Selenium assisted carbonylation with carbon monoxide

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Abstract

Selenium reacts with carbon monoxide and amines under mild conditions to give ammonium carbamoselenoates, which were then converted to corresponding ureas by aminolysis upon oxidation with molecular oxygen. Under the controlled conditions, the reaction proceeds with a catalytic amount of selenium, and its turnover number reached *ca.* 10^4. Successful applications of this Se/CO system include not only the synthetic reactions of a variety of carbamates, carbonates, and sulfur or selenium containing compounds but also metallurgical refinement of selenium and several important industrial processes as exemplified by isocyanate synthesis, water-gas shift reaction, and separation of carbon monoxide. The basis of these reactions is the facile *in situ* generation of carbonyl selenide, which possesses a potent reactivity toward a variety of nucleophiles.

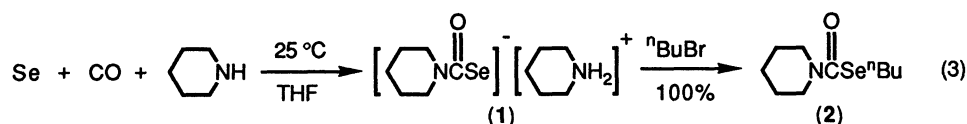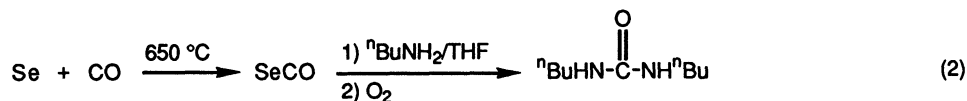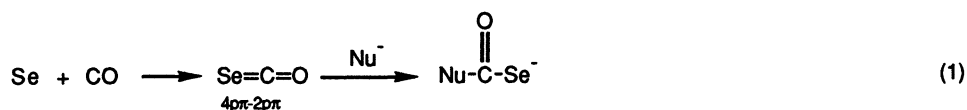## THE DISCOVERY OF SELENIUM CATALYZED CARBONYLATION WITH CARBON MONOXIDE

Water and carbon dioxide are very stable compounds, however, if (one of) the oxygen atom(s) in these molecules is replaced by one of the homologous chalcogen elements, the stabilities of these compounds decrease and their reactivities increase in the same order (Table 1). Hydrogen selenide is stable at ambient temperature like hydrogen sulfide but it is easily oxidized with molecular oxygen. Carbonyl selenide and hydrogen telluride are not stable at ambient temperature and gradually decompose to give elemental selenium or tellurium. Carbonyl telluride has not yet been identified.

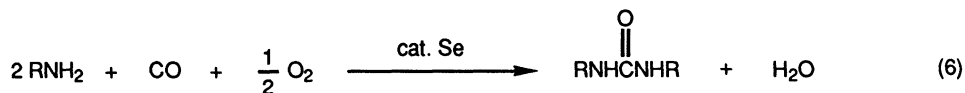TABLE 1. Comparison of physical constants of chalcogen elements.

X	O	S	Se	Te
electronegativity (Pauling)	3.5	2.5	2.4	2.1
bond energy (Kcal/mol), H-X of H_2X	119	91	73	64
bond length (Å), H-X	0.96	1.35	1.46	1.69
dissociation constant (pKa) of H_2X	14.0	7.0	3.7	2.6
bond energy (Kcal/mol), C-X of Et_2X	86.5	69.7	59.9	(<60)
π- bond energy (Kcal/mol, calculation value), $CH_2{=}X$	93	56	–	–
bond length (Å), C-X	1.42	1.82	1.96	2.12

