

Selective Reduction of α,β -Unsaturated Carbonyl Compounds with CO/H₂O Catalyzed by Selenium under Atmospheric Pressure

Fengshou Tian, Shiwei Lu*

National Engineering Research Center for Catalysis, Dalian Institute of Chemical Physics, Graduate School of the Chinese Academy of Sciences, 161 Zhongshan Road, Dalian, Liaoning 116011, P. R. China

Fax +86(411)83698749; E-mail: fengshoutian@163.com; E-mail: lusw@dicp.ac.cn

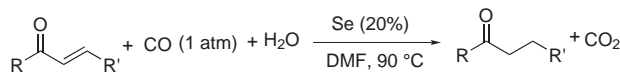
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Abstract: Selective reduction of α,β -unsaturated carbonyl compounds with carbon monoxide and water in the presence of a catalytic amount of selenium proceeded efficiently to afford the corresponding saturated carbonyl compounds in high yields under atmospheric pressure without use of a base.

Key words: selenium, carbon monoxide, α,β -unsaturated carbonyl compounds

Selective reduction of α,β -unsaturated carbonyl compounds is a useful functional group transformation in organic synthesis. The main problem of this reaction is to obtain an optimal selectivity in favor of the olefin or the carbonyl reduction. The common selective reducing agents are metal catalysts,¹ metal hydrides,² and metal or metal alloy.³ Furthermore, the carbon-carbon double bond of α,β -unsaturated carbonyl compounds can also be selectively reduced by PhSeH/hv,⁴ PhSeH/O₂,⁵ MSeH (M = Na or Li),⁶ or NaTeH.⁷ Although all these methods are successfully applied to selective reduction of α,β -unsaturated carbonyl compounds, these methods suffer from major disadvantages such as complex preparation process of reducing agents, the use of excess reducing agents, indispensable additive agents, harsh reaction conditions, complicated manipulations, low yields or low functional selectivity. Sonoda et al. found that elemental selenium could be readily reduced by carbon monoxide and water in the presence of base to produce hydrogen selenide which was successfully usable for the selective reduction of α,β -unsaturated carbonyl compounds.⁸ Although Sonoda's method is relatively convenient and can be easily manipulated, the process is also subject to the use of stoichiometric selenium, the strong base, relatively high pressure of CO (3.0 MPa), and long reaction time (24 h).

In the course of our ongoing studies on selenium-catalyzed reductive carbonylation of nitro aromatic compounds with carbon monoxide,⁹ we have developed a new reduction system, in which hydrogen selenide (HSe-) formed in situ from elemental selenium, carbon monoxide, and water in DMF under atmospheric pressure without use of a base. In this system, aromatic aldehydes can be reduced and selenated to symmetrical diselenides.¹⁰



R = aryl / heteroaryl R' = alkyl / aryl / heteroaryl

Scheme 1

Keeping this results in mind, we investigated the reaction of selective reduction of α,β -unsaturated carbonyl compounds and found that under similar conditions the Se(cat.)/CO/H₂O/DMF system was successfully usable for the selective reduction of α,β -unsaturated carbonyl compounds in the absence of base in high yields (Scheme 1).

Table 1 Selective Reduction of 1,3-Diphenyl-propenone (**1a**) to 1,3-Diphenyl-propan-1-one (**1b**) in the Presence of a Catalytic Amount of Selenium under Various Reaction Conditions

Entry ^a	Reaction temperature (°C)	Solvent	Yield (%) ^b
1	60	THF	1
2	75	EtOH	<1
3	75	MeCN	1
4	90	1,4-Dioxane	<1
5	90	Toluene	2
6	23	DMF	3
7	90	DMF ^c	2
8	90	FP ^d	62 ^e
9	90	DMSO	95 ^e
10	90	DMF	99 ^e
11	75	DMF	60 ^e
12	50	DMF	47 ^e

^a Reaction conditions: 1,3-diphenyl-2-propenone (**1a**, 2.5 mmol), Se (0.5 mmol), bubbling CO (0.1 MPa), H₂O (2 mL), solvent (20 mL), 2.0 h.

^b GC yield.

^c Without use of H₂O.

^d FP = 1-formylpiperidine.

^e Isolated yield of **1b**.

