

A NEW SYNTHESIS OF CARBONHYDRAZIDE, SEMICARBAZIDE, AND CARBAZATE

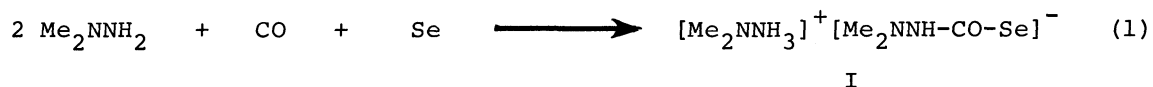
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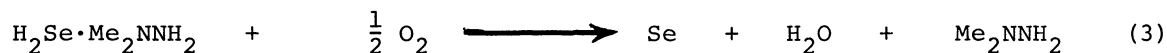
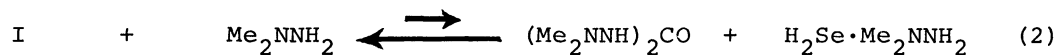
The reaction of carbon monoxide with N,N-dialkylhydrazine in the presence of selenium gave a salt of 3,3-dialkylselenocarbamic acid with hydrazine (I), which was oxidized quantitatively to give carbonohydrazide, water, and selenium. Aminolysis and alcoholysis of I followed by oxidation yielded semicarbazide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

In the previous communications we have reported the selenium catalyzed synthesis of ureas¹ and carbonates² 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)].

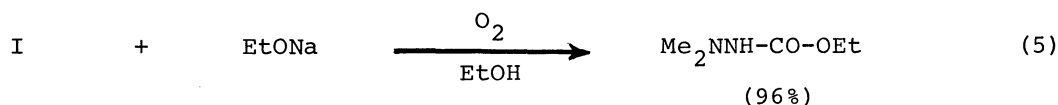
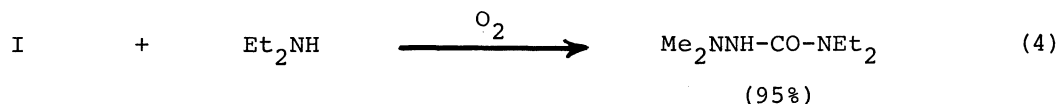


The oxidation of I with oxygen gave quantitatively carbonohydrazide, water, and Se, and this stoichiometric reaction might be described as follows [eqs. (2) and (3)].



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 O₂ (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)].



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

REFERENCES AND NOTE

- (1) N. Sonoda, T. Yasuhara, K. Kondo, T. Ikeda, and S. Tsutsumi, J. Amer. Chem. Soc., 93, 6344 (1971); K. Kondo, N. Sonoda, and S. Tsutsumi, Chem. Commun., 1972, 307; K. Kondo, N. Sonoda, K. Yoshida, M. Koishi, and S. Tsutsumi, Chem. Lett., 1972, 401.
- (2) K. Kondo, N. Sonoda, and S. Tsutsumi, Tetrahedron Lett., 1971, 4885.
- (3) Hydrogen selenide is an acid which may form a salt with base. See to K. Kondo, N. Sonoda, and H. Sakurai, Chem. Commun., 1973, 853.

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