Selenium-Catalyzed Deoxygenative Reduction of Aliphatic Nitro Compounds with Carbon Monoxide

Yutaka Nishiyama,* Sadatatsu Ikeda,
Hiroaki Nishida, and Rui Umeda

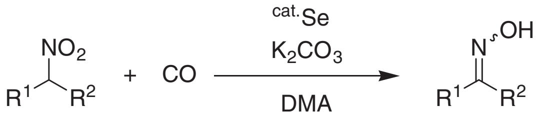
Department of Chemistry and Materials Engineering,
Faculty of Chemistry, Materials and Bioengineering,
Kansai University, Suita, Osaka 564-8680

Received December 28, 2009
E-mail: nishiya@kansai-u.ac.jp

A reduction method of aliphatic nitro compounds to oximes using carbon monoxide was developed. When aliphatic nitro compounds were treated with carbon monoxide in the presence of a selenium catalyst, the corresponding oximes were formed in moderate to good yields.

Carbon monoxide is widely accepted as a useful reducing agent as well as an extremely important agent for introducing carbonyl functions into organic molecules.[1] As to the synthetic reactions utilizing the reducing ability of carbon monoxide, transition-metal complexes are usually employed as the catalyst for the reduction or reductive carbonylation of various organic compounds with carbon monoxide. Recently, we and Chinese chemists have shown that elemental selenium, a non-transition metal, acts as a unique catalyst for the reduction or reductive carbonylation of aromatic nitro compounds with carbon monoxide giving the corresponding nitrogen-containing compounds.[2,3]

On the continuous study of the utility of carbon monoxide in organic synthesis, we now find that aliphatic nitro compounds are selectively reduced by carbon monoxide in the presence of a selenium catalyst under mild reaction temperature and carbon monoxide pressure producing the corresponding oximes in moderate to good yields (Scheme 1).[4,5] The preparation of oximes by the reductive deoxygenation of aliphatic nitro compounds has already been reported, however these methods have some disadvantages, namely (i) contamination of another reduction products, (ii) handling of agents unstable against moisture or air, (iii) limitation of substrates, and (iv) harsh reaction conditions.

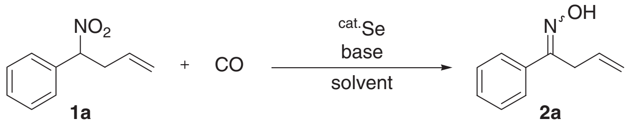


Scheme 1. Selenium-catalyzed reductive deoxygenation of aliphatic nitro compounds with carbon monoxide.

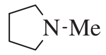
When 4-nitro-4-phenyl-1-butene (**1a**) was allowed to react with carbon monoxide (5 atm) in the presence of a catalytic amount of selenium (20 mol %) and three equivalent amounts of potassium carbonate in *N*,*N*-dimethylacetamide (DMA) at 25 °C for 0.5 h, reductive deoxygenation of **1a** smoothly proceeded to give 4-phenylbuten-4-one oxime (**2a**) in 98% yield without the formation of other nitrogen-containing compounds, such as amine, azo, azoxy, and nitroso (Entry 1 in Table 1). To determine the optimized reaction conditions, **1a**, which was chosen as a model compound, was treated with carbon monoxide in the presence of a selenium catalyst under various reaction conditions, and these results are shown in Table 1. When a tertiary amine, such as triethylamine and *N*-methylpyrrolidine was used as a base, the reductive deoxygenation of **1a** hardly proceeded under the same reaction conditions as Entry 1, and **1a** was recovered (Entries 2 and 3). In the case of DBU having a stronger basicity than that of triethylamine and *N*-methylpyrrolidine, **2a** was obtained in 72% yield (Entry 4). The use of *N*,*N*-dimethylformamide (DMF), acetonitrile, THF, and benzene instead of DMA as the solvent significantly decreased the yield of **2a** (Entries 5–8). Decreasing the amount of selenium as a catalyst (5 mol %) was successfully attained by extending the reaction time (Entries 9 and 10). When the reaction was carried out under an atmosphere of carbon monoxide, the yield of **2a** decreased (Entry 11).