Carbonyl selenide is an especially attractive compound because it involves a Se-C double bond consisted of a weak $4p\pi$-$2p\pi$ interaction, which facilitates the attack of nucleophiles at the carbon atom of carbonyl selenide (eq. 1). This prompted us to examine the reaction of carbonyl selenide with nucleophiles like

amines.   At the beginning of our study, gaseous carbonyl selenide was synthesized by the reaction of elemental selenium with carbon monoxide at 650 °C, and was introduced into the THF solution of n-butylamine.   The reaction successfully led to the formation of N,N'-dibutylurea together with selenium after treating of the reaction mixture with oxygen (eq. 2).   Further detailed examinations on this carbonylation of amines have made an important discovery that selenium reacts with carbon monoxide in the presence of an amine under very mild conditions (15 °C, 1 atm) to form in $situ$ carbonyl selenide, which then reacted with an amine to give the corresponding carbamoselenoate (1) as exemplified in eq. 3.   The formation of carbamoselenoate (1) was unambiguously confirmed by the alkylation with butyl bromide to give Se-butyl carbamoselenoate (2) quantitatively (refs. 1,2).

$$Se + CO \longrightarrow \underset{4p\pi\text{-}2p\pi}{Se=C=O} \xrightarrow{Nu^-} Nu\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}Se^- \qquad (1)$$

$$Se + CO \xrightarrow{650\,°C} SeCO \xrightarrow[2)\,O_2]{1)\ ^nBuNH_2/THF} {}^nBuHN\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}NH^nBu \qquad (2)$$

$$Se + CO + \underset{}{\text{〈 〉NH}} \xrightarrow[THF]{25\,°C} \left[\text{〈 〉N}\overset{\displaystyle O}{\overset{\|}{C}}Se\right]^- \left[\text{〈 〉NH}_2\right]^+ \xrightarrow[100\%]{^nBuBr} \text{〈 〉N}\overset{\displaystyle O}{\overset{\|}{C}}Se^nBu \qquad (3)$$
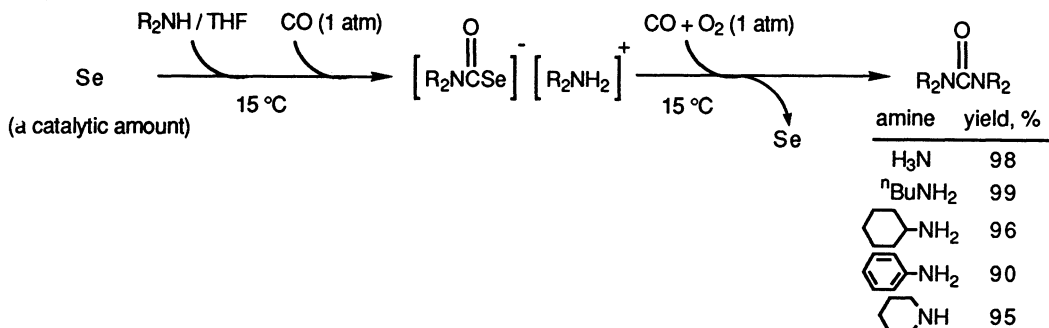$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (1) \qquad\qquad\qquad\qquad\qquad (2)$$

Stoichiometric reaction of primary amines with selenium and carbon monoxide afforded urea derivatives in excellent yields together with the concomitant formation of hydrogen selenide which may be present in the reaction medium as its ammonium salt (eq. 4).   Thus formed hydrogen selenide (or its ammonium salt) easily reacted with molecular oxygen at ambient temperature resulting in the regeneration of elemental selenium (eq. 5).   Considering that the similar oxidation of hydrogen sulfide does not proceed readily under such mild conditions, this reaction represents another characteristic feature of selenium.   The combination of eqs. 4 and 5 produces eq. 6, which indicates that the carbonylation can be performed using a catalytic amount of selenium when oxygen is present (ref. 1).

