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Selenium-Assisted Reduction of α- and β-Diketones with Carbon Monoxide and Water

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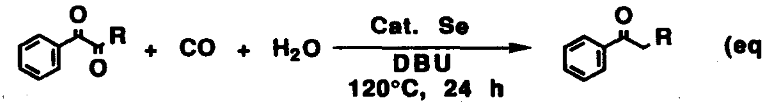
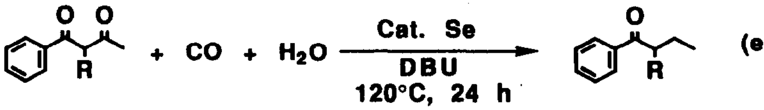
Summary: Phenyl substituted α- (PhC(=O)C(=O)R) and β-diketones (PhC(=O)CHRC(=O)R') are reduced by carbon monoxide and water in the presence of elemental selenium to give the corresponding aromatic ketones in moderate to good yields.

Several methods are available for the carbonyl to methylene conversion of carbonyl compounds,[1] but few methods have been developed for the selective reduction of one of the carbonyl groups of dicarbonyl compounds due to the side reactions of carbon-carbon bond cleavage, recyclization, or rearrangements.[2] In addition, to the best of our knowledge, there has been no report of a catalytic method for the conversion of dicarbonyl compounds to the corresponding monocarbonyl ones .

Recently we described that hydrogen selenide (or HSe^-), in situ generated from elemental selenium, carbon monoxide, and water in the presence of tertiary amine, exhibits a unique reducing ability towards various organic compounds.[1,3] Quite significantly, elemental selenium acts as a catalyst in these reductions.[1, 3a, 3c, 3e] In the course of our study on the utilization of this catalytic reaction system, we have found that selective reduction of the carbonyl groups adjacent to an alkyl groups of 1-phenyl-1,2- or 1,3-diketones takes place to give the corresponding aromatic ketone in moderate to good yields (eqs. 1 and 2).



(eq. 1)

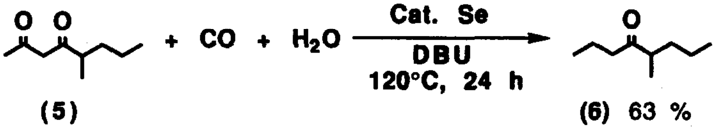


(eq. 2)

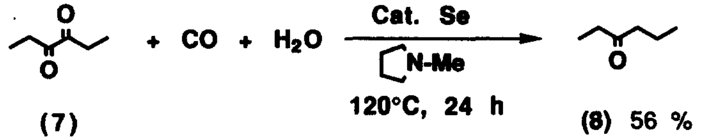
1-Phenyl-1,2-propanedione (2 mmol) was reacted with Se (1 mmol), H_2O (20 mmol), and CO (30 atm) in the presence of DBU (4 mmol) at 120 °C for 24 h giving 1-phenyl-1-propanone (**2a**) in 78 % (entry 1 in

Table I).[4] Quite surprising, no 1-phenyl-2-propanone was detected under these reaction conditions. To investigate the scope of this reduction, several 1-phenyl-1,2-diketones were reacted with selenium, carbon monoxide, and water (Table I). It is possible to diminish the quantity of selenium catalyst still further (entry 2). Treatment of **1a**, **1b**, and **1c** with CO and H_2O in the presence of selenium gave the corresponding aromatic ketones in 65-78 % yield, although the reaction of **1d** afforded a mixture containing 35 % yield of 1-phenyl-3-methyl-1-butanone (**2d**) and 40 % yield of 1-phenyl-3-methyl-2-butanone (**4d**) (entries 1 and 3-5). It seems likely that the alkyl group at the α position exerts a significant influence upon the distribution of the reduced products.[5] As well as α–diketones bearing aromatic ring, phenyl substituted β–diketones like 1-phenyl-1,3-butanedione (**1e**), 1-phenyl-2-methyl-1,3-butanedione (**1f**), and 1-phenyl-2-phenylmethyl-1,3-butanedione (**1g**) were also converted into the corresponding aromatic ketones in moderate to good yields (entries 6-8 in Table I).

To establish the scope of this catalytic reduction system, the reaction of non-aromatic α– and β–diketones with selenium, carbon monoxide, and water was carried out. The reaction of 5-methyl-2,4-octanedione (**5**) with CO and H_2O in the presence of selenium (0.5 equiv) gave 5-methyl-4-octanone (**6**) in 63 % yield (eq. 3).[6] On the other hand, the reaction of 3,4-hexanedione (**7**) with Se, CO, and H_2O in the presence of DBU provided the complex mixtures. Selective reduction of **7** to 3-hexanone (**8**) was achieved, however, by the use of N-methylpyrrolidine instead of DBU as the tertiary amine (eq. 4).



(eq. 3)



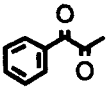
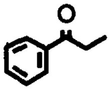
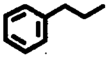
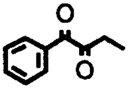
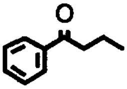
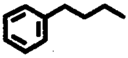
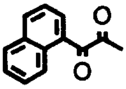
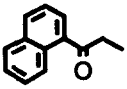
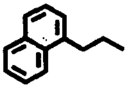
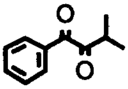
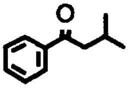
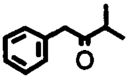
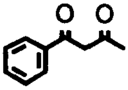
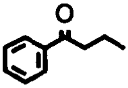
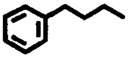
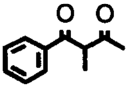
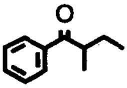
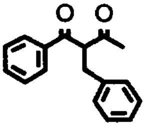
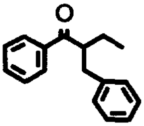
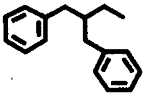
(eq. 4)

Although the details of the reduction mechanism are not clear yet, the present reduction may involve the deselenation of the corresponding α- and β-selenolketones.[7, 8] Further studies on the synthetic application of this selective reduction and the reaction mechanism are now progress.

