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A NEW SYNTHESIS OF CARBAMATES.
THE REACTION OF CARBON MONOXIDE WITH AMINE AND ALCOHOL IN THE CO-PRESENCE OF SELENIUM AND TRIETHYLAMINE

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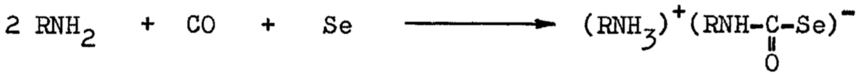
Carbamates have been synthesized conveniently by the reaction of carbon monoxide with amine and alcohol by the use of selenium and triethylamine under mild conditions.

Amine salt of selenocarbamic acid (I), prepared by the reaction of carbon monoxide with amine and selenium, gives urea derivative by the aminolysis followed by oxidation.[1] This salt (I) appeared to be a new type of carbamoylating reagent, and reaction with alcohols may yield corresponding carbamates.



$$2\ RNH_2 + CO + Se \longrightarrow (RNH_3)^+(RNH\text{-}\underset{\underset{O}{\|}}{C}\text{-}Se)^- \qquad (I)$$

Triethylamine salt of selenocarbamic acid (II) was successfully prepared by the reaction between equimolar amounts of Se and primary amine in the presence of excess amount of triethylamine under atmosphere of CO, and here we provide a conventional method for the synthesis of carbamates by the alcoholysis of II.

In a typical reaction, cyclohexylamine (0.01 mol), amorphous selenium (0.01g atom), Et_3N (0.1 mol), and methyl alcohol (0.1 mol) were added to 50 ml of THF, and CO was blown into the solution with vigorous stirring at room temperature until the Se was allowed to dissolve completely to give homogeneous solution. Thereafter O_2 was bubbled at a rate of 1 ml per min at 0°C until the Se deposited completely. After removal of the Se, methyl N-cyclohexylcarbamate was isolated in a 90 % yield by distillation. The results obtained from various combination of primary amine and alcohol under the same conditions are summarized in Table 1, and in each case small amount of urea derivative remained as a distillation residue.

The reaction process may be described by the following scheme, which involves nucleophilic addition of alcohol to the carbonyl group of the salt (II) to form an

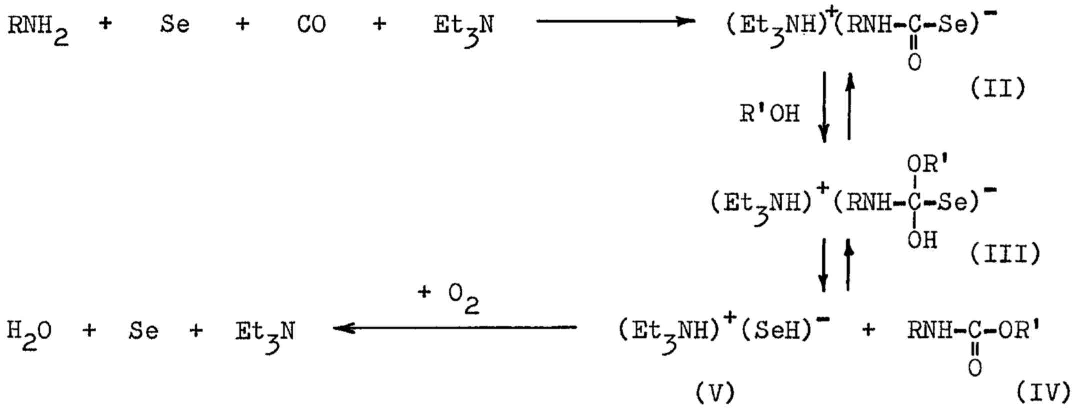
Table 1. The Yields of Carbamates from Amines and Alcohols.

RNH_2	$R'OH$	$\mathrm{RNH{-}\underset{\underset{O}{\|}}{C}{-}OR'}$
R	R'	Yield %*
n-Butyl	Methyl	60
n-Butyl	Ethyl	56
n-Butyl	n-Butyl	69
n-Butyl	i-Propyl	16
Cyclohexyl	Methyl	90
n-Octyl	Methyl	51
Phenyl	Methyl	30

* Yield % based on primary amine used.

intermediate (III), resulting in the formation of the carbamate (IV) and amine salt of hydrogen selenide (V).

Scheme



Conditions required are mild and procedures are simple as well as widely applicable to various sets of amine and alcohol. Further application of the present method to other amine and alcohol is now under investigation as well as the examination of the reactivity and utility of the salt (II) with a variety of substrates.

REFERENCES

(1) N. Sonoda, T. Yasuhara, K. Kondo, T. Ikeda, and S. Tsutsumi, J. Amer. Chem. Soc., 93, 6344 (1971).

(2) General synthesis of carbamates; see S.R. Sandler and W. Karo, " Organic Functional Group Preparations ", Vol.II, Academic Press, New York, (1971), p. 223.

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