$$Se + CO + 2\,RNH_2 \xrightarrow[THF]{} RNH\overset{\displaystyle O}{\overset{\|}{C}}NHR + H_2Se \qquad (4)$$

$$H_2Se + \tfrac{1}{2}O_2 \longrightarrow Se + H_2O \qquad (5)$$

$$2\,RNH_2 + CO + \tfrac{1}{2}O_2 \xrightarrow{cat.\ Se} RNH\overset{\displaystyle O}{\overset{\|}{C}}NHR + H_2O \qquad (6)$$
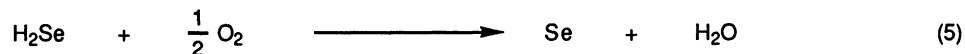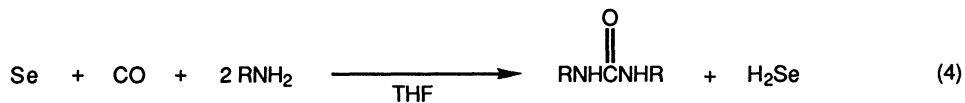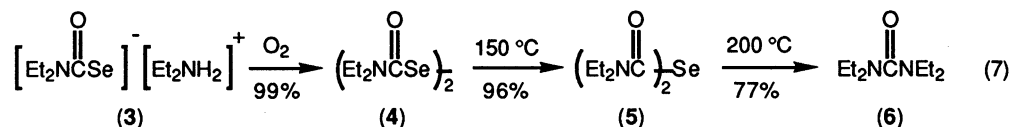
As depicted in Scheme 1, primary amines underwent carbonylation in the presence of 1 mol% of selenium at room temperature under an atmospheric pressure of carbon monoxide containing $ca.$ 5% of oxygen to give urea derivatives in excellent yields.   This method was also applicable to the synthesis of ureas from aromatic amines and several secondary amines such as piperidine and dimethylamine.

Scheme 1

$$Se \xrightarrow[15\,°C]{R_2NH/THF\quad CO\,(1\,atm)} \left[R_2N\overset{\displaystyle O}{\overset{\|}{C}}Se\right]^- \left[R_2NH_2\right]^+ \xrightarrow[15\,°C\quad \searrow Se]{CO+O_2\,(1\,atm)} R_2N\overset{\displaystyle O}{\overset{\|}{C}}NR_2$$

(a catalytic amount)

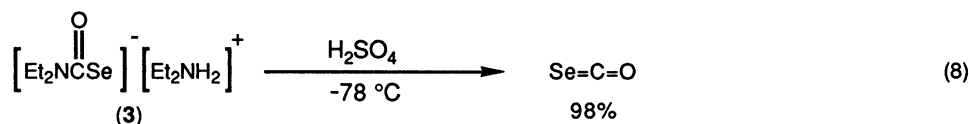| amine	yield, %
H_3N	98
$^nBuNH_2$	99
〈 〉-NH_2	96
〈 〉-NH_2	90
〈 〉NH	95

Contrary to this, dialkylamines other than dimethylamine did not afford the corresponding ureas. The oxidation of carbamoselenoate (3) arising from selenium, carbon monoxide, and diethylamine led to the formation of biscarbamoyl diselenide (4) almost quantitatively (eq. 7). Upon heating to 200 °C, however, biscarbamoyl diselenide (4) eliminated selenium and carbon monoxide to give N,N,N',N'-tetraethylurea (6) *via* biscarbamoyl selenide (5) (ref. 3).

$$\left[Et_2N\overset{O}{\overset{\|}{C}}Se\right]^{-}\left[Et_2NH_2\right]^{+} \xrightarrow[99\%]{O_2} \left(Et_2N\overset{O}{\overset{\|}{C}}Se\right)_2 \xrightarrow[96\%]{150\ °C} \left(Et_2N\overset{O}{\overset{\|}{C}}\right)_2 Se \xrightarrow[77\%]{200\ °C} Et_2N\overset{O}{\overset{\|}{C}}NEt_2 \quad (7)$$

$$\qquad\quad (3) \qquad\qquad\qquad (4) \qquad\qquad\qquad (5) \qquad\qquad\qquad (6)$$

Since it has become feasible to prepare carbamoselenoate (3) in a quantitative yield, we then attempted to establish a convenient method for generation of carbonyl selenide from 3 by acidifying its solution (ref. 4). Successful result was obtained only when 3 prepared in THF was cautiously added at -78 °C to the THF solution of a strong acid such as sulfuric acid or *p*-toluenesulfonic acid (eq. 8). The reverse addition resulted in the decomposition of 3 into selenium, carbon monoxide, and diethylamine.