In order to determine the scope and limitations of the preparation of aliphatic oximes by the reductive deoxygenation of nitro compounds with carbon monoxide, various aliphatic nitro compounds were treated with carbon monoxide in the

Table 1. Selenium-Catalyzed Reductive Deoxygenation of 4-Nitro-4-phenyl-1-butene (**1a**) with Carbon Monoxide[a)]



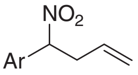
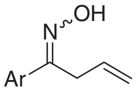
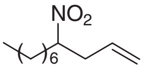
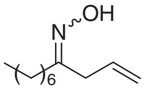
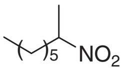
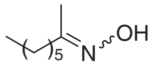
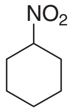
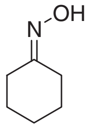
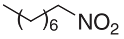
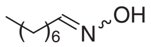
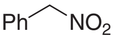
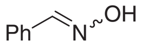
1a **2a**

Entry	Solvent	Base	Yield/%[b)]
1	DMA	K_2CO_3	98 (85)
2	DMA	Et_3N	9
3	DMA		7
4	DMA	DBU	72
5	DMF	K_2CO_3	53
6	CH_3CN	K_2CO_3	30
7	THF	K_2CO_3	7
8	C_6H_6	K_2CO_3	0
9[c)]	DMA	K_2CO_3	81
10[c),d)]	DMA	K_2CO_3	99
11[e)]	DMA	K_2CO_3	51

a) Reaction conditions: **1a** (0.30 mmol), Se (0.06 mmol), base (0.90 mmol), solvent (3 mL), and CO (5 atm) at 25 °C for 0.5 h. b) GC yield. The number in parenthesis shows the isolated yield. c) Se (0.015 mmol). d) For 3 h. e) CO (1 atm).

Published on the web June 30, 2010; doi:10.1246/bcsj.20090347

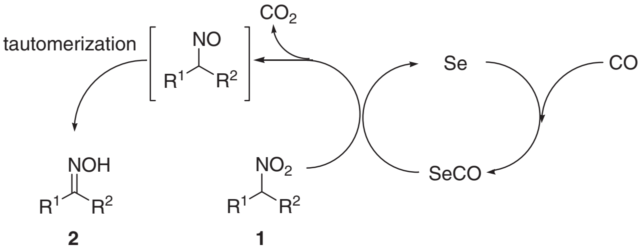
Table 2. Synthesis of Various Oximes[a)]

Entry	Substrate		Product		Yield/%[b)]
					
1	Ar = p-$CH_3C_6H_4$	**1b**		**2b**	90 (76)
2	Ar = p-$CF_3C_6H_4$	**1c**		**2c**	94 (73)
3	Ar = p-ClC_6H_4	**1d**		**2d**	98 (72)
4[c)]		**1e**		**2e**	77
5[d)]		**1f**		**2f**	54
6[d),e)]		**1g**		**2g**	77 (64)
7[d)]		**1h**		**2h**	94 (83)
8		**1i**		**2i**	33

a) Reaction conditions: substrate (0.30 mmol), Se (0.06 mmol), K_2CO_3 (0.90 mmol), DMA (3 mL), and CO (5 atm) at 25 °C for 0.5 h. b) GC yield. The numbers in parenthesis show the isolated yields. c) CO (20 atm) for 5 h. d) For 3 h. e) CO (50 atm).

