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A New Synthesis of Cyclic Ureas, Cyclic Urethanes, and a Quinazolinedione.[1] Selenium-Assisted Carbonylation of Aromatic Amines with Carbon Monoxide

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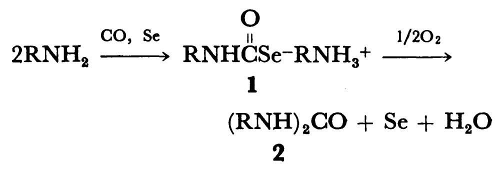
Five-, six-, and seven-membered cyclic ureas were synthesized in excellent yields from various aromatic diamines by reaction with carbon monoxide and a stoichiometric or excess amount of selenium in the presence of *N*-methylpyrrolidine. The carbonylation also proceeded using a catalytic amount of selenium in the presence of an oxidizing agent such as oxygen or dimethyl sulfoxide producing selectively the five- and six-membered cyclic ureas. In the case of 2-(2-aminoethyl)aniline under the catalytic conditions, intra- and intermolecular carbonylation competed resulting in the formation of a mixture of the seven-membered cyclic urea, 1,3,4,5-tetrahydro-2*H*-1,3-benzodiazepin-2-one and the acyclic urea, 1,3-bis[2-(2-aminophenyl)ethyl]-urea. The distribution ratio of these two products varied depending on the reaction conditions, but selective formation of the cyclic urea was attained only when a stoichiometric or excess amount of selenium was used. In addition to the above diamino compounds, 2-carbamoylaniline, 2-amino-3-pyridinol, and 2-(hydroxymethyl)-aniline also underwent similar carbonylation to give 2,4(1*H*,3*H*)-quinazolinedione, oxazolo[4,5-*b*]pyridin-2-(3*H*)-one, and 1,4-dihydro-2*H*-3,1-benzoxazin-2-one, respectively.

Many cyclic urea derivatives have been used as important precursors to pigments,[2] resins,[3] and bioactive compounds.[4] These cyclic ureas can be synthesized by intramolecular amination of in situ formed isocyanates via Hoffman, Curtius, or Lossen rearrangement,[5] or carbonylation of diamines using carbonylating reagents such as phosgene, ethyl chloroformate,[6] 1,1′-carbonyldiimidazole,[6] and 1,1′-[carbonylbis(oxy)]bis-2,5-pyrrolidinedione.[7]

In addition to these stoichiometric reactions, the catalytic *N*-carbonylation of diamines with carbon monoxide is an alternative approach to the synthesis of cyclic urea derivatives.[8] Although a number of studies on catalytic carbonylation of monoamines with carbon monoxide have been reported using a variety of transition metal complexes as the catalysts, these reaction often gave mixtures of urea, formamide, and oxamide.[9–15] The selectivity depends largely on the ligands as well as the metal used.[11] However, there are only two reports of the catalytic carbonylation of diamines: One uses $Mn_2(CO)_{10}$[16a] and the other $Ni(CO)_4$[16b]; selective formation of cyclic ureas has not been achieved using these two reaction systems.

Continuing an ongoing project on selenium-assisted carbonylation, we have established a convenient method for the synthesis of symmetrical ureas using a variety of amines which are reacted with carbon monoxide and oxygen in the presence of a catalytic amount of selenium under mild conditions.[17]

This catalytic reaction has been postulated[17a,b] to proceed via selenolcarbamate ammonium salt **1**[18] which undergoes aminolysis by the nucleophilic attack of a second amine molecule at the carbonyl carbon of **1** to form urea derivatives **2** in the presence of oxygen (Scheme 1). The intermediacy of the selenolcarbamate **1** is strongly supported by the facts that the selenolcarbamate derived from piperidine was isolated[17a] and that the selenolcarbamate from diethylamine was trapped by alkyl halides to give alkyl selenolcarbamates.[17b]

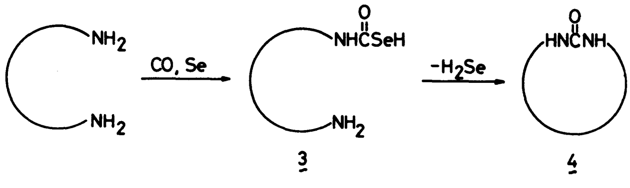


$$2RNH_2 \xrightarrow{CO,\ Se} \underset{\mathbf{1}}{RNH\overset{O}{\overset{\|}{C}}Se^{-}RNH_3^{+}} \xrightarrow{1/2O_2}$$

$$\underset{\mathbf{2}}{(RNH)_2CO} + Se + H_2O$$

Scheme 1.

We have expected that application of this reaction system to diamino compounds may provide a simple and convenient method for the synthesis of cyclic ureas **4**. In this paper, we will present full details of a study aimed at the selective formation of cyclic ureas from aromatic diamines by carbonylation with carbon monoxide using selenium (Scheme 2).[1]



Scheme 2.