$$\left[Et_2N\overset{O}{\overset{\|}{C}}Se\right]^{-}\left[Et_2NH_2\right]^{+} \xrightarrow[-78\ °C]{H_2SO_4} \qquad Se=C=O \qquad\qquad (8)$$

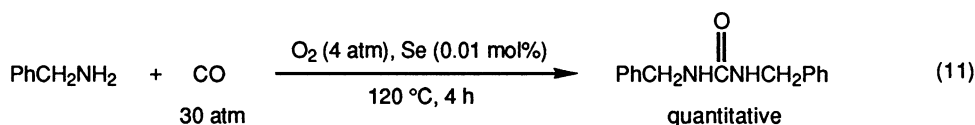$$\qquad\quad (3) \qquad\qquad\qquad\qquad\qquad\qquad 98\%$$

Since carbonyl selenide has now become readily available by our method, we examined its chemical behavior toward several reagents. Reactions of carbonyl selenide with phosphines and isocyanides resulted in the formation of phosphine selenides and isoselenocyanates, respectively, with the liberation of carbon monoxide (eqs. 9 and 10). A similar reaction with potassium cyanide gave potassium selenocyanate. It is interesting that carbonyl selenide decomposed quickly upon treatment with tertiary amines, although it reacted with primary or secondary amines to give urea derivatives (ref. 5).

$$SeCO \quad + \quad R_3P \quad \longrightarrow \quad R_3PSe \quad + \quad CO \qquad\qquad (9)$$

$$SeCO \quad + \quad RNC \quad \longrightarrow \quad RNCSe \quad + \quad CO \qquad\qquad (10)$$

The selenium-mediated carbonylation is based on the facile generation of carbonyl selenide from selenium and carbon monoxide in the presence of amines. Accordingly, carbonyl selenide can be regarded as a novel activated form of carbon monoxide. Compared with selenium, a similar reaction of sulfur with carbon monoxide requires much more severe conditions. Several synthetic applications of this Se/CO reaction system are demonstrated in the following sections.

## SELENIUM ASSISTED SYNTHESIS OF UREAS AND THE RELATED COMPOUNDS

The present selenium-catalyzed carbonylation of primary amines, which could proceed at room temperature under the atmosphere of carbon monoxide, was strongly accelerated at an elevated temperature and under pressurized conditions. For example, the carbonylation of 21.4 g of benzylamine (200 mmol) took place quantitatively by using only 0.8 mg of selenium (0.01 mmol) under 30 atm of CO at 120 °C (eq. 11).

$$PhCH_2NH_2 \quad + \quad CO \quad \xrightarrow[120\ °C,\ 4\ h]{O_2\ (4\ atm),\ Se\ (0.01\ mol\%)} \quad PhCH_2NH\overset{O}{\overset{\|}{C}}NHCH_2Ph \qquad (11)$$

$$\qquad\qquad\qquad 30\ atm \qquad\qquad\qquad\qquad\qquad\qquad quantitative$$

The turnover number of selenium reached *ca.* 10^4, which means the remarkably high catalytic activity of selenium for this carbonylation. Even so, this does not reflect the maximum activity of selenium but is simply a technical limitations in our laboratory.

The carbonylation of secondary amines is relatively slower than that of primary amines but afforded the corresponding urea derivatives in excellent yields upon using 1 mol % of selenium catalyst under similar

conditions. Some representative results are shown below. The fact that 2-methylpiperidine yielded only 6% of the corresponding urea along with recovery of a significant portion of unreacted amine under identical conditions suggests that this reaction is very sensitive to the steric bulk of the amine used.