presence of a selenium catalyst (20 mol %) under the same reaction conditions as that of Entry 1 in Table 1. These results are shown in Table 2. 4-(p-Methylphenyl)-, 4-(p-trifluoromethylphenyl)-, and 4-(p-chlorophenyl)-substituted 4-nitro-1-butenes were reductively deoxygenated by carbon monoxide to give the corresponding oximes **2b–2d** in 90, 94, and 98% yields, respectively (Entries 1–3). The conversion of the 4-nitro-1-undecene (**1e**) into 1-undecen-4-one oxime (**2e**) was successfully achieved using this system (Entry 4). When 2-nitrooctane (**1f**) and 1-nitrooctane (**1h**), which have no carbon–carbon double bond, were allow to react with carbon monoxide under mild reaction conditions, the yields of the corresponding oximes **2f** and **2h** decreased, however the product yields of **2f** and **2h** were improved by extending the reaction time (Entries 5 and 7). Similarly, nitrocyclohexane (**1g**) was reduced by carbon monoxide in the presence of a selenium catalyst to give cyclohexanone oxime (**2g**), which is an important intermediate in the preparation of nylon-6, in 77% yield (Entry 6). In the case of nitrophenylmethane, the yield of oxime **2i** was low due to the formation of various by-products (Entry 8).

A method for the preparation of carbonyl selenide (SeCO) via the acidolysis of secondary amine salts of the selenocarbamates generated by the reaction of elemental selenium with carbon monoxide and secondary amine has already been shown.[6] It was then proposed that the reductive deoxygenation of the nitro group of **1** with SeCO to generate the nitroso is the first step in this reaction. The tautomerization of nitroso compounds smoothly proceeded under the reaction conditions to give the oximes **2** (Scheme 2). When potassium carbonate, which was dried at 150 °C, was used, the yield of oxime was decreased (40%). Thus, another pathway including the reduction of nitro compound by hydrogen selenide, which was generated by the reaction of SeCO with H_2O, cannot be ruled out.[7]



Scheme 2. A plausible catalytic reaction pathway.

In summary, we found that the reaction of aliphatic nitro compounds with carbon monoxide in the presence of selenium catalyst gave the corresponding oximes in moderate to good yields with high selectivity.

Experimental

General Procedures. The ^1H and ^{13}C NMR spectra were recorded on 270 and 67.5 MHz spectrometers using $CDCl_3$ as the solvent with tetramethylsilane as the internal standard. The IR spectra were recorded on an FT-IR spectrometer. Gas chromatography (GC) was carried out using a flame-ionizing detector-equipped instrument and a capillary column (0.25 mm × 1200 mm).

Reagents. Selenium powder, amines, K_2CO_3, and nitrocyclohexane were commercially available and were used without further purification. The nitro compounds were prepared by literature methods and modification of these methods.[8] Other chemical agents were obtained commercially and were purified if necessary by distillation.

General Procedure for Selenium-Catalyzed Reaction of Aliphatic Nitro Compounds with Carbon Monoxide. In a 50 mL stainless steel autoclave were placed nitro compound (0.30 mmol), selenium (4 mg, 0.06 mmol), K_2CO_3 (124 mg, 0.90 mmol), and DMA (3 mL) and magnetic stirring bar. The apparatus was flushed three times and charged at 5–50 atm with carbon monoxide. The mixture was stirred at room temperature for 0.5–3 h. After the reaction, the carbon monoxide was purged in a well-ventilated hood. Aq. HCl was added to the reaction mixture, and the resultant solution was extracted with ethyl acetate (25 mL × 3). The organic layer was dried over $MgSO_4$. The resulting mixture was filtered and the filtrate was then concentrated. Purification of the residue by column chromatography on silica gel afforded the corresponding oxime. The product was characterized by comparing its spectral data with those of authentic sample or previous reports **2a**,[9] **2d**,[10] **2f**,[11] **2g**, **2h**,[11] and **2i**.[12] The structures of the products **2b**, **2c**, and **2e** were assigned by their ^1H and ^{13}C NMR, IR, and mass spectrum.

(*E*)-1-(*p*-Methylphenyl)-3-butene-1-one Oxime (2b): ^1H NMR (270 MHz, $CDCl_3$): δ 9.53 (br, 1H), 7.52 and 7.18 (AA′BB′, $J = 5.4$ Hz, 4H), 6.00–5.89 (m, 1H), 5.19–5.08 (m, 2H), 3.59 (d, $J = 4.1$ Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ 21.2, 31.0, 117.0, 126.2, 129.2, 132.2, 132.7, 139.3, 156.7; IR (KBr): 514, 592, 769, 816, 943, 1051, 1115, 1187, 1304, 1324, 1438, 1515, 1610, 1638, 3293 cm^{-1}; GC MS m/z 175 (M^+).

