carbonylation of phenyl derivative **1d** was slow, giving **4d** in a moderate yield (run 6). Under similar conditions, fluorene (R = H) gave a complex mixture of products including only 8% of **4a** probably due to an equilibrium of benzylic anions arising from the abstraction of the second benzylic proton of intermediates.

Scheme 1

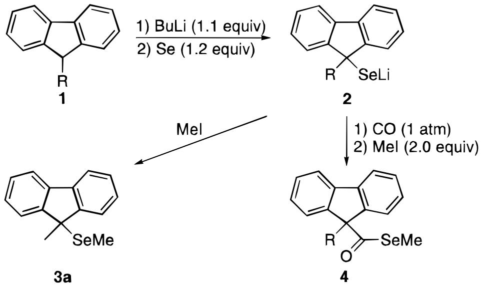
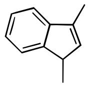
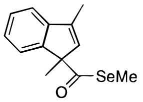
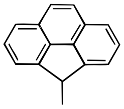
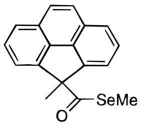
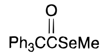
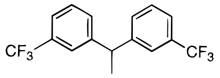
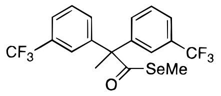
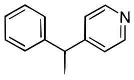
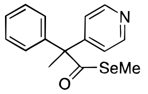
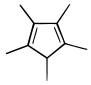
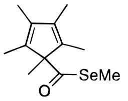


Table 1. Carbonylation of Fluorene Derivatives[a]

run	substrate	R	temp (°C)	time (min)	product	isolated yield (%)
1[b]	**1a**	Me	20	90	**4a**	93
2	**1a**	Me	20	40	**4a**	96
3	**1a**	Me	−23	60	**4a**	93
4	**1b**	*n*-Bu	20	40	**4b**	93
5	**1c**	*c*-C_6H_{11}	20	50	**4c**	98
6	**1d**	Ph	20	120	**4d**	47

[a] Conditions: **1** (2.0 mmol), *n*-BuLi (2.2 mmol), THF (25 mL), HMPA (6.0 mmol), −78 °C, 30 min; Se (2.4 mmol), −78 to ∼+20 °C (or −23 °C in run 3), 30 min; CO (1 atm), under conditions specified in the table; MeI (4.0 mmol), 0 °C (or −23 °C in run 3), 30 min. [b] Without HMPA.

Table 2. Carbonylation of Acidic Hydrocarbons[a]

run	substrate	product	time (h)	isolated yield (%)
1			1	40
2			1	77
3[b]	Ph_3CH	 $Ph_3CC(=O)SeMe$	2	55
4			37	39
5			17	35
6			1	74

[a] Substrate (2.0 mmol), *n*-BuLi (2.2 mmol), Se (2.4 mmol), CO (1 atm), MeI (4.0 mmol), THF (25 mL), HMPA (6.0 mmol). Methyl iodide was added after absorption of carbon monoxide ceased. [b] *t*-BuLi (2.2 mmol) was used instead of *n*-BuLi in the presence of TMEDA (3.0 mmol).

To examine the generality of the present carbonylation, several benzylic substrates were tested under similar conditions, and the results are presented in Table 2. 1,3-Dimethylindene and 4-methyl-4*H*-cyclopenta[*def*]phenanthrene were carbonylated in 40% and 77% yields, respectively (runs 1 and 2). Carbonylation of triphenylmethane and 1,1-diarylethanes also proceeded to give the desired selenol esters in moderate yields (runs 3−5). As an example of allylic substrates, we tested

---

[†] Osaka University.

[‡] Osaka Dental University.

(1) For reviews of ester synthesis *via* carbonylation, see: (a) Tkatchenko, I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds; Pergamon Press: Oxford, 1982; Vol. 8, pp 101−223. (b) Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation: Direct Synthesis of Carbonyl Compounds*; Plenum Press: New York, 1991; pp 111−143.

(2) (a) Falbe, J. *New Syntheses with Carbon Monoxide*; Springer-Verlag: New York, 1980; Chapter 3. (b) Bates, R. W. In *Comprehensive Organometallic Chemistry II*, Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds; Pergamon Press: Oxford, 1995; Vol. 12, pp 349−386.