| 100% | 99% | 96% | 99% |
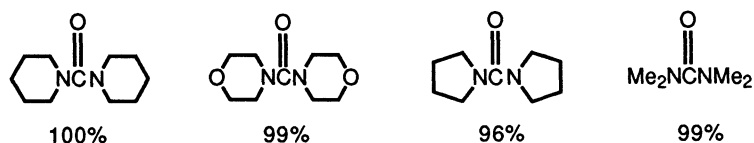
This Se/CO reaction system could be applied to the syntheses of a variety of cyclic (or acyclic) ureas, carbamates, carbonates and their analogues such as thiocarbonates, when using bifunctional compounds as the substrate (refs. 6-9). These reactions were accelerated by the addition of a tertiary amine such as N-methylpyrrolidine (NMP) or triethylamine. Equation 12 represents a typical example: amino alcohols underwent carbonylation with carbon monoxide in two different fashions, i.e., intermolecularly and intramolecularly. The selectivity could be controlled by the reaction conditions employed. The intermolecular reaction was favored when the reaction was conducted at low temperatures under concentrated conditions as can easily be expected. What should be emphasized here is that the reaction course can be alternated almost perfectly by changing the amount of selenium used. This may be explained by assuming that 5-aminopentanol reacts with selenium and carbon monoxide exclusively on the amino group due to its higher nucleophilicity in comparison to the hydroxy groups, forming the ammonium salts of 7. In the catalytic reactions, the intermediate (7) undergoes intermolecular aminolysis by reaction with the remaining starting material to produce an acyclic urea. On the other hand, upon using stoichiometric or excess amounts of selenium, all of the starting material is converted to the intermediate (7) before the intermolecular reaction takes place. Therefore, the only possibility for reaction is intramolecularly.

$$(12)$$
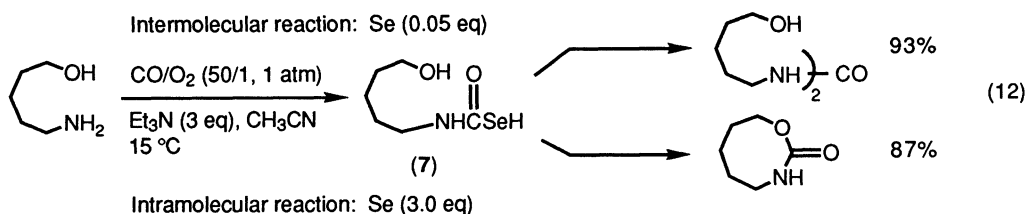
The reaction of amines with a stoichiometric amount of selenium in methanol under atmospheric pressure of carbon monoxide afforded the corresponding carbamates in high yields after usual workup (eq. 13). This reaction demonstrates one of the important applications of this Se/CO reaction system to industrial chemistry, because the thermolysis of carbamates provides corresponding isocyanates on elimination of methanol (vide infra).

$$RNH_2 \ + \ MeOH \ + \ CO \xrightarrow[\text{THF, 25 °C}]{\text{Se (1 eq), Et}_3\text{N (1 eq)}} RNHCOMe \qquad (13)$$
(1 atm)
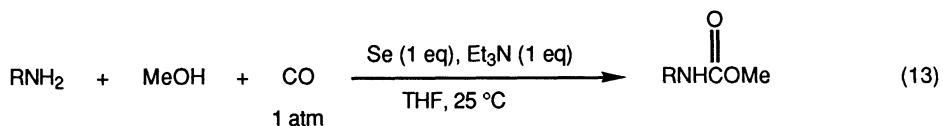
Likewise, aliphatic alcohols were successfully carbonylated under the pressure of carbon monoxide by the use of sodium alkoxide as a base in the presence of a catalytic amount of selenium and a small amount of oxygen (eq. 14).

$$ROH \ + \ CO \xrightarrow[\text{THF (or ROH), 20 °C}]{\text{Se (cat.), RONa, O}_2} ROCOR \qquad (14)$$
(1 atm)
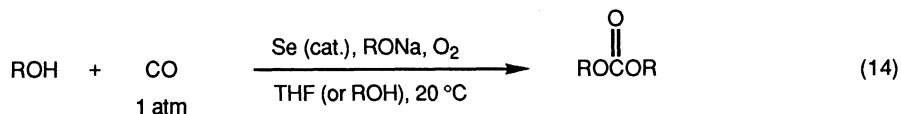
In addition to the carbonylation at heteroatom sites, C-carbonylation can also be performed by the use of a strong base such as 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU). As shown in Scheme 2, 4-hydroxy-coumarin as an important precursor of an effective anticoagulant (Warfarin), was synthesized easily from o-hydroxyacetophenone by using a catalytic amount of selenium and nitrobenzene as the oxidizing agent (ref. 10).