Results and Discussion

Carbonylation of Aromatic Diamines with Carbon Monoxide Using Stoichiometric Amount of Selenium. We have shown that aliphatic amines react with carbon monoxide at room temperature in the presence of stoichiometric amount of selenium leading to the selenolcarbamate **1**.[17a,b)] Oxidation of **1** with oxygen afforded corresponding ureas in good yields.[17a)] Alternatively, aromatic amines such as anilines were less reactive, and the reaction of aromatic amines required a tertiary amine as the base and higher reaction temperature.[17c)]

A solution of *o*-phenylenediamine (**5**) was allowed to react at 100 °C with 31 kg cm^{-2} of carbon monoxide and a stoichiometric amount of selenium in the presence of *N*-methylpyrrolidine (NMP) in THF. The uptake of carbon monoxide ceased within 20 h. After the reaction was complete, the remaining carbon monoxide was purged and the mixture was stirred for 1 h under air to oxidize the resulting hydrogen selenide (see Scheme 2). The following workup gave an 89% yield of the cyclic urea **17**. Unreacted starting

Table 1. Intramolecular Carbonylation of Aromatic Amines with Carbon Monoxide

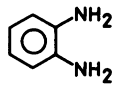
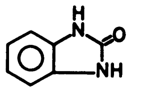
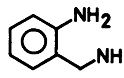
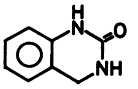
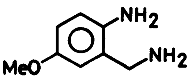
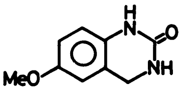
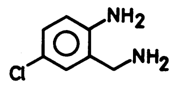
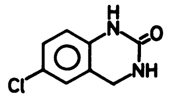
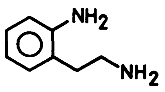
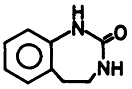
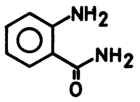
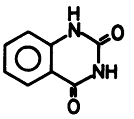
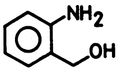
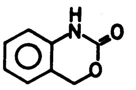
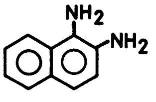
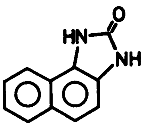
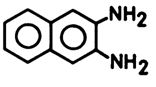
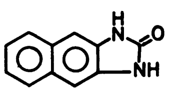
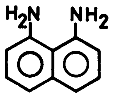
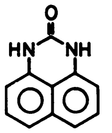
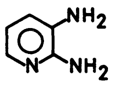
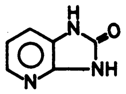
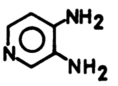
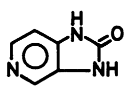
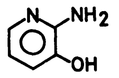
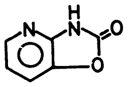
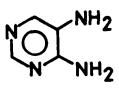
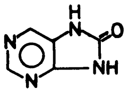
Entry	Substrate		Product		Yield/% (Conditions)[a)]	
					Excess	Catalytic
1		**5**		**17**	99(A)	99(E) 98(I)
2		**6a**		**18a**	86(A)	92(F)
3		**6b**		**18b**	92(A)	—
4		**6c**		**18c**	86(A)	—
5		**7**		**19**	81(A)	b)
6		**8**		**20**	21(B)	20(G) 23(J)
7		**9**		**21**	—	85(F)
8		**10**		**22**	98(A)	96(E) 97(I)
9		**11**		**23**	98(A)	97(E)
10		**12**		**24**	97(A)	96(E) 95(I)
11		**13**		**25**	98(C)	97(G)
12		**14**		**26**	96(C)	98(G)

Table 1. (Continued)

Entry	Substrate		Product		Yield/% (Conditions)[a]	
					Excess	Catalytic
13		15		27	75(D)	71(H) 74(I)
14		16		28	87(D)	89(H) 83(I)

