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Selective Catalytic Oxidative Carbonylation of Amino Alcohols to Ureas

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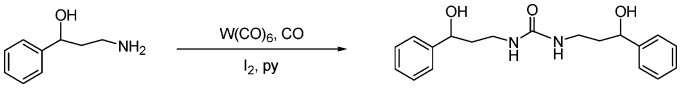


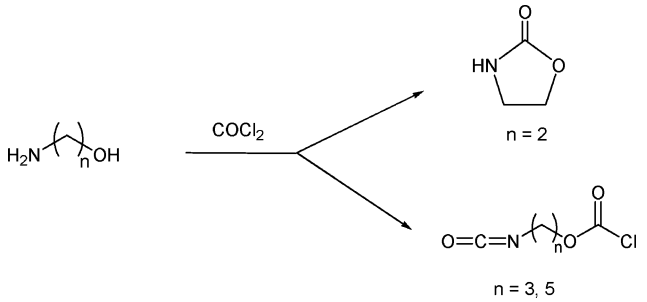
Amino alcohols undergo $W(CO)_6$-catalyzed oxidative carbonylation to the corresponding hydroxyalkylureas without protection of the hydroxyl group. Selected examples of 1,2-, 1,3-, 1,4-, and 1,5-amino alcohols were converted to the ureas in good to excellent yields, with only small amounts of the cyclic carbamates being formed. In contrast, the phosgene derivatives CDI and DMDTC undergo stoichiometric reactions with the amino alcohol substrates to afford ureas and cyclic carbamates with variable selectivity.

Introduction

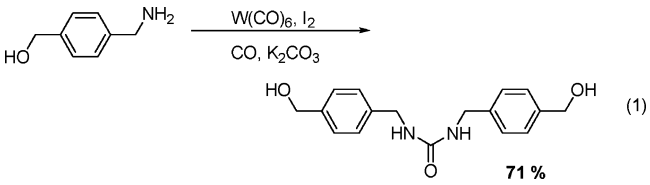
Conversion of amines to ureas commonly involves nucleophilic displacement of leaving groups from phosgene or a phosgene derivative.[1] Phosgene and its derivatives are not selective for the carbonylation of amines, reacting with other functionalities such as hydroxyl groups. In fact, phosgene reacts with both functional groups of amino alcohols to form products such as cyclic carbamates[2] or isocyanate chloroformates (Scheme 1).[3,4] Although transamination of ureas,[5] selenium-catalyzed carbonylation,[6] and condensation with *S*,*S*′-dimethyl dithiocarbonate (DMDTC)[7] have been used to generate hydroxyalkylureas from amino alcohols under circumstances where formation of the cyclic carbamate is disfavored, selective reactivity of amino alcohols with a phosgene derivative often requires protection of one functional group to avoid forming mixtures of ureas and carbamates.

As an alternative to phosgene and phosgene derivatives, we recently reported the catalytic carbonylation of aliphatic amines to ureas using $W(CO)_6$ as the catalyst and I_2 as the oxidant.[8−11]

SCHEME 1



A functional group compatibility study demonstrated that the catalyst was tolerant of −OH groups (eq 1), at least in the case



of [4-(aminomethyl)phenyl]methanol, in which the corresponding urea was produced without competing carbamate or carbonate formation.[8] However, in the carbonylation reaction of eq 1, the −OH group is para with respect to the amine so as to eliminate the possibility of intramolecular formation of a cyclic

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(2) Scholtissek, C. *Chem. Ber.* **1956**, *89*, 2562−2565.
(3) Hayashi, K.; Iwakura, Y. *Makromol. Chem.* **1966**, *94*, 132−139.
(4) Kurita, K.; Matsumura, T.; Iwakura, Y. *J. Org. Chem.* **1976**, *41*, 2070−2071.
(5) Kielbania, A. J.; Kukkala, P.; Lee, S.; Leighton, J. C. U.S. Patent 5,858,549, 1999.
(6) Sonoda, N.; Yamamoto, G.; Natsukawa, K.; Kondo, K.; Murai, S. *Tetrahedron Lett.* **1975**, 1969−1972.
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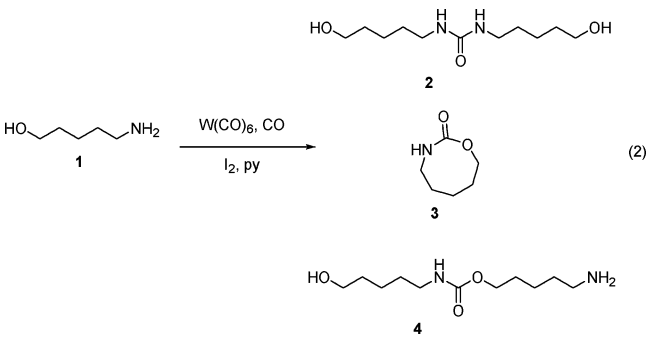
carbamate. We now report the catalytic carbonylation of a series of amino alcohols of varying tether lengths and substitution patterns to evaluate the selectivity of the $W(CO)_6/I_2$ carbonylation system for reactivity of alcohols vs amines. These results are compared to reaction of the same amino alcohol substrates with the phosgene derivatives DMDTC and 1,1′-carbonyldiimidazole (CDI).