(*Z*)-1-(*p*-Methylphenyl)-3-butene-1-one Oxime (2b):

^{1}H NMR (270 MHz, CDCl$_3$): δ 8.89 (br, 1H), 7.41 and 7.22 (AA′BB′, $J = 5.4$ Hz, 4H), 5.88–5.78 (m, 1H), 5.14–5.06 (m, 2H), 3.29 (d, $J = 4.6$ Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (67.5 MHz, CDCl$_3$): δ 21.3, 39.8, 117.8, 127.9, 128.9, 130.0, 133.2, 139.0, 156.5; IR (KBr): 475, 518, 574, 640, 659, 719, 747, 812, 902, 930, 980, 1020, 1065, 1109, 1190, 1245, 1326, 1397, 1426, 1513, 1611, 1644, 1655, 3247 cm^{-1}; GC MS m/z 175 (M$^+$).

(*E*)-1-(*p*-Trifluoromethylphenyl)-3-butene-1-one Oxime (2c): ^{1}H NMR (270 MHz, CDCl$_3$): δ 9.12 (br, 1H), 7.66 and 7.55 (AA′BB′, $J = 6.8$ Hz, 4H), 5.91–5.77 (m, 1H), 5.13–5.02 (m, 2H), 3.53 (dt, $J = 1.7$, 5.4 Hz, 2H); ^{13}C NMR (67.5 MHz, CDCl$_3$): δ 21.5, 30.9, 117.6, 125.4, 125.5, 125.5, 126.7, 131.5, 156.0; IR (KBr): 501, 577, 610, 670, 754, 773, 836, 901, 931, 976, 1017, 1076, 1120, 1161, 1322, 1408, 1427, 1618, 1645, 3234 cm^{-1}; GC MS m/z 229 (M$^+$).

(*Z*)-1-(*p*-Trifluoromethylphenyl)-3-butene-1-one Oxime (2c): ^{1}H NMR (270 MHz, CDCl$_3$): δ 8.91 (br, 1H), 7.61 and 7.51 (AA′BB′, $J = 5.4$ Hz, 4H), 5.79–5.69 (m, 1H), 5.08–5.02 (m, 2H), 3.23 (dt, $J = 0.8$, 4.6 Hz, 2H); ^{13}C NMR (67.5 MHz, CDCl$_3$): δ 39.7, 118.6, 125.1, 125.2, 125.2, 125.3, 128.4, 132.3, 155.7; IR (KBr): 511, 834, 951, 1013, 1051, 1095, 1294, 1320, 1399, 1438, 1495, 1596, 1638, 3294 cm^{-1}; GC MS m/z 229 (M$^+$).

(*E*)-1-Undecene-4-one Oxime (2e): ^{1}H NMR (270 MHz, CDCl$_3$): δ 7.77 (br, 1H), 5.91–5.76 (m, 1H), 5.18–5.10 (m, 2H), 2.94 (dt, $J = 1.4$, 7.0 Hz, 2H), 2.34 (t, $J = 7.7$ Hz, 2H), 1.31–1.23 (m, 10H), 0.88 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (67.5 MHz, CDCl$_3$): δ 14.1, 22.6, 26.1, 29.0, 29.2, 31.7, 32.4, 33.9, 117.3, 132.1, 159.4; IR (KBr): 914, 969, 1637, 2928, 3247 cm^{-1}; GC MS m/z 182 (M$^+$).