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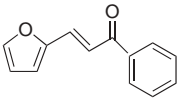
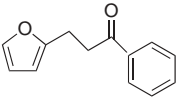
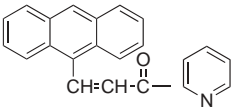
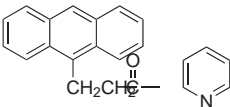
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The reaction conditions for the selective reduction of 1,3-diphenyl-propenone (**1a**) to 1,3-diphenyl-propan-1-one (**1b**) were examined in detail and some of the results are shown in Table 1. When reduction solvents such as THF, EtOH, MeCN, 1,4-dioxane, and toluene were used as the reaction solvents, selective reduction of **1a** almost did not occur (Table 1, entries 1–5). It is noteworthy that selective reduction of **1a** did almost not proceed in DMF at ambient

temperature or without use of water (Table 1, entries 6 and 7). 1-Formyl piperidine and DMSO as solvents were available for the selective reduction of **1a** to **1b** (Table 1, entries 8 and 9). When **1a** was treated with carbon monoxide (bubbling) and water (2 mL) in the presence of a catalytic amount of selenium (0.2 equiv) in DMF solution at 90 °C for 2 hours, selective reduction of **1a** efficiently proceeded to give **1b** in 99% yield (Table 1, entry 10).

Table 2 Selective Reduction of α,β -Unsaturated Carbonyl Compounds to Saturated Carbonyl Compounds in the Presence of a Catalytic Amount of Selenium

Entry ^a	α,β -Unsaturated carbonyl compound	Product	Mp (°C)	Reaction time (h)	Yield (%) ^b
1	PhCH=CHCOPh 1a	PhCH ₂ CH ₂ COPh 1b	68–69 (69) ¹¹	2	99
2	<i>p</i> -CH ₃ OC ₆ H ₄ CH=CHCOPh 2a	<i>p</i> -CH ₃ OC ₆ H ₄ CH ₂ CH ₂ COPh 2b	62–63 (66) ¹²	2	98
3	<i>p</i> -ClC ₆ H ₄ CH=CHCOPh 3a	<i>p</i> -ClC ₆ H ₄ CH ₂ CH ₂ COPh 3b	53–54 (58) ¹²	2	84
4	PhCH=CHCOC ₆ H ₄ Cl- <i>p</i> 4a	PhCH ₂ CH ₂ COC ₆ H ₄ Cl- <i>p</i> 4b	73–75 (78) ¹²	2	98
5	PhCH=CHCOC ₆ H ₄ F- <i>p</i> 5a	PhCH ₂ CH ₂ COC ₆ H ₄ F- <i>p</i> 5b	37–39 (35–36.5) ¹³	2	86
6	<i>p</i> -ClC ₆ H ₄ CH=CHCOC ₆ H ₄ F- <i>p</i> 6a	<i>p</i> -ClC ₆ H ₄ CH ₂ CH ₂ COC ₆ H ₄ F- <i>p</i> 6b	46–48 (–) ¹³	2	95
7	<i>p</i> -CH ₃ OC ₆ H ₄ CH=CHCOC ₆ H ₄ Cl- <i>p</i> 7a	<i>p</i> -CH ₃ OC ₆ H ₄ CH ₂ CH ₂ COC ₆ H ₄ Cl- <i>p</i> 7b	63–65 (–) ¹³	2	97
8	<i>p</i> -CH ₃ OC ₆ H ₄ CH=CHCOC ₆ H ₄ OCH ₃ - <i>p</i> 8a	<i>p</i> -CH ₃ OC ₆ H ₄ CH ₂ CH ₂ COC ₆ H ₄ OCH ₃ - <i>p</i> 8b	36–38 (–) ¹⁴	2	76
9	PhCH=CHCOCH ₃ 9a	PhCH ₂ CH ₂ COCH ₃ 9b	Yellow liquid ¹⁵	2	95
10			Yellow liquid ¹⁶	3	88
11			91–93	3	90
12	PhCH=CHCOCH=CHPh 12a	PhCH ₂ CH ₂ COCH ₂ CH ₂ Ph 12b	Yellow liquid ¹⁷	4	96
13	PhCH=CHCH=CHCOPh 13a	PhCH ₂ CH ₂ CH ₂ CH ₂ COPh 13b	Yellow liquid ¹⁸	4	86
14	PhCH=CHCN 14a	No reaction		4	–
15	PhCH=CH ₂ 15a	No reaction		4	–
16	PhCH=CHCH(OH)Ph 16a	No reaction		4	–

^a Reaction conditions: α,β -unsaturated carbonyl compound (2.5 mmol), Se (0.5 mmol), bubbling CO (0.1 MPa), water (2 mL), DMF (20 mL), 90 °C.

^b Isolated yield.

1,3-Diphenyl-propan-1-ol or 1,3-diphenyl-prop-2-en-1-ol was not detected from the reaction mixture. With DMF as the reaction solvent, while lowering the reaction temperature, the yield of **2a** decreased correspondingly (Table 1, entries 10–12).