Acknowledgment.

We would like to thank Prof. N. Sonoda and Dr. A. Ogawa (Osaka University) for their helphul discussions on this research. We thank the Ministry of Education, Science, and Culture, Japan, for financial support to this work.

Table I. Reduction of α- and β-Diketones with Carbon Monoxide and Water in the Presence of Selenium[a]

entry	diketone	yields and products[b]	
1	 1a	 2a 78 % (73%)	 3a 8 % (5 %)
2[c]	1a	2a 63 %	3a 5 %
3	 1b	 2b 76 % (70 %)	 3b 5 % (3 %)
4	 1c	 2c 65 % (61 %)	 3c 23 % (18 %)
5	 1d	 2d 35 %	 4d 40 %
6	 1e	 2e 73 % (67 %)	 3e 5 % (4 %)
7	 1f	 2f 68 % (62 %)	 3f 14 % (11 %)
8	 1g	 2g 64 % (63 %)	 3g 5 % (3 %)

a) Reaction conditions: diketone (2 mmol), Se (1 mmol), H_2O (20 mmol), DBU (4 mmol), and CO (30 atm) 120°C for 24 h. b) ^1H NMR yields. Isolated yields were given in parentheses. c) Selenium (0.2 mmol) was used.

References and Notes

1. Many methods for the carbonyl to methylene conversion of carbonyl compounds have been developed hitherto. See: Nishiyama, Y.; Hamanaka, S.; Ogawa, A.; Kambe, N.; Sonoda, N. *J. Org. Chem.* **1988**, 53, 1326 and references cited therein.
2. a) Mayer, R.; Hiller, G.; Nitzschke, M.; Jentzsch, J., *Angew. Chem.* **1963**, 75, 1011; b) Sicher, J.; Svoboda, M.; Zavada, J. *Collect. Czech. Chem. Commun.* **1965**, 30, 421; c) Reusch, W.; LeMahieu, R. *J. Am. Chem. Soc.* **1964**, 86, 3068; d) Seibert, W. *Chem. Ber.* **1947**, 80, 494; e) Wenkert, E.; Kariv, E. *Chem. Commun.* **1965**, 570; f) Stephenson, L. M.; Falk, L. C. *J. Org. Chem.* **1976**, 41, 2928.
3. a) Miyata, T.; Kondo, K.; Murai, S.; Hirashima, T.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1980**, 19, 1008; b) Nishiyama, Y.; Hamanaka, S.; Ogawa, A.; Murai, S.; Sonoda, N. *Synthetic Commun.* **1986**, 16, 1059; c) Ogawa, A.; Nishiyama, Y.; Kambe, N.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1987**, 28, 3271; d) Nishiyama, Y.; Makino, Y.; Hamanaka, S.; Ogawa, A.; Sonoda, N. *Bull. Chem. Soc. Jpn.* **1989**, 62, 1682; e) Nishiyama, Y.; Katsuen, S.; Jounen, Y.; Hamanaka, S.; Ogawa, A.; Sonoda, N. *J. Heteroatom Chem.* **1990**, 1, 467; f) Ref. (1)
4. Typical Procedure as follows: In a 50 mL stainless steel autoclave were placed diketone (2 mmol), Se (1 mmol), H_2O (20 mmol), DBU (4 mmol), and THF (5 mL), and the mixture was heated at 120 °C for 24 h under the pressure of CO (30 atm: initial pressure at 25 °C). After the reaction was complete, carbon monoxide was purged in a well ventilated hood, and air was blown into the solution for 10 min in order to oxidize the remaining hydrogen selenide to elemental selenium. Selenium deposited was filtered off, the filtrate was acidified to slightly acidic end with hydrochloric acid (2N), and then the product was extracted with Et_2O (30 mL x 3). The combined extracts were dried over $MgSO_4$. Evaporation of the solvent and purification by column chromatography on silica gel gave the corresponding products.
5. When the reaction of 1-phenyl-3,3-dimethyl-1,2-butanedione with Se, CO, and H_2O was carried out under the similar conditions, 1-phenyl-3,3-dimethyl-2-butanone was formed in 45 % yield and diketone was recovered in 48 % yield.
6. In the case of linear β-diketone such as 2,4-decanedione, di-4-decyl diselenide, which was further reductive selenated product, was formed in 63 % yield.
7. In our previous papers, we assumed that the reduction of α,β-unsaturated carbonyl compounds with Se-CO-H_2O or NaSeH to the corresponding carbonyl compounds would occur *via* the β-selenol ketone intermediate. See: Nishiyama, Y.; M. Yoshida, M.; Ohkawa, S.; Hamanaka, S. *J. Org. Chem.* **1991**, 56, 6720, and Ref (3c).
8. We have already reported that the reaction of aromatic ketones with CO and H_2O in the presence of a catalytic amount of selenium gave the corresponding aromatic hydrocarbons in good yields. See: Ref (1).

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