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A New Synthesis of Carbonates.
The Reaction of Carbon Monoxide with Alkolates in the Presence of Selenium.

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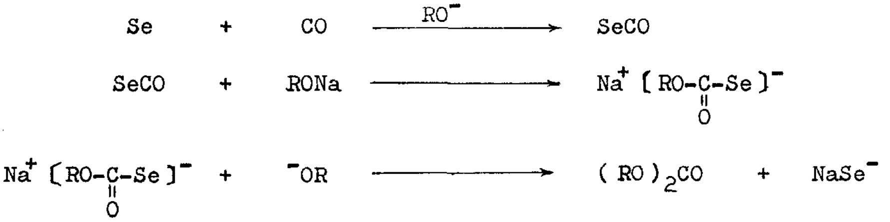
In the previous communication we reported the synthesis of ureas from aliphatic amines and carbon monoxide using selenium as a catalyst.[1] The experimental evidence suggested the presence of carbonyl selenide (SeCO) as an active species, which is formed by the reaction of Se with CO in the presence of a base catalyst, and it is of great interest to investigate the applicability of the reaction system to other substrates than amines. In this communication we wish to report the novel synthesis of carbonates from carbon monoxide and aliphatic alkolates in the presence of selenium. Conditions required are mild and procedures are quite simple.[2] The following procedure for the preparation of dimethyl carbonate is representative.

For instance, 0.04 mol of sodium methylate in 0.3 mol of methyl alcohol was dissolved in 50 ml of tetrahydrofuran to which was added 0.002 g. atom sample of amorphous selenium,[3] and carbon monoxide was blown into the resultant solution at a rate of 60 ml/min for 4 hr with vigorous stirring. Thereafter oxygen was blown at a rate of 10 ml/min for 30 min. Filtration of the deposited solid followed by distillation gave dimethylcarbonate in a stoichiometric yield based on the selenium used. All qualitative and quantitative analyses were done by glpc method.

Using a temperature of 20° and one atmospheric pressure of CO, we prepared carbonates from methyl alcohol, ethyl alcohol, n-propyl alcohol, and n-butyl alcohol in yields ranging from 94 to 99%. Benzyl alcohol gave the corresponding carbonate under these conditions in 76% yield. With secondary alcohols such as isopropyl alcohol and cyclohexyl alcohol, and with tert-butyl alcohol yields were 6 to 16% under these conditions. Aromatic phenols did not react under the same conditions. Benzene, cyclohexane, and ether were poor solvents for the present reaction, while THF was effectively used.

It is currently suggested that the process goes in at least three steps which can be described by the following equations:



$$\mathrm{Se} + \mathrm{CO} \xrightarrow{\mathrm{RO}^-} \mathrm{SeCO} \qquad (1)$$

$$\mathrm{SeCO} + \mathrm{RONa} \longrightarrow \mathrm{Na}^+[\mathrm{RO{-}}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\mathrm{{-}Se}]^- \qquad (2)$$

$$\mathrm{Na}^+[\mathrm{RO{-}}\underset{\overset{\|}{\mathrm{O}}}{\mathrm{C}}\mathrm{{-}Se}]^- + {}^-\mathrm{OR} \longrightarrow (\mathrm{RO})_2\mathrm{CO} + \mathrm{NaSe}^- \qquad (3)$$

These reactions may provide a convenient and facile route to various carbonates. Work is continuing on the further application to various alcohols and phenols, and elucidation of full mechanism and development of circulatory use of selenium are currently under investigation.

REFERENCES

1. N. Sonoda, T. Yasuhara, K. Kondo, T. Ikeda, and S. Tsutsumi, *J. Amer. Chem. Soc.*, in press.
2. R. B. Wagner and H. D. Zook, " Synthetic Organic Chemistry ", New York; John Wiley & Sons, Inc.,1961, p.483.
3. Metallic selenium was also applicable, and there seemed to be no difference in the reactivity.