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Selenium Catalyzed Synthesis of of Carbonates. The Reaction of Alkoxide with Carbon Monoxide and Oxygen in the Presence of Selenium

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A novel selenium catalyzed synthetic reaction of carbonates was investigated. The reaction of alkoxides with carbon monoxide in the presence of stoichiometric amount of selenium gave carbonates in high yields under atmospheric pressure at 20 °C in THF. When the resultant reaction solution was made to react continuously with the mixture gas of carbon monoxide and oxygen, catalytic formation of carbonates was achieved. Isolation of Se-alkyl monoselenocarbonate from the reaction mixture by addition of alkyl halide indicated that carboalkoxy sodium selenide might be formed as an intermediate in the course of present reaction. In connection with these reactions, the reaction of carbonyl selenide with sodium alkoxide in alcohol was also studied.

There are many reports on the synthesis of carbonates,[1] and a very common synthesis is one by the reaction of phosgene with alcohol. Synthesis of carbonates by the reaction of cupric alkoxide and carbon monoxide was reported[2,3] by Saegusa *et al.*, and it was described[4] that carbonylation of ethanol by palladium chloride in the presence of sodium carbonate proceeded under mild conditions to give diethyl carbonate. Recently we reported[5-7] a novel synthesis of urea derivatives by the reaction of amine with carbon monoxide in the presence of selenium under mild conditions with simple operations. From further investigations on the reaction between carbon monoxide and selenium in the presence of a base, it has been noticed[8] that stoichiometric amount of carbonates based on used selenium was found to be formed by the reaction of carbon monoxide with aliphatic alkoxides under mild conditions.

Now we wish to report full results of the reaction of alkoxides with mixture gas of carbon monoxide and oxygen in the presence of selenium, which provides a new, convenient method for catalytic synthesis of carbonates [reaction (1)].

$$\mathrm{RONa} + \mathrm{CO} + \frac{1}{2}\mathrm{O_2} \xrightarrow[\substack{20^\circ\mathrm{C},\ 1\ \mathrm{atm.} \\ \mathrm{ROH,\ THF}}]{\mathrm{Se}} (\mathrm{RO})_2\mathrm{CO} + \mathrm{NaOH} \qquad (1)$$

Thus various carbonates were prepared under mild conditions with simple operations. From the investigation of the reaction path, a key intermediate was successfully trapped in the form of Se-alkyl monoselenocarbonate by alkylation with alkyl halide, and sodium hydrogen selenide was found to play an important role for the circulation of selenium. It was also confirmed that reaction of carbonyl selenide, prepared from direct reaction between carbon monoxide and selenium at elevated temperature, with sodium alkoxides was closely resembled to the present synthetic reaction.

Results and Discussion

It was confirmed that sodium alkoxide reacted easily with metallic selenium and carbon monoxide to form dialkyl carbonate [reaction (2)]. For instance, sodium ethylate and ethyl alcohol were dissolved in tetrahydrofuran (THF), to which was added metallic selenium at 20 °C, and carbon monoxide was blown into the solution for 2 hr with vigorous stirring. At this stage of the reaction, quantitative formation of diethyl carbonate based on selenium used in the reaction mixture was confirmed from glpc analyses. It is notable that the procedure is very simple. The results are shown in Table 1.

$$\mathrm{Se} + \mathrm{CO} + \mathrm{NaOR} \xrightarrow[20^\circ\mathrm{C},\ 1\ \mathrm{atm.}]{\mathrm{ROH,\ THF}} (\mathrm{RO})_2\mathrm{CO} + \mathrm{NaSeH}\ \text{and/or}\ \mathrm{Na_2Se} \qquad (2)$$

Table 1. Stoichiometric synthesis[a] of carbonates

Run No.	RONa R	ROH mol	$(RO)_2CO$ Yield %[b]
1	Me	0.04	99
2	Et	0.04	99
3	Et	0.04	99[c]
4	Et	0.10	95
5	*n*-Pr	0.10	99
6	*n*-Bu	0.10	80
7	Benzyl	0.10	76
8	*i*-Pr	0.10	16
9	Cyclohexyl	0.10	6
10	*t*-Bu	0.10	14
11	Ph	0.10	—[d]

a) Metallic selenium (0.001 g atom), sodium alkoxide (0.04 mol), and alcohol were made to react with carbon monoxide (60 ml/min) at 20 °C in 50 ml THF for 2 hr with vigorous stirring. b) Yield % based on selenium used. c) Amorphous selenium was used. d) No reaction took place.