Similar reactions were investigated and the results of reduction of various α,β -unsaturated carbonyl compounds are shown in Table 2. During the reduction reaction, the chloro-, fluoro-, and methoxy group were unaffected (Table 2, entries 2–8). However, selective reduction of **8a** was not complete under the same reaction conditions to give **8b** in only 76%. Alkyl group instead of phenyl group was investigated; the selective reaction still could take place in high yield (Table 2, entry 9). The carbon-carbon double bonds of **10a** and **11a** underwent reduction without affecting the furyl- and pyridyl groups. At the same time, 1,5-diphenyl-1,4-pentadien-3-one and 1,5-diphenyl-2,4-pentadien-1-one, which possess two conjugated carbon-carbon bonds, were completely reduced to saturated carbonyl compounds (Table 2, entries 12 and 13). Unfortunately, cinnamitrile would not be reactive in the current reducing system (Table 2, entry 14). When cinnamaldehyde was carried out under the similar conditions, side reactions took place to afford a complex mixture. In addition, styrene and 1,3-diphenyl-2-en-1-ol also did not react at all (Table 2, entries 15 and 16), which implies that the isolated carbon-carbon double bonds are inactive to this reaction.

Although the detail of the mechanism has not been elucidated, it is likely that the selective reduction of α,β -unsaturated carbonyl compounds **a** may involve formation of intermediate Michael adduct **C**^{6,8} by the addition of in situ formed H_2Se to the carbon-carbon double bond of α,β -unsaturated carbonyl compounds **a**. Further decomposition of **C** give the product **b** and selenium, and then the catalyst selenium proceeds to the next cycle (Figure 1).

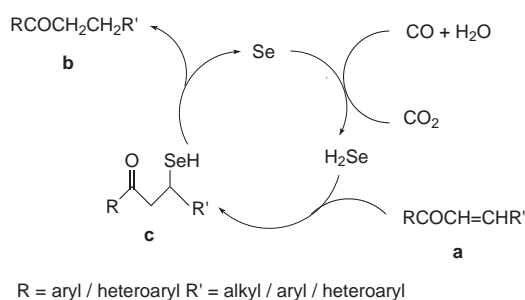


Figure 1 Proposed pathway to saturated carbonyl compounds **b**

In summary, we have developed an efficient and convenient method for the selective reduction of α,β -unsaturated carbonyl compounds with $\text{CO}/\text{H}_2\text{O}$ in the presence of a catalytic amount of selenium under atmospheric pressure in the absence of base.

Typical Reduction Procedure:

A 100 mL three-necked flask was charged with α,β -unsaturated carbonyl compound (2.5 mmol), selenium (0.5 mmol), H_2O (2 mL) and DMF (20 mL). Carbon monoxide was introduced and bubbled into the reaction mixture with vigorous stirring at 90°C for 2–4 h. The reaction was monitored by TLC determination. After the reaction was complete, CO bubbling was ceased and the resultant mixture was stirred in air at ambient temperature for 30 min. To this mixture 20 mL water was added and extracted with Et_2O (3×40 mL). The organic phase was dried over anhyd MgSO_4 , filtered and evaporated the volatiles under reduced pressure to afford the crude product. Further purification by column chromatography on silica gel or recrystallization gave the pure product. All products were identified by NMR and/or compared with the authentic samples.

3-Anthracen-9-yl-1-pyridin-2-yl-propan-1-one (**13b**):

Green solid; mp $91\text{--}93^\circ\text{C}$. $^1\text{H NMR}$ (400 MHz, CDCl_3 , 23°C): δ = 8.60 (d, 1 H, CH), 8.33–8.37 (m, 3 H, CH), 8.09 (d, 1 H, CH), 7.97 (s, 1 H, CH), 7.99 (s, 1 H, CH), 7.78 (d, 1 H, CH), 7.51–7.38 (m, 5 H, CH), 3.69 (t, 2 H, CH_2), 4.05 (t, 2 H, CH_2). $^{13}\text{C NMR}$ (400 MHz, CDCl_3 , 23°C): δ = 201.92 (C=O), 153.73, 149.61, 137.51, 134.20, 132.25, 130.23, 129.86, 127.81, 126.68, 126.35, 125.50, 124.94, 122.47, 40.08 (s, CH_2), 23.21 (s, CH_2).