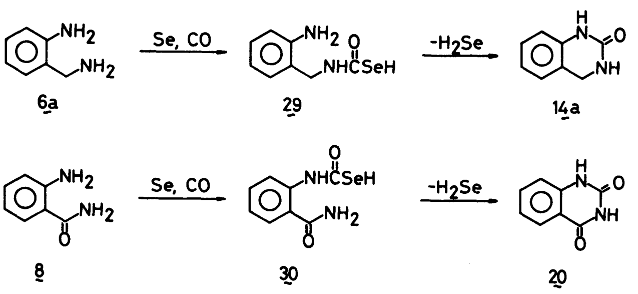
a) Conditions: (A) Substrate (2.5 mmol), selenium (7.5 mmol), *N*-methylpyrrolidine (0.79 mL, 7.5 mmol), THF (10 mL), carbon monoxide (31 kg cm^{-2}), 100 °C, 20 h. (B) Substrate (2.5 mmol), selenium (7.5 mmol), *N*-methylpyrrolidine (0.79 mL, 7.5 mmol), DMF (10 mL), carbon monoxide (31 kg cm^{-2}), 100 °C, 20 h. (C) Substrate (5 mmol), selenium (15 mmol), THF (10 mL), carbon monoxide (31 kg cm^{-2}), 100 °C, 20 h. (D) Substrate (5 mmol), selenium (15 mmol), DMSO (1 mL), carbon monoxide (31 kg cm^{-2}), 100 °C, 20 h. (E) Substrate (2.5 mmol), selenium (0.125 mmol), *N*-methylpyrrolidine (0.79 mL, 7.5 mmol), THF (10 mL), carbon monoxide (29 kg cm^{-2}), oxygen (2 kg cm^{-2}), 100 °C, 20 h. (F) Substrate (2.5 mmol), selenium (0.125 mmol), *N*-methylpyrrolidine (0.79 mL, 7.5 mmol), THF (10 mL), under atmospheric pressure of a gas mixture of carbon monoxide (0.94 kg cm^{-2}) and oxygen (0.06 kg cm^{-2}), 15 °C, 10 h. (G) Substrate (2.5 mmol), selenium (0.125 mmol), THF (10 mL), carbon monoxide (29 kg cm^{-2}), oxygen (2 kg cm^{-2}), 100 °C, 20 h. (H) Substrate (2.5 mmol), selenium (0.125 mmol), DMSO (1 mL), carbon monoxide (29 kg cm^{-2}), oxygen (2 kg cm^{-2}), 100 °C, 20 h. (I) Substrate (2.5 mmol), selenium (0.125 mmol), *N*-methylpyrrolidine (0.79 mL, 7.5 mmol), THF (10 mL), DMSO (250 mg), carbon monoxide (31 kg cm^{-2}), 100 °C, 20 h. (J) Substrate (2.5 mmol), selenium (0.125 mmol), DMSO (2 mL), carbon monoxide (31 kg cm^{-2}), 100 °C, 20 h. b) See Table 2.

diamine was recoverd. When the reaction was carried out at 25 °C, only the starting material was recovered. In the absence of NMP, **5** gave **17** in 67% yield under similar conditions. This carbonylation was accelerated by using excess amounts of selenium. For example, when three-fold excess of selenium was used, **17** was obtained in 99% yield. Table 1 summarizes the results obtained when the reaction was carried out at 100 °C with 31 kg cm^{-2} of carbon monoxide and three-fold excess of selenium (conditions A-D in Table 1).

Other aniline derivatives having an aminoalkyl substituent in the ortho position **6a**—**c** and **7** underwent similar carbonylation to yield the corresponding cyclic ureas **18a**—**c** and **19** in good yields.

It should be noted that the carbamoyl nitrogen could be carbonylated under similar conditions as demonstrated by the reaction of 2-carbamoylaniline **8** in DMF (Entry 6 in Table 1). In this reaction, unreacted starting material was recovered. In THF, **8** did not react, probably due to the low solubility of **8** in THF.

The present carbonylation reaction is postulated to proceed via a selenolcarbamate intermediate formed by the reaction of the diamines with carbon monoxide and selenium (Scheme 3). The aliphatic amino group is more reactive than the aromatic one and may react faster with carbon monoxide in the presence of selenium, so that 2-(aminomethyl)aniline (**6a**) is preferentially converted to selenolcarbamate **29**.[19] In case of 2-carbamoylaniline **8**, the selenolcarbamate is formed at the site of the aromatic amino group, because of the low reactivity of the carbamoyl nitrogen.



Scheme 3.

The intermediates **29** and **30** then undergo aminolysis by the intramolecular nucleophilic attack of the remaining NH_2 group to give the corresponding cyclic ureas **14a** and **20**, respectively, together with the formation of hydrogen selenide.

Naphthalene-, pyridine-, and pyrimidinediamines were also examined. The reaction of 1,2-, 2,3-, and 1,8-naphthalenediamine **10**—**12** under similar conditions gave rise to cyclic ureas **22**—**24**, respectively in good yields. Pyridine- and pyrimidinediamines **13**, **14**, and **16** which have the tertiary amino moiety in the aromatic ring underwent similar carbonylation even in the absence of NMP to give the corresponding cyclic ureas **25**, **26**, and **28** in good yields. In case of 2-amino-3-pyridinol **15**, the carbonylation reaction also proceeded without NMP to afford the corresponding cyclic urethane **27** in 87% yield.