The yield of carbonates from primary alcohols was higher than that from secondary or tertiary alcohols, and in the case of phenol no reaction took place. These results clearly showed the excellent and novel oxidizing ability of selenium[9] in the presence of a strong base. Then, catalytic reaction [reaction (1)] could be successfully performed by passing mixture gas of carbon monoxide and oxygen continuously into the resultant reaction mixture given by the reaction (2). The

Table 2. Catalytic synthesis[a)] of carbonates

Run No.	RONa R	Catalytic reaction time[b)] (hr)	Oxidizing efficiency %[c)]
1	Me	0	99
2	Me	1	225
3	Et	0	99
4	Et	1	240
5	Et	2	310
6	Et	4	520
7	*n*-Bu	2	292
8	*t*-Bu	2	113
9	$-CH_2CH_2OH$	2	270[d)]
10	$-CH_2CHMeOH$[e)]	2	220[d)]

a) RONa (0.05 mol), ROH (0.05 mol), and metallic selenium (0.001 g atom) were made to react with carbon monoxide for 30 min, and then with mixture gas of carbon monoxide and oxygen (60 ml/min and 1 mmol/hr respectively) in 50 ml THF at 20 °C for catalytic reaction time. b) The time (hr) for which mixture gas of carbon monoxide and oxygen was bubbled, and the results at catalytic reaction time 0 hr corresponded to those in Table 1. c) See to Ref. 10. d) DMF (50 ml) was used for the solvent in the case of glycols. e) $-CHMe-CH_2OH$ may be contained.

results obtained by the present catalytic reaction were shown in Table 2. The circulation of selenium in the reaction system was shown in terms of oxidizing efficiency[10)] of selenium, and the efficiency decreased as catalytic reaction time prolonged. This tendency might be explained by the facts that sodium hydroxide formed in the reaction system interferred the formation of carbonate and prolonged contact of carbonate with sodium hydroxide in alcohol decreased the amount of formed carbonate. Cyclic aliphatic carbonates such as ethylene carbonate, propylene carbonate were similarly synthesized when dimethylformamide[11)] (DMF) was used.

The circulation of selenium in the catalytic system may be explained by the following Eqs. (3) and (4), which exhibit the regeneration[12)] of selenium by the facile oxidation of hydrogen selenide with oxygen.

$$\mathrm{Na_2Se} \underset{\mathrm{RONa}}{\overset{\mathrm{ROH}}{\rightleftarrows}} \mathrm{NaSeH} \underset{\mathrm{RONa}}{\overset{\mathrm{ROH}}{\rightleftarrows}} \mathrm{H_2Se} \qquad (3)$$

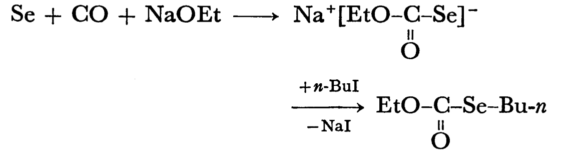
$$\mathrm{H_2Se} + \frac{1}{2}\mathrm{O_2} \longrightarrow \mathrm{H_2O} + \mathrm{Se} \qquad (4)$$

In order to examine if the sodium hydrogen selenide played a significant role in the catalytic reaction, the reaction of alcoholic sodium alkoxide with the mixture gas of carbon monoxide and oxygen in the presence of sodium hydrogen selenide[13)] in THF was carried out and was found to proceed successfully, clarifying that the catalytic reaction (1) might be rewritten as following equation.