Scheme 2

SELENIUM CATALYSIS OF THE CARBONYLATION

In order to gain insight into the reaction mechanism for this selenium-catalyzed carbonylation, the reaction of selenium with piperidine and carbon monoxide was followed by ^{1}H, ^{13}C, and ^{77}Se NMR and some control experiments have been done (ref. 11). The proposed reaction pathway is summarized in Scheme 3, which may be true for the carbonylation of secondary amines. Metallic selenium reacted with piperidine and carbon monoxide at 25 °C to give a homogeneous solution of ammonium salt of **8** (R_2N = piperidino), the formation of which was confirmed by successful isolation under nitrogen atmosphere (mp 80-81 °C) and characterization by IR and NMR spectra and elemental analysis. The introduction of oxygen into the THF solution of **8** at 25 °C caused the deposition of selenium from the reaction medium resulting in the quantitative formation of a urea (**11**). These results suggest that the direct aminolysis of ammonium salt of **8** to give **11** and hydrogen selenide is not likely in the case of secondary amines at least under these mild conditions. When the oxidation of **8** was carried out at 0 °C, diselenide (**9**) was obtained as the major product (82%). The intermediacy of **9** in the urea formation was supported by the fact that the reaction of **9** with 2 equivalents of piperidine at 25 °C in the presence of oxygen led to **11** and selenium in 89% and 86% yields, respectively. The reaction may proceed by the nucleophilic attack of piperidine at the carbonyl carbon of **9** to give **11** and **10**. The intermediate (**10**) then eliminates selenium to regenerate **8**. Alternatively, **10** reacts directly with carbon monoxide to form carbonyl selenide and **8** without elimination of selenium. These processes are supported by the following experiment: after performed the reaction of **9** with piperidine in the absence of oxygen, the addition of benzyl bromide into the resulting mixture led to successful trapping of **8** to give Se-benzylcarbamoselenoate.

Scheme 3

As to the mechanism for the carbonylation of primary amines, the formation of an ammonium carbamoselenoate (**12**) was also confirmed by NMR in the reaction of *tert*-butylamine with selenium and carbon monoxide. This indicates the intermediacy of carbamoselenoates as well as the case of secondary amines. Unlike secondary amines, however, an alternative pathway *via* isocyanates may operate in the

subsequent aminolysis step as shown in Scheme 4. This possibility is supported by the facts that the carbonylation of primary amines proceeded much more readily than secondary amines and that ureas could be formed from primary amines even in the absence of oxygen under certain conditions.

Scheme 4

APPLICATIONS OF Se/CO REACTION SYSTEM

Carbon monoxide is not only a useful carbonylating agent but also is a highly potent reducing agent. Since carbon monoxide itself rarely reacts with usual organic molecules directly, the synthetic application of carbon monoxide as a reducing reagent has been attained only by the aid of transition metal complexes. We have found that selenium is reduced to hydrogen selenide *via* selenocarbonic acid formed from selenium, carbon monoxide and water in the presence of a tertiary amine as shown in Scheme 5 (ref. 12). The resulting hydrogen selenide forms an ammonium salt which could be expected to act as an efficient reducing agent toward a variety of organic molecules (refs. 13-17).