Selenium-Catalyzed Carbonylation with Carbon Monoxide Using Oxidizing Agents. In addition to the stoichiometric reaction described above, a similar carbonylation using a catalytic amount of selenium in the presence of an oxidizing agent was developed.[17a,c]

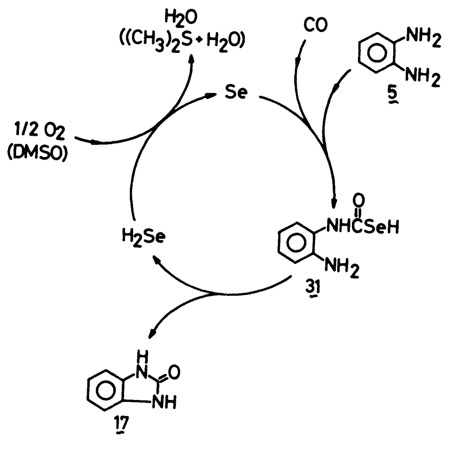
Reaction of *o*-phenylenediamine (**5**) was carried out at 100 °C using 0.05 equiv of selenium with 3 equiv of NMP under a gas mixture of carbon monoxide (29 kg cm^{-2}) and oxygen (2 kg cm^{-2}). After a similar workup as previously mentioned, the cyclic urea **17** was obtained in 99% yield. At room temperature **5** gave **17** in 77% yield.[20]

Other aromatic diamines **10**—**12** underwent intramolecular carbonylation catalytically in a similar manner to afford the corresponding cyclic compounds in good yields (Table 1). As described in the stoichiometric reactions, a tertiary amine was not required in the catalytic carbonylation of **13**—**16**. 2-Carbamoylaniline **8** and 2-amino-3-pyridinol **15** also afforded 2,4(1*H*,3*H*)-quinazolinedione **20** (20%) and **27** (71%).

This selenium-catalyzed carbonylation also proceeded using dimethyl sulfoxide[21] as the oxidizing agent instead of oxygen. Formation of dimethyl sulfide was confirmed by capillary gas chromatography and ^{1}H NMR.

Scheme 4 shows a plausible reaction path for this catalytic carbonylation under these reaction conditions.[22]

The catalytic carbonylation was found to proceed under much milder conditions in comparison with those of stoichiometric reactions.[20] For example, at room temperature under atmospheric pressure of a mixture of carbon monoxide and oxygen, 2-(aminomethyl)aniline **6a** and 2-(hydroxymethyl)aniline **9** were converted to the corresponding cyclic urea **18a** and urethane **21** in good yields, respectively, although the reaction using a stoichiometric amount of selenium in the absence of oxygen at room temperature resulted in the recovery of the starting materials. Under the catalytic conditions at room temperature in the presence of oxygen, 2-(2-aminoethyl)aniline (**7**) gave acyclic urea **33** (95%) together with a trace amount of cyclic urea **19** (<1%). In the stoichiometric reaction **19** was the sole product.



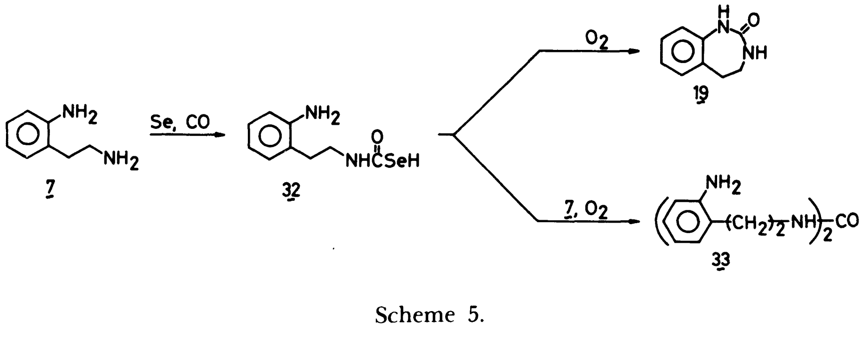
Scheme 4.

Selectivity between Intra- and Intermolecular Reactions of Selenium-Catalyzed Carbonylation of 2-(2-Aminoethyl)aniline (7). As mentioned above, intra- and intermolecular carbonylations competed in case of 2-(2-aminoethyl)aniline (**7**). Then we examined the effects of temperature, concentration, carbon monoxide and oxygen pressure, and amount of selenium used on the selectivity. The representative results were summarized in Table 2.

The cyclic urea **19** was preferentially formed under more dilute conditions (compare Entries 1, 6, and 7) and at higher temperatures (compare Entries 1, 2, and 3). The acyclic urea **33** was obtained selectively when the reaction was carried out at room temperature (Entries 3 and 4). Selective formation of cyclic urea **19** was attained only when a stoichiometric or excess amount of selenium was used (Entry 5).

These results are interpreted as follows. The aliphatic amino group of **7** is more nucleophilic than the aromatic amino group and reacts faster with selenium and carbon monoxide to form selenolcarbamate **32**. Therefore when a stoichiometric or excess amount of selenium is used, all of the aliphatic amino groups are converted rapidly to selenolcarbamate moieties which undergo intramolecular cyclization by the attack of the aromatic amino group.

