Selenium-assisted Carbonylation of *o*-Hydroxyacetophenone with Carbon Monoxide

Akiya Ogawa, Kiyoshi Kondo, Shinji Murai, and Noboru Sonoda*

Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

Selenium-assisted carbonylation of o-hydroxyacetophenone (1) with carbon monoxide in the presence of a strongly basic tertiary amine gave 4-hydroxycoumarin (2) as a *C*-carbonylated product in a high yield.

During our studies on selenium-catalysed carbonylation, we have shown that amines or alcohols react with carbon monoxide under mild conditions to give ureas or carbonates as the *N*- or *O*-carbonylated products, respectively.¹⁻⁴ We considered that the key step in these reactions is the nucleophilic attack of amines or alcohols on the carbonyl selenide that is produced *in situ* by the reaction of carbon monoxide with selenium.^{2,4} These selenium-catalysed carbonylations are novel since most of the known carbonylations employ transition metals as catalysts.

We now report the first example of a selenium-assisted carbonylation with carbon monoxide leading to the formation of a C-carbonylated product. The reaction of o-hydroxyacetophenone (1) with selenium (1 equiv.) and carbon monoxide (30 kg/cm^2) in tetrahydrofuran (THF) in the presence of DBU (1,5-diazabicyclo[5.4.0]undec-5-ene; 40 mmol)† at 90 °C gave 4-hydroxycoumarin (2)‡ in quantitative



[†] 4-Hydroxycoumarin (2) was not obtained if tertiary amines such as triethylamine, *N*-methylpyrrolidine, and DABCO (1,4diazabicyclo[2.2.2]octane) were used instead of DBU.

[‡] The following data fully support structure (2): v_{max} (KBr) 3600–2000 (OH), 1680 (C=O), and 1605 (C=C) cm⁻¹; δ (CD₃SOCD₃) 5.60 (s, 1H), and 7.20–7.86 (m, 4H); *m/z* 162 (*M*⁺); m.p. 206.7–207.2 °C (lit.,⁶ 206 °C).

yield [reaction (1)]. After the reaction, the hydrogen sclenide generated during the reaction was easily converted into elemental selenium on exposure to air.

The similar reaction of acetophenone (3) with carbon monoxide and selenium followed by quenching with nbutylamine gave the amide (4) in 28% yield [reaction (2)]. The product (4) may be derived from aminolysis of the intermediate seleno-acid (5) generated by the reaction of the enolate anion of acetophenone with carbonyl selenide.¹

It was expected that the carbonylation would proceed with a catalytic amount of selenium if the hydrogen selenide produced could be oxidised to selenium *in situ*. Several oxidising agents were examined for this, and nitrobenzene was found to be effective. Thus, a stirred mixture of *o*-



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hydroxyacetophenone (10 mmol), selenium (2 mmol), DBU (40 mmol), nitrobenzene (5 mmol), and THF (5 ml) was heated under CO (30 kg/cm²) at 90 °C for 30 h. The product (2) (6.8 mmol, 68%) was isolated by extraction with ether

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after neutralization. Nitrobenzene was reduced concomitantly to aniline⁵ during the reaction (Scheme 1). A plausible reaction path for the formation of 4-hydroxycoumarin (2) is shown in Scheme 2.

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References

- 1 N. Sonoda, T. Yasuhara, K. Kondo, T. Ikeda, and S. Tsutsumi, J. Am. Chem. Soc., 1971, 93, 6344.
- 2 K. Kondo, N. Sonoda, and H. Sakurai, Bull. Chem. Soc. Jpn., 1975, 48, 108.
- 3 K. Kondo, N. Sonoda, and S. Tsutsumi, Chem. Lett., 1972, 373.
- 4 K. Kondo, S. Yokoyama, N. Miyoshi, S. Murai, and N. Sonoda, *Angew. Chem.*, *Int. Ed. Engl.*, 1979, **18**, 692.
- 5 T. Miyata, K. Kondo, S. Murai, T. Hirashima, and N. Sonoda, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 1008.
- 6 R. Anschütz, Liebigs Ann. Chem., 1909, 367, 196.