Scheme 5
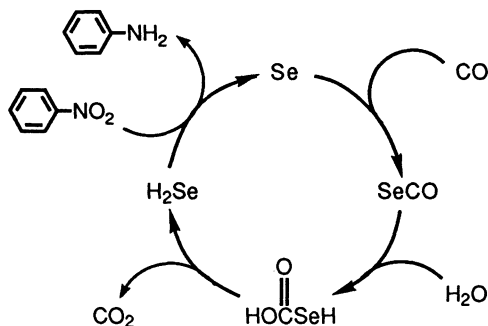
For example, aromatic ketones (ref. 13), α,β-unsaturated carbonyls (ref. 14), α-halo ketones or *vic*-dihalides (ref. 15), diselenides or disulfides (ref. 16), and nitroarenes (ref. 17) could be easily reduced in this Se/CO/H$_2$O reaction medium to the corresponding arylalkanes, saturated carbonyls, dehalogenated ketones or alkenes, selenols or thiols, and aromatic amines, respectively. Most of these reductions have been performed successfully using a catalytic amount of selenium. One of the fascinating applications of this Se/CO system is the direct conversion of nitroarenes to the corresponding carbamates, where the reductive carbonylation has been achieved in one process. The industrial importance of this process will be suggested by eq. 15, which provides a shortcut way to toluenediisocyanate (TDI), a significant precursor of polyurethane.
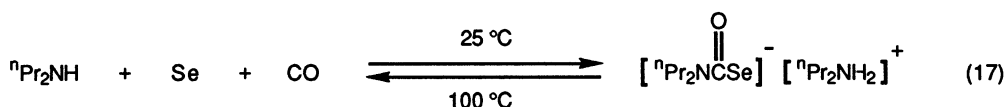

(15)
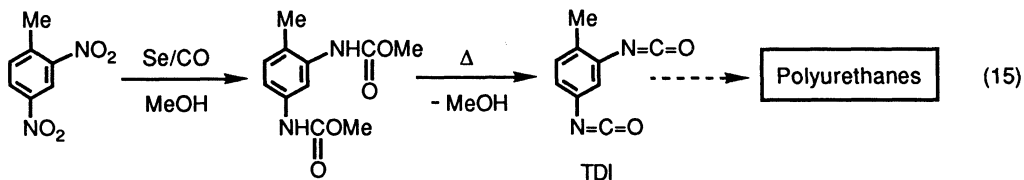
Reaction of nitriles with hydrogen selenide generated *in situ* from Se/CO/H$_2$O afforded selenoamides in good yields (refs. 18,19). Deselenative coupling of the selenoamides by treatment with copper powder provides a powerful tool for preparing *vic*-diaminoalkenes (eq. 16) (ref. 20). When the reaction of selenium with CO and H$_2$O was conducted in the presence of platinum black catalyst, the hydrogen selenide
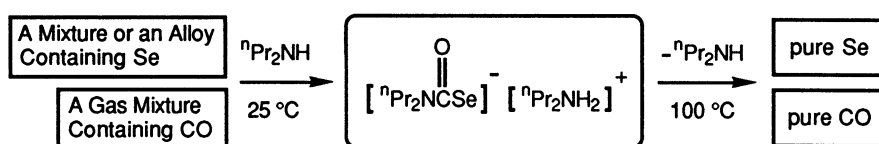
generated *in situ* was decomposed to hydrogen and selenium leading to the development of a new water-gas shift reaction ($H_2O + CO \rightarrow H_2 + CO_2$) catalyzed by selenium and platinum (ref. 21).
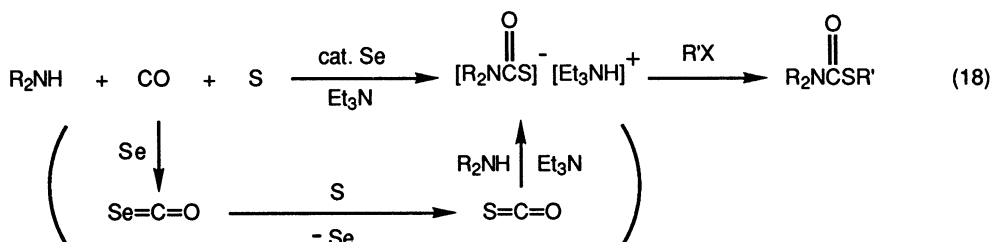
$$[H_2Se] \xrightarrow{RCN} \overset{\overset{\displaystyle Se}{\|}}{RCNH_2} \xrightarrow[-NH_3]{R'_2NH} \overset{\overset{\displaystyle Se}{\|}}{RCNR'_2} \xrightarrow{Cu(0)} \underset{R'_2N \quad R}{\overset{R \quad NR'_2}{C=C}} \quad (16)$$

