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A NEW SYNTHESIS OF CARBONOHYDRAZIDE, SEMICARBAZIDE, AND CARBAZATE

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The reaction of carbon monoxide with N,N-dialkylhydrazine in the presence of selenium gave a salt of 3,3-dialkylselenocarbazic acid with hydrazine (I), which was oxidized quantitatively to give carbonohydrazide, water, and selenium. Aminolysis and alcoholysis of I followed by oxidation yielded semicarbazide and carbazate respectively in excellent yields under mild conditions.

In the previous communications we have reported the selenium catalyzed synthesis of ureas[1] and carbonates[2] by the reaction of CO with amines and with alkoxides respectively. In this communication we wish to describe the novel synthesis of carbonohydrazide, semicarbazide, and carbazate by the reaction of N,N-dialkylhydrazine with CO and Se in the presence of hydrazine, amine, and alcohol, respectively, under mild conditions in excellent yields with simple operations.

For instance, 10 mmol of N,N-dimethylhydrazine was dissolved in 50 ml tetrahydrofuran to which was added 5 mmol of metallic Se, and CO was bubbled at a rate of 60 ml/min for 30 min at 25°C with vigorous stirring to give homogeneous clean solution. At this stage of the reaction, stoichiometric amount of an intermediate (I) was isolated by the evaporation of the solvent [eq. (1)].

$$2\ Me_2NNH_2 + CO + Se \longrightarrow \underset{\text{I}}{[Me_2NNH_3]^+[Me_2NNH\text{-}CO\text{-}Se]^-} \quad (1)$$

The oxidation of I with oxygen gave quantitatively carbonohydrazide, water, and Se, and this stoichiometric reaction might be described as follows [eqs. (2) and (3)].

$$\mathrm{I} + \mathrm{Me_2NNH_2} \overset{\rightarrow}{\longleftarrow} \mathrm{(Me_2NNH)_2CO} + \mathrm{H_2Se \cdot Me_2NNH_2} \qquad (2)$$

$$\mathrm{H_2Se \cdot Me_2NNH_2} + \tfrac{1}{2}\,\mathrm{O_2} \longrightarrow \mathrm{Se} + \mathrm{H_2O} + \mathrm{Me_2NNH_2} \qquad (3)$$

Equation (3) shows the regeneration of selenium by the facile oxidation of hydrogen selenide.[3] Thus catalytic synthesis of carbonohydrazide could successfully be performed in the presence of 30 mmol of N,N-dimethylhydrazine and 5 mmol of I by addition of mixture gas of CO and O_2 (60 ml/min and 5 ml/min respectively) under atmospheric pressure at 25°C for two hours. Removal of Se followed by evaporation of the solvent gave 19.9 mmol of carbonohydrazide, which corresponded to 99.5 % yield based on used N,N-dimethylhydrazine and showed 4 times circulation of Se as a catalyst.

The aminolysis and alcoholysis of I followed by oxidation with oxygen afforded corresponding semicarbazide and carbazate respectively in excellent yields as shown in the typical reactions [eqs. (4) and (5)].

$$\mathrm{I} + \mathrm{Et_2NH} \xrightarrow{\mathrm{O_2}} \underset{(95\%)}{\mathrm{Me_2NNH\text{-}CO\text{-}NEt_2}} \qquad (4)$$

$$\mathrm{I} + \mathrm{EtONa} \xrightarrow[\mathrm{EtOH}]{\mathrm{O_2}} \underset{(96\%)}{\mathrm{Me_2NNH\text{-}CO\text{-}OEt}} \qquad (5)$$

The study on the reaction of other hydrazines with carbon monoxide and selenium is now in progress.

REFERENCES AND NOTE

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