(3) Chapter 5 in ref 2a.

(4) (a) Holmquist, H. E.; Carnahan, J. E. *J. Org. Chem.* **1960**, *25*, 2240. (b) Antebi, S.; Alper, H. *Tetrahedron Lett.* **1985**, *26*, 2609. (c) Kuniyasu, H.; Ogawa, A.; Miyazaki, S. -I.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1991**, *113*, 9796.

(5) Crudden, C. M.; Alper, H. *J. Org. Chem.* **1995**, *60*, 5579.

(6) (a) Reppe, W. *Justus Liebigs Ann. Chem.* **1953**, *582*, 1. (b) Reppe, W.; Kröper, H. *Justus Liebigs Ann. Chem.* **1953**, *582*, 38. (c) Antebi, S.; Alper, H. *Organometallics* **1986**, *5*, 596.

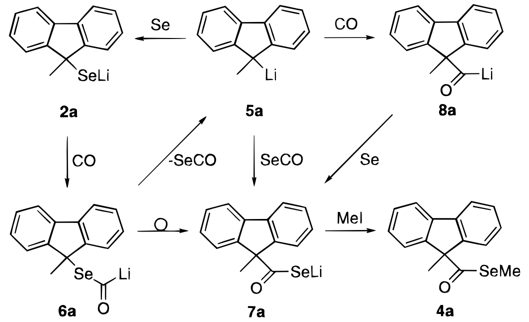
(7) Uemura, S.; Takahashi, H.; Ohe, K.; Sugita, N. *J. Organomet. Chem.* **1989**, *361*, 63.

(8) (a) Seyferth, D.; Hui, R. C. *Organometallics* **1984**, *3*, 327. (b) Seyferth, D.; Hui, R. C. *Tetrahedron Lett.* **1984**, *25*, 2623.

(9) (a) Gould, E. S.; McCullough, J. D. *J. Am. Chem. Soc.* **1951**, *73*, 1109. (b) Engman, L.; Hellberg, J. S. E. *J. Organomet. Chem.* **1985**, *296*, 357.

S0002-7863(96)01699-X CCC: $12.00

Scheme 2



1,2,3,4,5-pentamethylcyclopentadiene, which underwent carbonylation efficiently to give the corresponding selenol ester in 74% under the same conditions (run 6).

Plausible pathways of the present carbonylation are shown in Scheme 2. Reaction of **5a** with selenium affords **2a**, which then reacts with CO to give selenocarboxylate **7a** probably *via* formal rearrangement of **6a**. It is still a question whether the rearrangement proceeds intramolecularly or intermolecularly *via* **5a** with elimination of carbonyl selenide.[10] Selenol ester **4a** is formed by trapping of **7a** with methyl iodide. An alternative pathway *via* generation of acyllithium **8a** by the direct reaction of **5a** with CO and subsequent trapping with selenium (which is similar to that proposed by Seyferth in the thiol ester synthesis[8]) seems unlikely since **5a** may not be present in substantial concentration in the reaction media. This was supported by the fact mentioned above that **3a** was obtained in a quantitative yield by the addition of MeI to a mixture of **5a** and selenium in the absence of CO. Moreover, even if **8a** is generated, decarbonylation seems to be much faster under the present reaction conditions than intermolecular trapping with selenium.[11] When BuLi was employed instead of fluorenyllithiums under the same conditions, only BuSeMe was obtained without any carbonylated products. This result may suggest that migration of the butyl group does not proceed, probably due to the thermodynamic instability of the butyl anion.

Carbonylation at benzylic and allylic positions with CO has been attained by means of transition-metal-catalyzed reaction of the corresponding halides. But these reactions have been applied to only relatively simple compounds, and no precedents have been reported for carbonylation of fluorene, indene, and triphenylmethane derivatives.[12] Alternative methods without the use of transition metals are not suitable for carbonylation of these benzylic and allylic compounds. For example, acid-catalyzed carbonylation of benzyl cations occurs at the *para* position in the phenyl ring,[13] and CO reacts sluggishly with di- or triaryl-substituted benzylic cations.[14] Carbonylation of benzyl anions hardly proceeds.[15] Carbonylation of benzyl radicals with CO has never been attained because of fast reverse decarbonylation.[16]

Selenol esters[17] are synthetically very useful compounds as precursors of acyl radicals[18] and acyl cations.[19] They can also be converted easily to the corresponding acids,[20] esters,[20] amides,[20] ketones,[21] aldehydes,[22] and alkenyl selenides.[23] Hydrocarbons employed in this study have pK_a values ranging from 18 to 31,[24] and the present reaction provides a useful method for carbonylation of these compounds.