The formation of ammonium carbamoselenoates from selenium, carbon monoxide and amines is an equilibrium process, and when secondary amines bearing bulky substituents were used, the carbamoselenoates decomposed completely to the starting materials on heating without the formation of ureas (eq. 17). Therefore, this Se/CO/amine system provides a unique separation procedure of pure selenium and pure carbon monoxide by the method of temperature swing, because only selenium in a solid mixture or an alloy containing other elements and only carbon monoxide in a gas mixture of hydrogen, methane etc. react with amine to give a homogeneous solution as shown in Scheme 6 (ref. 22).
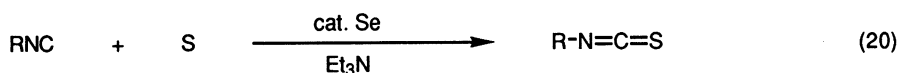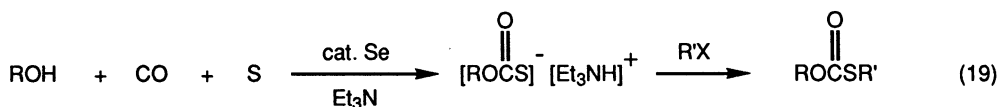
$$^nPr_2NH + Se + CO \underset{100\,°C}{\overset{25\,°C}{\rightleftharpoons}} [\,^nPr_2N\overset{\overset{\displaystyle O}{\|}}{C}Se\,]^- [\,^nPr_2NH_2\,]^+ \quad (17)$$

Scheme 6

We have found a novel carbonyl exchange reaction of carbonyl selenide with elemental sulfur in the presence of a tertiary amine, which provides carbonyl sulfide and elemental selenium (i.e., SeCO + S → SCO + Se). This finding led us to develop a new selenium-catalyzed synthesis of thiocarbamates from elemental sulfur, carbon monoxide, and amines under mild conditions (eq. 18). A variety of S-alkyl thiocarbamates, including important agrochemicals such as herbicides, can be prepared by this method (ref. 23).

$$R_2NH + CO + S \xrightarrow[Et_3N]{cat.\ Se} [R_2N\overset{\overset{\displaystyle O}{\|}}{C}S]^- [Et_3NH]^+ \xrightarrow{R'X} R_2N\overset{\overset{\displaystyle O}{\|}}{C}SR' \quad (18)$$

$$\left(\begin{array}{c} Se \downarrow \\ Se=C=O \xrightarrow[-\ Se]{S} S=C=O \xleftarrow{\ R_2NH\ \big\uparrow\ Et_3N\ } \end{array} \right)$$

Further extension of this selenium catalysis in the sulfur reaction provided a facile synthesis of thiocarbonates and isothiocyanates having an isoelectronic structure with carbonyl sulfide, as shown in eqs. 19 and 20, respectively (refs. 24, 25).

$$ROH + CO + S \xrightarrow[Et_3N]{cat.\ Se} [RO\overset{\overset{\displaystyle O}{\|}}{C}S]^- [Et_3NH]^+ \xrightarrow{R'X} RO\overset{\overset{\displaystyle O}{\|}}{C}SR' \quad (19)$$

$$RNC + S \xrightarrow[Et_3N]{cat.\ Se} R-N=C=S \quad (20)$$

In conclusion, selenium readily reacted with carbon monoxide in the presence of a base under mild conditions to generate carbonyl selenide, and this simple principle was successfully applied to the catalytic carbonylation of amines, alcohols, etc., providing the unique, powerful, and useful tools for preparing ureas, carbamates, carbonates, and the related compounds. This is the first example of the carbonylation with carbon monoxide catalyzed by non-transition elements, and to our great delight, the selenium catalyzed

carbonylation described here is sometimes called "SONODA REACTION".   In addition to the carbonylation, various types of applications, such as the selenium catalyzed reduction with carbon monoxide, the synthesis of selenium or sulfur containing compounds, separation and purification of selenium and carbon monoxide, could also be developed based on this Se/CO system.

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