(*Z*)-1-Undecene-4-one Oxime (2e): ^{1}H NMR (270 MHz, CDCl$_3$): δ 8.47 (br, 1H), 5.93–5.78 (m, 1H), 5.18–5.06 (m, 2H), 3.13 (dt, $J = 1.5$, 6.5 Hz, 2H), 2.19 (t, $J = 7.6$ Hz, 2H), 1.3–1.2 (m, 10H), 0.88 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (67.5 MHz, CDCl$_3$): δ 14.1, 21.5, 22.6, 25.5, 27.3, 29.0, 29.8, 31.7, 117.6, 133.4, 167.7; IR (KBr): 916, 976, 1655, 2928, 3247 cm^{-1}; GC MS m/z 182 (M$^+$).

This research was supported by a Grant-in-Aid for Science Research, and Strategic Project to Support the Formation of Research Bases at Private Universities from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

1 For recent reviews of carbonylation with carbon monoxide, see: a) *Modern Carbonylation Methods*, ed. by L. Kollar, Wiley-VCH Verlag, Weinheim, Germany, **2008**. b) M. Dugal, D. Koch, G. Naberfeld, C. Six, *Applied Homogeneous Catalyst with Organometallic Compounds*, 2nd ed., Wiley-VCH Verlag, Weinheim, Germany, **2002**, Vol. 3. c) *Handbook of Organopalladium Chemistry for Organic Synthesis*, ed. by E. Negishi, John Wiley & Sons, New York, **2002**, pp. 2681–2704. d) R. Skoda-Foldes, L. Kollar, *Curr. Org. Chem.* **2002**, *6*, 1097. e) R. W. Bates, in *Comprehensive Organometallics Chemistry*, ed. by E. W. Abel, F. G. A. Stone, G. Wilkinson, Pergamon Press, Oxford, UK, **1995**, Vol. 12, pp. 349–386. f) H. M. Colquhoun, D. J. Thompson, M. V. Twigg, *Carbonylation: Direct Synthesis of Carbonyl Compounds*, Plenum Press, New York, **1991**.

2 a) Y. Nishiyama, M. Fujimoto, N. Sonoda, *Synlett* **2006**, 109. b) Y. Nishiyama, Y. Naitoh, N. Sonoda, *Synlett* **2004**, 886. c) Y. Nishiyama, M. Hirose, W. Kitagaito, N. Sonoda, *Tetrahedron Lett.* **2002**, *43*, 1855. d) Y. Nishiyama, R. Maema, K. Ohno, M. Hirose, N. Sonoda, *Tetrahedron Lett.* **1999**, *40*, 5717.

3 a) X. Zhang, H. Jing, *J. Mol. Catal. A: Chem.* **2009**, *302*, 137. b) X. Liu, S. Lu, *J. Mol. Catal. A: Chem.* **2009**, *300*, 36. c) X. Zhang, H. Jing, J. Miao, S. Lu, *Huaxue Jinzhan* **2008**, *20*, 1102. d) X.-P. Zhang, S.-W. Lu, *J. Chem. Res.* **2008**, 589. e) X. Wang, P. Li, X. Yuan, S. Lu, *J. Mol. Catal. A: Chem.* **2006**, *253*, 261. f) X. Liu, S. Lu, *Cuihua Xuebao* **2005**, *26*, 74. g) X. Wang, G. Ling, Y. Xue, S. Lu, *Eur. J. Org. Chem.* **2005**, 1675. h) X. Zhang, S. Lu, *Synlett* **2005**, 1535. i) J. Chen, G. Ling, Z. Yu, S. Wu, X. Zhao, X. Wu, S. Lu, *Adv. Synth. Catal.* **2004**, *346*, 1267. j) X. Wang, S. Lu, Z. Yu, *Adv. Synth. Catal.* **2004**, *346*, 929. k) X. Liu, Q. Liu, S. Lu, *Cuihua Xuebao* **2004**, *25*, 597. l) X. Liu, S. Lu, *J. Mol. Catal. A: Chem.* **2004**, *212*, 127. m) X. Liu, A. Peng, S. Lu, *Cuihua Xuebao* **2003**, *24*, 731. n) J. Mei, S. Lu, *Cuihua Xuebao* **2003**, *24*, 321. o) J. Chen, G. Ling, S. Lu, *Tetrahedron* **2003**, *59*, 8251. p) J. Mei, S. Lu, *Cuihua Xuebao* **2002**, *23*, 321. q) J. Mei, S. Lu, *Huaxue Jinzhan* **2002**, *14*, 433. r) Y. Xue, S. Lu, *Chihua Xuebao* **2001**, *22*, 387. s) Y. Yang, S. Lu, *Tianragi Huagong* **2000**, *25*, 457. t) Y. Yang, S. Lu, *Chihua Xuebao* **1999**, *20*, 224. u) Y. Yang, S. Lu, *Tetrahedron Lett.* **1999**, *40*, 4845.