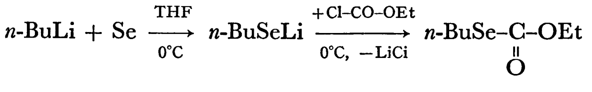
$$\mathrm{RONa} + \mathrm{CO} + \frac{1}{2}\mathrm{O_2} \xrightarrow[\mathrm{ROH,\,THF}]{\mathrm{NaSeH}} \mathrm{(RO)_2CO} + \mathrm{NaOH} \qquad (5)$$

The catalytic reaction was found to stop if oxygen-rich mixture gas was treated, and the ratio of carbon monoxide to oxygen was found to be such that sodium hydrogen selenide could be present in the catalytic reaction system.

In order to attain the knowledge of the reaction path, we have tried to trap an intermediate by addition of excess amount of alkyl halide into the reaction mixture. Gas-Mass spectroscopic analyses of the reaction mixture of sodium ethylate, carbon monoxide, selenium and *n*-butyl iodide at 0 °C showed the formation of di-*n*-butyl selenide and di-*n*-butyl diselenide together with the trace amount of formation of Se-*n*-butyl ethyl monoselenocarbonate, which might be formed by the reaction (6). The authentic sample of monoselenocarbonate[14)] was prepared by the following unambiguous route [reaction (7)].



$$\mathrm{Se + CO + NaOEt \longrightarrow Na^+[EtO{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}Se]^-} \xrightarrow[-\mathrm{NaI}]{+n\text{-}\mathrm{BuI}} \mathrm{EtO{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}Se{-}Bu}\text{-}n \qquad (6)$$



$$n\text{-}\mathrm{BuLi} + \mathrm{Se} \xrightarrow[0^\circ\mathrm{C}]{\mathrm{THF}} n\text{-}\mathrm{BuSeLi} \xrightarrow[0^\circ\mathrm{C},\ -\mathrm{LiCi}]{+\mathrm{Cl{-}CO{-}OEt}} n\text{-}\mathrm{BuSe{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}OEt} \qquad (7)$$

ca. 15%

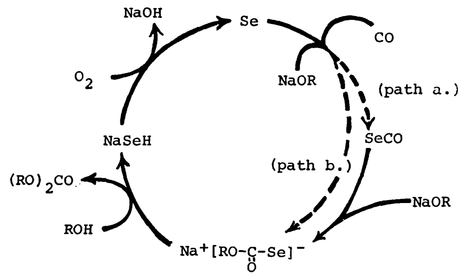
The retention time of the gas chromatography and the fragmentation pattern in the mass spectra of the trapped selenocarbonate were identical with those of the authentic sample. Very fast alcoholysis of the intermediate, ethoxycarbonyl sodium selenide[15)] would yield the carbonate and sodium hydrogen selenide, and the driving force of the alcoholysis reaction would be attributed to the precipitation of the sodium hydrogen selenide in THF.

It was suggested[5)] that carbon monoxide was readily oxidized with selenium in the presence of a strong base under mild conditions to give carbonyl selenide (SeCO).[17)] Then we performed the reaction of isolated carbonyl selenide prepared by the reaction[18)] of carbon monoxide with selenium at elevated temperature (550—600 °C) trapped at −120 °C, into which was added an alcoholic solution of sodium alkoxide at −80 °C. Gas chromatographic analyses revealed the quantitative formation of carbonates (dimethyl, diethyl, and di-*n*-butyl carbonate) [reaction (8)].

$$\mathrm{SeCO} + \mathrm{RONa} \xrightarrow[-80^\circ\mathrm{C}]{\mathrm{ROH}} \mathrm{(RO)_2CO} + \mathrm{NaSeH\ and/or\ Na_2Se} \qquad (8)$$

The reaction of carbonyl selenide with sodium alkoxide was so fast and almost quantitative even at low temperature that it might be impossible to detect the formation of free SeCO, even if it were generated, from the reaction mixture under any reaction condition at room temperature.