On the other hand, in the catalytic reaction, there remains most of the starting material possessing the aliphatic amino group which can attack the carbamoyl carbon of **32** intermolecularly to form acyclic urea **33**. Thus, both intra- and intermolecular reactions take place competitively (Scheme 5).



Scheme 5.

Table 2. Selenium-Assisted Carbonylation with Carbon Monoxide

Entry	**7**	CO	O_2	Se	Temp	THF	Yield/%	
	mmol	kg cm^{-2}		mmol	°C	mL	**19**	**33**
1	2.5	29	2	0.125	100	10	61	29
2	2.5	29	2	0.125	65	10	49	45
3	2.5	29	2	0.125	15	10	<1	96
4	2.5	0.8	0.2	0.125	15	10	<1	95
5	2.5	29	2	2.5	100	10	85	<1
6	2.5	29	2	0.125	100	0.3	24	64
7	0.5	29	2	0.025	100	20	79	12

NMP (0.79 mL, 7.5 mmol)

Experimental

Apparatus. Melting points were determined on a Yanagimoto HP-S2 and were uncorrected. ^{1}H NMR spectra were recorded on a Hitachi R-24B or a JEOL JNM-PS-100 with Me_4Si as an internal standard. ^{13}C NMR spectra were obtained on a JEOL FX-60s with Me_4Si as an internal standard. Infrared spectra were obtained on a Shimadzu IR-400. Mass spectra were recorded on a Hitachi Model RMU-6E. Gas chromatography were carried out on a Shimadzu GC-8A using a 0.2 mm×25 m fused silica capillary column CBP1-M25-025. Elemental analyses were performed on a Yanagimoto CHN-Corder MT-2.

Materials. THF was freshly distilled from sodium–benzophenone prior to use. DMF and DMSO were distilled from CaH_2. Metallic selenium (99.9%) and carbon monoxide (99.9%) were purchased from Nakarai Chemicals, Ltd. and Seitetsu Chem., Co., respectively. *N*-Methylpyrrolidine (NMP) was distilled from CaH_2. 2-(Aminomethyl)aniline **6a**[23] and its derivatives **6b** and **6c**, and 2-(2-aminoethyl)aniline **7**[24] were prepared from nitriles following the procedures reported. All other starting materials were purchased from commercial sources and purified by distillation or recrystallization.

Carbonylation of *o*-Substituted Aromatic Diamines with Carbon Monoxide Using a Stoichiometric or Excess Amount of Selenium.

Formation of 2*H*-benzimidazol-2(3*H*)-one 17 as a Typical Experiment. *o*-Phenylenediamine (**5**) (270 mg, 2.5 mmol), selenium (592 mg, 7.5 mmol), NMP (0.79 mL, 7.5 mmol), and THF (10 mL) were placed in a 50 mL stainless-steel autoclave under a nitrogen atmosphere. Carbon monoxide (31 kg cm^{-2}) was introduced to the system, and the reaction vessel was heated to 100 °C with stirring. After 20 h, the apparatus was cooled to room temperature, and the remaining carbon monoxide was evacuated and the resulting mixture was stirred in the air for 1 h to oxidize resulting hydrogen selenide. The reaction mixture was extracted into THF (50 mL) by a Soxhlet extractor and the extract was evaporated in vacuo. The crude solid was recrystallized from THF–hexane to give 331 mg (99%) of **17**: Mp 299—300 °C (lit,[25] mp 300 °C); ^{1}H NMR (DMSO-d_6) δ=10.58 (br s, 2H), 7.02 (s, 4H); IR (KBr) 3025, 1715, 1020, 868, 714 cm^{-1}; MS *m/z* 134 (M$^+$). When a stoichiometric amount of selenium was used, **17** was obtained in 89% (295 mg) yield by a similar procedure.

Reactions under the same conditions and similar workup as described above gave cyclic ureas **18a—c**, **19**, and **21—23**.

3,4-Dihydro-2(1*H*)-quinazolinone (18a): 86%; mp 241—242 °C; ^{1}H NMR (DMDO-d_6) δ=9.08 (br s, 1H), 7.50—6.80 (m, 5H), 4.40 (s, 2H); IR (KBr) 3240, 1720, 1264, 740 cm^{-1}; MS *m/z* 148 (M$^+$). Found: C, 64.60; H, 5.20; N, 18.95. Calcd for $C_8H_8N_2O$: C, 64.85; H, 5.44; N, 18.92.