4 The preparation of oximes by the reduction of aliphatic nitro compounds, see: a) A. Gissot, S. N'Gouela, C. Matt, A. Wagner, C. Mioskowski, *J. Org. Chem.* **2004**, *69*, 8997. b) V. M. Danilenko, A. A. Tishkov, S. L. Ioffe, I. M. Lyapkalo, Y. A. Strelenko, V. A. Tartakovsky, *Synthesis* **2002**, 635. c) J. R. Hwu, W. N. Tseng, H. V. Patel, F. F. Wong, D.-N. Horng, B. R. Liaw, L. C. Lin, *J. Org. Chem.* **1999**, *64*, 2211. d) D. Albanese, D. Landini, M. Penso, *Synthesis* **1990**, 333. e) J. R. Hwu, S.-C. Tsay, *Tetrahedron* **1990**, *46*, 7413. f) M. Bartra, P. Romea, F. Urpí, J. Vilarrasa, *Tetrahedron* **1990**, *46*, 587. g) D. H. R. Barton, I. Fernandez, C. S. Richard, S. Z. Zard, *Tetrahedron* **1987**, *43*, 551. h) G. A. Olah, S. C. Narang, L. D. Field, A. P. Fung, *J. Org. Chem.* **1983**, *48*, 2766. i) P. A. Wehrli, B. Schaer, *Synthesis* **1977**, 649. j) J. R. Hanson, *Synthesis* **1974**, 1. k) J. F. Knifton, *J. Org. Chem.* **1973**, *38*, 3296. l) H. H. Baer, W. Ramk, *Can. J. Chem.* **1972**, *50*, 1292. m) W. K. Seifert, P. C. Condit, *J. Org. Chem.* **1963**, *28*, 265.

5 It was reported that aliphatic nitro compounds were reduced by carbon monoxide in the presence of selenium catalyst, however there are some disadvantages on these methods: (i) high pressure (50 atm) of carbon monoxide, (ii) high reaction temperature (130–150 °C), (iii) low yield (<49%) and low selectivity, and (iv) limitation of the substrate. see: J. J. McCoy, J. G. Zajacek, K. E. Fuger, U.S. Patent 3989755, **1976**.

6 K. Kondo, S. Yokoyama, N. Miyoshi, S. Murai, N. Sonoda, *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 691.

7 N. Sonoda, K. Kondo, K. Nagano, N. Kambe, F. Morimoto, *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 308.

8 a) X. Gu, J. M. Ndungu, W. Qiu, J. Ying, M. D. Carducci, H. Wooden, V. J. Hruby, *Tetrahedron* **2004**, *60*, 8233. b) H. Ishibashi, S. Harada, M. Okada, M. Ikeda, K. Ishiyama, H. Yamashita, Y. Tamura, *Synthesis* **1986**, 847.

9 W. A. Wasylenko, N. Kebede, B. M. Showalter, N. Matsunaga, A. P. Miceli, Y. Liu, L. R. Ryzhkov, C. M. Hadad, J. P. Toscano, *J. Am. Chem. Soc.* **2006**, *128*, 13142.

10 D. Jiang, J. Peng, Y. Chen, *Org. Lett.* **2008**, *10*, 1695.

11 K. P. Park, C.-Y. Shiue, L. B. Clapp, *J. Org. Chem.* **1970**, *35*, 2065.

12 N. Jain, A. Kumar, S. M. S. Chauhan, *Tetrahedron Lett.* **2005**, *46*, 2599.