Acknowledgment. This work was supported in part by a Grant-in-Aid from the Ministry of Education, Science and Culture, Japan. Thanks are due to the Instrumental Analysis Center, Faculty of Engineering, Osaka University.

Supporting Information Available: Experimental procedure and spectral data (5 pages). See any current masthead page for ordering and Internet access instructions.

JA9616995

---

[10] The intermolecular process may not be ruled out since 56% of **4a** was obtained from the reaction of **5a** with carbonyl selenide at −78 °C followed by trapping with methyl iodide. A similar pathway has been proposed for selenium-catalyzed urea synthesis from amines and CO: Sonoda, N. *Pure Appl. Chem.* **1993**, *65*, 699.

[11] Seyferth carried out the reaction of organolithiums with CO at −78 °C or below; see ref 8. When the reaction of **5a** with CO was conducted at 20 °C without selenium, absorption of CO was not observed.

[12] Migratory insertion of carbon monoxide into benzylic or allylic carbon−transition metal bonds is slower than that into alkyl carbon−transition metal bonds, probably due to thermodynamic disadvantage; see: (a) Nagy-Magos, Z.; Bor, G.; Markó, L. *J. Organomet. Chem.* **1968**, *14*, 205. (b) Craig, P. J.; Green, M. *J. Chem. Soc., Sect. A* **1969**, 157. (c) Fachinetti, G.; Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1977**, 1946. (d) Sonnenberger, D. C.; Mintz, E. A.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 3484.

[13] (a) Booth, B. L.; El-Fekky, T. A.; Noori, G. F. M. *J. Chem. Soc., Perkin Trans. 1* **1980**, 181. (b) Olah, G. A.; Laali, K.; Farooq, O. *J. Org. Chem.* **1985**, *50*, 1483.

[14] Takahashi, Y.; Yoneda, N.; Nagai, H. *Chem. Lett.* **1985**, 1733.

[15] There is only one example of the efficient carbonylation of a benzyllithium with CO where a transiently generated acyllithium was trapped by intramolecular silicon migration: Murai, S.; Ryu, I.; Iriguchi, J.; Sonoda, N. *J. Am. Chem. Soc.* **1984**, *106*, 2440.

[16] For rate constants of decarbonylation of phenylacetyl radical, see: (a) Cozens, F. L.; Scaiano, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 5204. (b) Tsentalovich, Y. P.; Fischer, H. *J. Chem. Soc., Perkin Trans. 2* **1994**, 729 and references cited therein.

[17] Hitherto known preparative methods of selenol esters are based on acylation or aroylation of selenols or their metal salts; see: Ogawa, A.; Sonoda, N. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 6, pp 461−484.

[18] Pfenninger, J.; Heuberger, C.; Graf, W. *Helv. Chim. Acta* **1980**, *63*, 2328.

[19] Kozikowski, A. P.; Ames, A. *Tetrahedron* **1985**, *41*, 4821.

[20] Kozikowski, A. P.; Ames, A. *J. Org. Chem.* **1978**, *43*, 2735.

[21] (a) Sviridov, A. F.; Ermolenko, M. S.; Yashunsky, D. V.; Kochetkov, N. K. *Tetrahedron Lett.* **1983**, *24*, 4355. (b) Back, T. G.; Kerr, R. G. *Tetrahedron* **1985**, *41*, 4759.

[22] Kuniyasu, H.; Ogawa, A.; Higaki, K.; Sonoda, N. *Organometallics* **1992**, *11*, 3937.

[23] Petasis, N. A.; Lu, S. -P. *Tetrahedron Lett.* **1995**, *36*, 2393.

[24] For acidities of these compounds in DMSO; see: Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.