These experimental findings suggested that present selenium catalyzed synthesis of carbonates might well be described by the reaction Scheme 1, in which the intervention of carbonyl selenide as an intermediate in the catalytic cycle would offer a reasonable interpretation (path a), though there should be another path, in which intermediacy of carbonyl selenide might not necessarily be required (path b).



Scheme 1. Reaction path for the formation of carbonates.

In every synthesis of carbonates, however, small amounts of formates[19] were detected as the by-products, which have long been known to be produced by a base catalyzed reaction of carbon monoxide.[20]

Experimental

Materials. Alcohols (methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *t*-butyl, cyclohexyl, benzyl alcohol, ethylene glycol, propylene glycol, and phenol) were all purchased from commercial sources, and purification was carried out by distillation over corresponding sodium alkoxide under nitrogen and each purity was qualified by glpc. Metallic selenium (99.99%) of Nakarai Chem. Co. and amorphous selenium prepared by reduction of selenium dioxide with sulfur dioxide were used. Carbon monoxide (99.999%) of Seitetsu Chem. Co. and oxygen (99.999%) of Osaka Sanso Co. were applied. The chemical grade of metallic sodium, sodium hydride, and sodium borohydride were used for the sodium-metallation of alcohols or preparation of sodium hydrogen selenide. The chemical grade of *n*-butyl lithium (Merck Co.), *n*-butyl iodide, ethyl chloroformate were also commercially available. Tetrahydrofuran (THF) stored with KOH were dried over sodium wire and lithium aluminum hydride, and freshly distilled under nitrogen just before use. Dimethylformamide (DMF) was distilled under vacuum just before use. Authentic samples of the carbonates and formates were purchased or synthesized by the use of phosgene or formic acid with sodium alkoxide in alcohol.

Apparatus. The product analyses were generally carried out by gas chromatography with use of PEG-20M and SE-30 in 1 or 3 meter stainless steel column. They were performed by means of Shimadzu Model GC-3BF with ion flame detector, Varian Aerograph Model 90-P, Hitachi Model K-53 with thermal conductivity detector for separation, and Hitachi Model O63 with ion collector detector for Gas-Mass. IR spectra (Shimadzu IR-27C, and Hitachi EPI-S2) and NMR spectra (Hitachi Perkin-Elmer R-20) were also used for the analyses. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-60 or on a Hitachi Model RMS-4 Mass Spectrometer for Gas-Mass.

Procedures. Reactions were generally carried out in a three necked 100 ml flask fitted with a thermometer, a cooler at whose top the gas outlet was equipped, and a gas inlet tube. Gas flow meter and nujol-sealed gas bubbler were attached between the gas inlet tube and gas supply. Gas outlet tube was also connected to the nujol-sealed gas bubbler. In catalytic synthesis of carbonates oxygen was supplied by use of 20 ml syringe. A magnetic stirrer was used for effective vigorous stirring of the reaction mixture.

The Stoichiometric Synthesis of Carbonates. A preparative example of the stoichiometric synthesis of diethyl carbonate was as follows; 0.05 mol of sodium ethylate and 0.05 mol of ethyl alcohol were dissolved in 50 ml THF to which was added 0.01 g atom sample of metallic selenium at 20 °C, and carbon monoxide was blown into the resultant solution at a rate of 60 ml/min for 2 hr with vigorous stirring. At this stage of the reaction glpc analyses revealed the quantitative formation of diethyl carbonate based on selenium in the reaction mixture. Thereafter oxygen was added into the solution at a rate of 10 ml/min without the addition of carbon monoxide. Filtration followed by distillation gave diethyl carbonate (1.086 g, 92% based on selenium used). In order to see the relative reactivity of alcohols, we showed the results of controlled experiments with the use of mole ratio of reactants as shown in Table 1, taking identical procedures as described in this section.

