

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

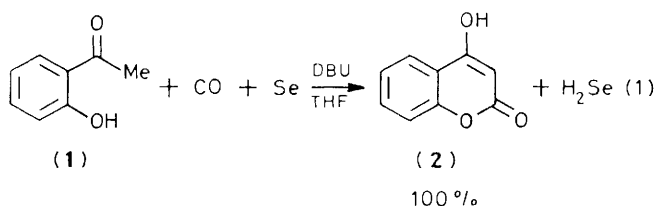
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Selenium-assisted carbonylation of *o*-hydroxyacetophenone (**1**) with carbon monoxide in the presence of a strongly basic tertiary amine gave 4-hydroxycoumarin (**2**) as a *C*-carbonylated product in a high yield.

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/cm²) 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



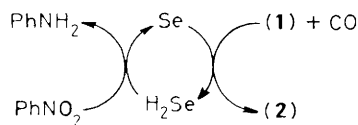
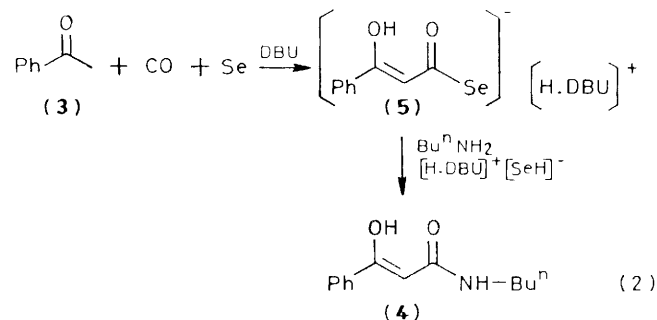
† 4-Hydroxycoumarin (**2**) was not obtained if tertiary amines such as triethylamine, *N*-methylpyrrolidine, and DABCO (1,4-diazabicyclo[2.2.2]octane) were used instead of DBU.

‡ The following data fully support structure (**2**): ν_{\max} (KBr) 3600–2000 (OH), 1680 (C=O), and 1605 (C=C) cm^{-1} ; δ (CD_3SOCD_3) 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).

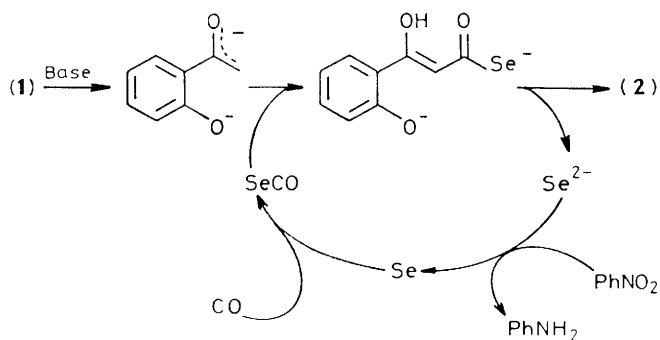
yield [reaction (1)]. After the reaction, the hydrogen selenide generated during the reaction was easily converted into elemental selenium on exposure to air.

The similar reaction of acetophenone (**3**) with carbon monoxide and selenium followed by quenching with *n*-butylamine 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*-



Scheme 1



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

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.

Received, 2nd August 1982; Com. 904

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