6-Methoxy-3,4-dihydro-2(1*H*)-quinazolinone (18b): 92%; mp 230—231 °C; ^{1}H NMR (DMSO-d_6) δ=8.81 (br s, 1H), 6.81 (s, 3H) 6.66 (br s, 1H), 4.32 (s, 2H), 3.71 (s, 3H); IR (KBr) 2970, 1660, 1031, 763 cm^{-1}; MS *m/z* 178 (M$^+$). Found: C, 60.28; H, 5.55; N, 15.60. Calcd for $C_9H_{10}N_2O_2$: C, 60.66; H, 5.66; N, 15.72.

6-Chloro-3,4-dihydro-2(1*H*)-quinazolinone (18c): 86%; mp 285—286 °C; ^{1}H NMR (DMSO-d_6) δ=9.38 (br s, 1H), 7.45—6.80 (m, 4H), 4.43 (s, 2H); IR (KBr) 3200, 1678, 1191, 802, 757 cm^{-1}; MS: *m/z* 182 (M$^+$). Found: C, 52.55; H, 3.77; N, 15.40. Calcd for $C_8H_7N_4ClO$: C, 52.62; H, 3.86; N, 15.34.

1,3,4,5-Tetrahydro-2*H*-1,3-benzodiazepin-2-one (19): 81%: mp 170.5—171 °C (lit,[26] mp 169—171 °C); ^{1}H NMR (DMSO-d_6) δ=8.90 (br s, 1H), 7.22—6.55 (m, 5H), 3.21 (m, 2H), 2.85 (m, 2H); IR (KBr) 3225, 1685, 1241, 750 cm^{-1}; MS *m/z* 162 (M$^+$).

2,4(1*H*,3*H*)-Quinazolinedione (20). A similar treatment of 2-carbamoylaniline (**8**) (340 mg, 2.5 mmol) with selenium (593 mg, 7.5 mmol), NMP (0.79 mL, 7.5 mmol) in DMF (10 mL) under a pressure of carbon monoxide (31 kg cm^{-2}), followed by a similar workup as described for the preparation of **17** afforded 85 mg (21%) of **20**: Mp >300 °C; ^{1}H NMR (DMSO-d_6) δ=11.50 (br s, 1H), 11.20 (br s, 1H), 8.07—6.59 (m, 4H); IR (KBr) 3200, 1704, 1141, 758, 683 cm^{-1}; MS *m/z* 162 (M$^+$). **20** showed the spectral data in complete accordance with those of the authentic sample (Aldrich).

1*H*-Naphth[1,2-*d*]imidazol-2(3*H*)-one (22): 98%; mp 347—347.5 °C; ^{1}H NMR (DMSO-d_6) δ=11.55 (br s, 1H), 10.75 (br s, 1H), 7.88—7.45 (m, 6H); IR (KBr) 3020, 1705, 787, 728 cm^{-1}; MS: *m/z* 184 (M$^+$). Found: C, 71.34; H, 4.41; N, 15.04. Calcd for $C_{11}H_8N_2O$: C, 71.73; H, 4.38; N, 15.21.

1*H*-Naphth[2,3-*d*]imidazol-2(3*H*)-one (23): 98%; mp >340 °C; ^{1}H NMR (DMSO-d_6) δ=10.65 (br s, 2H), 7.95—7.00 (m, 4H), 7.29 (s, 2H); IR (KBr) 3012, 1751, 825, 760, 700 cm^{-1}; MS *m/z* 184 (M$^+$). **23** showed the spectral data in complete accordance with the authentic sample.[27]

1*H*-Perimidin-2(3*H*)-one (24): 97%; mp >310 °C. ^{1}H NMR (DMSO-d_6) δ=10.11 (br s, 2H), 7.41—6.98 (m, 4H), 6.64—6.46 (m, 2H); IR (KBr) 3200, 1714, 813, 758 cm^{-1}; MS m/z 184 (M$^+$). **24** showed the spectral data in complete accordance with the authentic sample.[4b]

1*H*-Imidazo[4,5-*b*]pyridin-2(3*H*)-one (25). Treatment of 2,3-pyridinediamine (**13**) (546 mg, 5 mmol) with selenium (1.184 g, 15 mmol), in THF (10 mL) under pressure of carbon monoxide (31 kg cm^{-2}) at 100 °C for 20 h, followed by a similar workup as described for the preparation of **17** gave 660 mg (98%) of **21**: Mp 272—273 °C (lit,[28] mp 270—273 °C); ^{1}H NMR (DMSO-d_6) δ=10.99 (br s, 1H), 10.49 (br s, 1H), 6.74 (d, J=4.0 Hz, 1H), 7.56 (dd, J=4.0, 7.0 Hz, 1H), 7.06 (d, J=7.0 Hz, 1H); IR (KBr): 3000, 1685, 1459, 1107, 862, 714 cm^{-1}; MS: m/z 135(M$^+$).