The Catalytic Synthesis of Carbonates. As already described in the section of Results and Discussion, the procedure of the catalytic synthesis only differed from the stoichiometric synthesis in the way that the catalytic reaction was successfully performed by passing continuously the mixture gas of carbon monoxide and oxygen into the resultant solution afforded by the stoichiometric reaction. The ratio of the reaction mixture was as shown in Table 2. In this experimental section was shown the typical example of catalytic synthesis of diethyl carbonate by the reaction of sodium ethylate (0.05 mol) and ethyl alcohol (0.05 mol) with carbon monoxide (60 ml/min) in the presence of metallic selenium (0.001 g atom) dissolved in 50 ml THF for 30 min with vigorous stirring. Catalytic reaction was then performed by adding the mixture gas of carbon monoxide and oxygen for the time given in Table 2. The flow rate of carbon monoxide was 60 ml/min and oxygen was added 1 mmol/hr. At the end of the catalytic reaction, the feed of carbon monoxide was stopped, and only oxygen gas was added (10 ml/min) for 30 min. Isolation of carbonate was identical with example in the case of stoichiometric synthesis.

The Catalytic Synthesis of Diethyl Carbonate in the Presence of Sodium Hydrogen Selenide. Sodium hydrogen selenide (0.005 mol) was prepared according to the method,[13] to which were added THF (50 ml) solution of sodium ethylate (0.05 mol) and ethanol (0.05 mol), and then the mixture gas of carbon monoxide (60 ml/min) and oxygen (0.005 mmol/hr) for 2 hr. About 0.012 mol of diethyl carbonate was found to be formed from glpc.

An Attempted Experiment for the Trapping of the Intermediate. Sodium ethylate (0.05 mol) and ethyl alcohol (0.05 mol) were dissolved in 50 ml THF to which was added 0.01 g atom sample of metallic selenium at 0 °C, and carbon monoxide was added at a rate of 60 ml/min for 30 min with vigorous stirring. Then cold (0 °C) THF solution (25 ml) of *n*-butyl iodide (0.1 mol) was added dropwise in 20 min; during the addition, a gentle flow of carbon monoxide (10 ml/min) was continued. The product analyses were performed by use of Gas-Mass Spectrometer (Hitachi Model O63 Gas Chromatograph and Hitachi Model RMS-4 Mass Spectrometer) with 3 meter PEG-20M column. The chromatogram with its retention time between those of di-*n*-butyl selenide and di-*n*-butyl diselenide was attributed to Se-*n*-butyl ethyl selenocarbonate (*ca.* 0.5%) from the mass spectrum.

*The Synthesis of Authentic Sample of Se-*n*-Butyl Ethyl Mono selenocarbonate.* Metallic selenium (0.05 g atom) was stirred vigorously under nitrogen at 0 °C in 50 ml THF well dried over $LiAlH_4$ and freshly distilled under nitrogen, to which was added 0.052 mol of *n*-butyl lithium in hexane dropwise. THF (25 ml) solution of ethyl chloroformate (0.06 mol) at 0 °C was added dropwise and the resultant solution was kept stirring for 15 hr at 0 °C. Filtration of the lithium chloride followed by distillation under vacuum gave Se-*n*-butyl ethyl monoselenocarbonate (*n*-Bu–Se–CO–

OEt) (1.58 g, 15%) with very unpleasant odor: bp 85 °C/5 mmHg IR (direct) 1717 cm^{-1} (ν_{CO}). Mass (70 eV) *m/e* 210 (M$^+$), 165 (*n*-Bu–Se–CO$^+$), 137 (*n*-Bu–Se$^+$), 108 (SeCO$^+$), 73 (EtO–CO$^+$). Found: C, 40.04; H, 6.83%. Calcd for $C_7H_{14}O_2Se$: C, 40.20; H, 6.75%.