References

- (1) (a) Sakaguchi, S.; Yamaga, T.; Ishii, Y. *J. Org. Chem.* **2001**, *66*, 4710. (b) Kitamura, T.; Joh, T.; Hagihara, N. *Chem. Lett.* **1975**, 203. (c) Selvam, P.; Sonavane, S. U.; Mohapatra, S. K.; Jayaram, R. V. *Tetrahedron Lett.* **2004**, *45*, 3071. (d) Yoshinaga, K.; Kito, T.; Ohkubo, K. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 178. (e) Saburi, M.; Ohnuki, M.; Ogasawara, M.; Takahashi, T.; Uchida, Y. *Tetrahedron Lett.* **1992**, *33*, 5783.
- (2) (a) Brown, H. C.; Mathew, C. P.; Pyun, C.; Son, J. C.; Yoon, N. M. *J. Org. Chem.* **1984**, *49*, 3091. (b) Brown, H. C.; Krishnamuthy, S. *Tetrahedron* **1979**, *35*, 567. (c) Noyori, R.; Ishigami, T. *J. Org. Chem.* **1972**, *37*, 1542. (d) Yamashita, M.; Kato, Y.; Suemitsu, R. *Chem. Lett.* **1980**, 847. (e) Goetz, R. W.; Orchin, M. *J. Am. Soc. Chem.* **1963**, *85*, 2782.
- (3) (a) Contento, M.; Saroia, D.; Trombini, C.; Umani-Ronochi, A. *Synthesis* **1979**, 30. (b) Cortese, N. A.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 3985. (c) Cabrera, A.; Alper, H. *Tetrahedron Lett.* **1992**, *33*, 5007. (d) Alonso, F.; Yus, M. *Tetrahedron* **1998**, *54*, 1921. (e) Lee, H. Y.; An, M. *Tetrahedron Lett.* **2003**, *44*, 2775.
- (4) Perkins, M. J.; Smith, B. V.; Turner, E. S. *J. Chem. Soc., Chem. Commun.* **1980**, 977.
- (5) Masawaki, T.; Uchida, Y.; Kambe, N.; Miyoshi, N.; Sonoda, N. *J. Phys. Org. Chem.* **1988**, *1*, 115.
- (6) Nishiyama, Y.; Yoshida, M.; Ohkawa, S.; Hamanaka, S. *J. Org. Chem.* **1991**, *56*, 6720.
- (7) (a) Yamashita, M.; Kato, Y.; Suemitsu, R. *Chem. Lett.* **1980**, 847. (b) Geethamalika, G.; Suguna Sundari, A.; Shanmugam, P.; Rajendran, S. P. *Indian J. Chem., Sect. B* **2004**, *43* (3), 674.
- (8) Nishiyama, Y.; Makino, Y.; Hamanaka, S.; Ogawa, A.; Sonoda, N. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1682.
- (9) (a) Yang, Y.; Lu, S. W. *Tetrahedron Lett.* **1999**, *40*, 4845. (b) Mei, J. T.; Yang, Y.; Xue, Y.; Lu, S. W. *J. Mol. Catal. A: Chem.* **2003**, *191*, 135. (c) Ling, G.; Chen, J. Z.; Lu, S. W. *J. Mol. Catal. A: Chem.* **2003**, *202*, 23. (d) Chen, J. Z.; Ling, G.; Lu, S. W. *Eur. J. Org. Chem.* **2003**, *17*, 3446. (e) Chen, J. Z.; Lu, S. W. *Appl. Catal., A* **2004**, *261*, 199. (f) Liu, X. Z.; Lu, S. W. *Chem. Lett.* **2003**, *32*, 1142. (g) Liu, X. Z.; Lu, S. W. *J. Mol. Catal. A: Chem.* **2004**, *212*, 127.

- (10) Tian, F. S.; Yu, Z. K.; Lu, S. W. *J. Org. Chem.* **2004**, *69*, 4520.
- (11) Kursanov, D. N.; Loim, N. M.; Baranova, V. A.; Moiseeva, L. V.; Zalukaev, L. P.; Parnes, Z. N. *Synthesis* **1973**, 420.
- (12) Sasson, Y.; Cohen, M.; Blum, J. *Synthesis* **1973**, 359.
- (13) Katiyar, S.; Latithambica, M. *Indian J. Chem., Sect. A* **1980**, *19 (10)*, 956.
- (14) Baker, B. R. *J. Am. Chem. Soc.* **1943**, *65*, 1572.
- (15) Nishiyama, Y.; Yoshida, M.; Ohhawa, S.; Hamanaka, S. *J. Org. Chem.* **1991**, *56*, 6720.
- (16) Persephone, C.; Mohamed, A. *Tetrahedron Lett.* **1983**, *49*, 5519.
- (17) Nightingale, D.; Wadsworth, F. T. *J. Am. Chem. Soc.* **1947**, *69*, 1181.
- (18) Narasaka, K.; Sakurai, H. *Chem. Lett.* **1993**, 1269.