1*H*-Imidazo[4,5-*c*]pyridin-2(3*H*)-one (26). Reaction of 3,4-pyridinediamine (**14**) (546 mg, 5 mmol) under the same conditions followed by a similar workup as described for the preparation of **25**, gave 648 mg (96%) of **26**: Mp 312—313 °C (lit,[29] mp 315 °C); ^{1}H NMR (DMSO-d_6) δ=11.57—10.09 (br, 2H), 8.33 (s, 1H), 8.32 (d, J=7.0 Hz, 1H), 7.20 (d, J=7.0 Hz, 1H); IR (KBr) 3000, 1710, 1227, 998, 905, 760, 697 cm^{-1}; MS m/z 135 (M$^+$).

Oxazolo[4,5-*b*]pyridin-2(3*H*)-one (27). 2-Amino-3-pyridinol (**15**) (550 mg, 5 mmol), selenium (1.184 g, 15 mmol), and DMSO (1 mL) was reacted under a pressure of carbon monoxide (31 kg cm^{-2}) at 100 °C for 20 h. The carbon monoxide and resulting dimethyl sulfide was evacuated through aqueous calcium hypochlorite solution. A similar workup as described for the preparation of **17** gave 517 mg (75%) of **27**: Mp 211—212 °C (lit,[29] 211—212 °C) ^{1}H NMR (DMSO-d_6) δ=10.31 (br s, 1H), 8.08 (d, J=5.0 Hz, 1H), 7.62 (d, J=7.0 Hz, 1H), 7.12 (dd, J=5.0, 7.0 Hz); IR (KBr) 3000, 2700, 1772, 1221, 791, 703 cm^{-1}; MS m/z 136 (M$^+$).

7*H*-Purin-8(9*H*)-one (28). Reaction of 4,5-pyrimidinediamine (**16**) (555 mg, 5 mmol) under the same conditions as described for the preparation of **27**, followed by a similar workup gave 682 mg (87%) of **28**: Mp >330 °C (lit,[30] 305—307 °C); ^{1}H NMR (DMSO) δ=11.76 (br s, 1H) 10.98 (br s, 1H), 8.54 (s, 1H), 8.04 (s, 1H); IR (KBr): 3050, 1730, 1459, 1107, 989, 714 cm^{-1}; MS m/z 136 (M$^+$). **28** showed the spectral data in complete accordance with the authentic sample.[30]

Carbonylation with Carbon Monoxide Using a Catalytic Amount of Selenium in the Presence of Oxygen. A typical experimental procedure is as follows. In a 50 mL stainless-steel autoclave, were placed *o*-phenylenediamine **5** (270 mg, 2.5 mmol), selenium (10 mg, 0.125 mmol), NMP (0.79 mL, 2.5 mmol), and THF (10 mL) under nitrogen atmosphere. The autoclave was charged with oxygen (2 kg cm^{-2}), and carbon monoxide (29 kg cm^{-2}) to the total pressure of 31 kg cm^{-2}. The reaction mixture was stirred at 100 °C for 20 h, and then cooled to room temperature. After evacuation of the remaining gas, the product was extracted into THF (50 mL) with a Soxhlet extractor. The solvent was evaporated in vacuo, and the residue was recrystallized from THF–hexane to give 328 mg (99%) of **17**.

The reactions of 2-carbamoylaniline (**8**), and 1,2-, 2,3-, 1,8-naphthalenediamine (**9**—**11**), were performed in a similar manner as exemplified by *o*-phenylenediamine (**5**).

Under similar conditions 1,2- and 3,4-pyridinediamine (**13**) and (**14**) (273 mg, 2.5 mmol) reacted with selenium (10 mg, 0.125 mmol), carbon monoxide (31 kg cm^{-2}), and oxygen (2 kg cm^{-2}) in the absence of NMP and gave **25** (98%, 327 mg) and **26** (96%, 324 mg), respectively. Similar reactions of 2-amino-3-pyridinol (**15**) (275 mg, 2.5 mmol), and 4,5-pyrimidinediamine (**16**) (278 mg, 2.5 mmol) in DMSO (1 mL) gave (**27**) (71%, 261 mg) and **28** (89%, 306 mg), respectively.

Catalytic Carbonylation under Atmospheric Pressure. A typical experimental procedure is as follows. In a three-necked 100 mL flask, were placed 2-(aminomethyl)aniline (**6a**) (305 mg, 2.5 mmol), selenium (10 mg, 0.125 mmol), NMP (0.79 mL, 7.5 mmol), and THF (10 mL) and carbon monoxide (4.5 mL min^{-1}) was bubbled into the reaction mixture at room temperature with stirring. All of metallic selenium reacted and a colorless homogeneous solution was obtained within 1 h. Oxygen (0.3 mL min^{-1}) was bubbled into the mixture, and after 3 h, the feed of carbon monoxide was stopped. The addition of oxygen was increased to 20 mL min^{-1}, and was continued for another 2 h. At this time, all of the selenium used was deposited. The product was extracted into THF (50 mL) with a Soxhlet extractor. The extract was evaporated in vacuo, and the residual solid was recrystallized from THF–hexane to give 315 mg (92%) of **18a**.