The Reaction of Carbonyl Selenide with Sodium Alkoxide. The preparation of carbonyl selenide was carried out as described in the literature.[18] For the trapping of generated carbonyl selenide gas, we used EtBr-cold bath (−120 °C) with liq. N_2. Carbonyl selenide was then treated with excess sodium alkoxide in alcohol at −80 °C. Addition of oxygen at room temperature to the reaction mixture followed by filtration was found to contain stoichiometric amount of corresponding carbonate from glpc.

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1) R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley & Sons, New York, N.Y. (1961), p. 483.

2) T. Saegusa, T. Tsuda, K. Isayama, and K. Nishijima, *Tetrahedron Lett.*, **1968**, 831.

3) T. Saegusa, T. Tsuda, and K. Isayama, *J. Org. Chem.*, **35**, 2976 (1970).

4) M. Graziani, P. Uguagliati, and G. Carturan, *J. Organometal. Chem.*, **27**, 275 (1971).

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

6) K. Kondo, N. Sonoda, and S. Tsutsumi, *Chem. Commun.*, **1972**, 307.

7) K. Kondo, N. Sonoda, K. Yoshida, M. Koishi, and S. Tsutsumi, *Chem. Lett.*, **1972**, 401.

8) K. Kondo, N. Sonoda, and S. Tsutsumi, *Tetrahedron Lett.*, **1971**, 4885.

9) Selenium with its oxidation number 0 was found to be formally reduced to selenide anion, Se^{2-} with its oxidation number -II.

$$\underset{(0)}{\mathrm{Se}} + \mathrm{Substrate} \longrightarrow \underset{(-\mathrm{II})}{\mathrm{Se}^{2-}} + \mathrm{Product}$$

10) (Oxidizing Efficiency) %=[(mmol of formed $(RO)_2CO$)/(mg atom of Se used)]×100

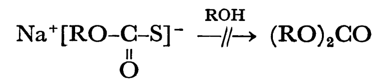
11) The reaction in DMF gave somewhat better yield of carbonates than that in THF.

12) Equation (1) was thus derived by the combination of Eqs. (2), (3), and (4).

13) D. L. Klayman and J. S. Griffin, *J. Amer. Chem. Soc.*, **95**, 197 (1973).

14) To the best of our knowledge, reaction (7) provides the first synthesis of monoselenocarbonate.

15) The reaction of carbonyl sulfide with sodium alkoxide in alcohol was reported[16] to give sodium alkoxy carbonyl sulfide, which was called Bender's salt, and not to give carbonates.



$$\mathrm{SCO} + \mathrm{RONa} \xrightarrow{\mathrm{ROH}} \mathrm{Na^+[RO\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-}S]^-} \xrightarrow[\not\;]{\mathrm{ROH}} \mathrm{(RO)_2CO}$$

16) J. G. Weeldenberg, *Rec. Trav. Chim.*, **47**, 496 (1928); R. J. Ferm, *Chem. Revs.*, **57**, 621 (1957).

17) Some inorganic reactions of carbonyl selenide were known. For instance,

$$\mathrm{SeCO} + 4\mathrm{NaOH} \longrightarrow \mathrm{Na_2CO_3} + \mathrm{Na_2Se_2} + 2\mathrm{H_2O};$$

See to O. Glemser and T. Risler, *Z. Naturforsch*, **3B**, 1 (1948). Present reaction showed a novel utilization of carbonyl selenide in organic synthetic reaction, which would be highly reactive because of small overlap of Se–C 4pπ–2pπ bond in comparison with C–O 2pπ–2pπ bond.

18) T. G. Pearson and P. L. Robinson, *J. Chem. Soc.*, **1932**, 652.

19) The trace experiment in the presence and in the absence of selenium under the identical reaction conditions revealed that the formate generation was neither enhanced nor retarded by selenium, and that the rate of its formation was found to be much slower by 100 times than that of the formation of carbonate in the present reaction conditions.

20) M. Orchin and I. Wender, "Catalysis", Vol. 5, ed. by P. H. Emmett, Reinhold Pub. Co., New York, N.Y. (1957) p. 1.