1,4-Dihydro-(2*H*)-3,1-benzoxazin-2-one (21). 2-(Hydroxymethyl)aniline(**9**) (307 mg. 2.5 mmol) was reacted under the same conditions as descrived above. A similar workup afforded 316 mg (85%) of **21**: Mp 118.5—119 °C (lit,[31] 118—120 °C); ^{1}H NMR (CDCl$_3$) δ=9.07 (br s, 1H), 7.67—6.43 (m, 4H), 5.40 (s, 2H); IR (KBr) 2980, 1701, 1446, 730 cm^{-1}; MS m/z 149 (M$^+$).

1,3-Bis[2-(2-aminophenyl)ethyl]urea (33). In a three-necked 50 mL flask, were placed 2-(2-aminoethyl)aniline (**7**) (340 mg, 2.5 mmol) selenium (10 mg, 0.125 mmol), NMP (0.79 mL, 7.5 mmol), and THF (5 mL). Carbon monoxide was bubbled (5 mL min^{-1}) into the reaction mixture at room temperature for 1 h. Oxygen was bubbled at a rate of 0.3 mL min^{-1} through the system for 3 h. The flow of carbon monoxide was then stopped, and the resulting mixture was stirred for another 1 h under oxygen. The selenium was filtered off and the solvent was evaporated in vacuo, and the residue was recrystallized from THF–pentane to afford 365 mg (95%) of **33**: Mp 103—104 °C; ^{1}H NMR (CDCl$_3$) δ=7.25—6.27 (m, 8H), 4.64 (br s, 2H), 3.39 (br s, 4H), 3.31 (t, J=7.6 Hz, 4H), 2.66 (t, J=7.6 Hz, 4H); ^{13}C NMR (DMSO-d_6) δ=162.74, 130.37, 127.57, 127.36, 123.38, 116.82, 115.31, 40.55, 40.12; IR (KBr) 3330, 2930, 1630, 1562, 1270, 1043, 752 cm^{-1}; MS m/z 298 (M$^+$). Found: C, 75.92; H, 7.53; N, 10.43. Calcd for $C_{17}H_{24}N_4O$: C, 76.09; H, 7.51; N, 10.44.

Catalytic Carbonylation with Carbon Monoxide Using a Catalytic Amount of Selenium in the Presence of Dimethyl Sulfoxide. In a 50 mL stainless-steel autoclave, were placed *o*-phenylenediamine (**5**) (270 mg, 2.5 mmol), selenium (10 mg, 0.125 mmol), DMSO (250 mg, 3.2 mmol), NMP (0.79 mL, 7.5 mmol), and THF (10 mL). The autoclave was charged with carbon monoxide (31 kg cm^{-2}) and the reaction was carried out at 100 °C for 20 h. The remaining carbon monoxide was purged, and the resulting mixture was analyzed by capillary gas chromatography, and the yield of dimethyl sulfide was found to be 85% (2.1 mmol) using octane as the internal standard. A similar workup gave **17** in 98% yield (328 mg).

In a similar manner, **8**, **10**, **12**, **15**, and **16** were converted to **20**, **22**, **24**, **27**, and **28**, respectively, in 23—98% yields.

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18) The intermediate, selenolcarbamic acid **1** may exist as the ammonium salt in the actual reaction mixture (Scheme 1). However, in the following Schemes 2—6, it will be shown in the free state for simplification.

19) In case of the carbonylation of 2-(aminomethyl)-aniline (**6a**), theoretical amount of carbon monoxide was absorbed at room temperature. Unfortunately, an attempt for the trapping of the corresponding selenolcarbamate with butyl iodide under nitrogen failed resulting in the formation of a mixture of cyclic urea **14a** and *N*-alkylated compounds of **14a**.

20) The fact that the intramolecular carbonylation of *o*-phenylendiamine (**5**) proceeded even at room temperature under catalytic conditions indicates that an alternative path may exist in the presence of oxygen. One of the possible paths is the intramolecular aminolysis of the corresponding diselenide which is formed in situ by the oxidation of the selenolcarbamate **31** with oxygen.[17c] An attempt for the isolation of the diselenide failed. In the absence of an oxidizing reagent (i.e., in the stoichiometric reaction), the cyclization via aminolysis of **31** may occur only at elevated temperatures to give **17** and hydrogen selenide (Scheme 4).

21) The use of dimethyl sulfoxide as an oxidizing agent rather than that of oxygen is recommended, because the limit of inflammablility of carbon monoxide in oxygen has large extent ranging from 15.5 to 93.9%. See, R. C. Wheast, "CRC Handbook of Chemistry and Physics," CRC Press, Inc. Boca Raton, Florida (1985), p. D-124.

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