Results and Discussion

The amino alcohol substrates for this study were chosen with varying tether lengths between the functional groups and varying steric hindrance at the active sites. The substrates were then subjected to $W(CO)_6$-catalyzed oxidative carbonylation for evaluation of the selectivity of the $W(CO)_6/I_2$ system toward formation of the ureas or carbamates, either cyclic or acyclic. As a comparison of the stoichiometric reactions of phosgene derivatives to the catalytic $W(CO)_6/I_2$ methodology, 1,1′-carbonyldiimidazole (CDI) and dimethyl dithiocarbonate (DMDTC) were also used for the carbonylation of the amino alcohol substrates.

Carbonylation of 5-Aminopentanol. Carbonylation of 5-aminopentanol (**1**) was investigated to determine the preference of a 1,5-amino alcohol to form the corresponding acyclic urea **2** or the eight-membered cyclic carbamate **3** (eq 2). The optimal



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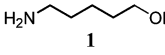
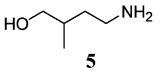
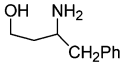
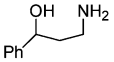
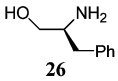
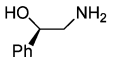
reaction conditions of a substrate concentration of 4 M, 40 °C, 80 atm CO and a reaction time of 18 h afforded the bis(hydroxyalkyl)urea **2** in 64% yield and the cyclic carbamate **3** in only 2% yield. The acyclic carbamate **4** was not detected in the reaction mixtures. However, the presence of unreacted starting material was observed by TLC prior to purification of the products.

When potassium carbonate was used as the base, as was reported in prior studies,[8,12] formation of urea **2** was confirmed by various spectroscopic methods. No evidence of the acyclic carbamate **4** was found. Purification of **2** by the previously described method proved difficult. The problem is similarity in the solubilities of the hydroxyalkylurea product and potassium iodide, which is a byproduct of carbonylation in the presence of K_2CO_3. Consequently, it was difficult to purify the urea by methods such as chromatography or selective extraction. These difficulties with the workup could be avoided by changing the base to pyridine, which allowed purification of the products to be carried out without chromatography. The modified workup for the recovery of the urea and carbamate is described in detail in the Experimental Section.

(12) McCusker, J. E.; Grasso, C. A.; Main, A. D.; McElwee-White, L. *Org. Lett.* **1999**, *1*, 961−964.

TABLE 1. Carbonylation of Amino Alcohols to Ureas and Carbamates

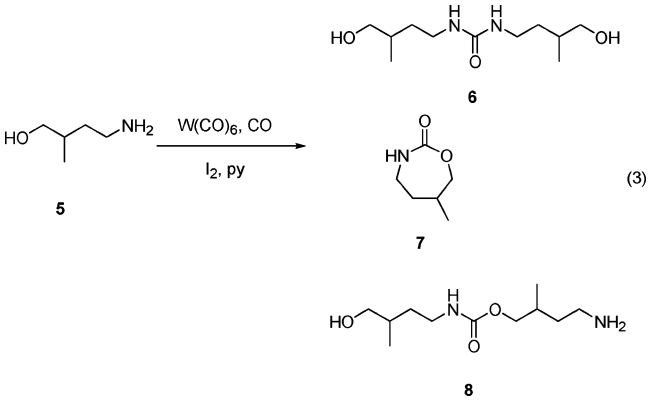
Entry	Substrate	Reagent	Urea (%)	Cyclic Carbamate (%)
1	 **1**	$W(CO)_6$/CO	64	2
		CDI	80	trace
		DMDTC	45	0
2	 **5**	$W(CO)_6$/CO	93	0
		CDI	70	trace
		DMDTC	93	0
3	 **10**	$W(CO)_6$/CO	95	trace
		CDI	36	60
		DMDTC	30	8
4	 **14**	$W(CO)_6$/CO	72	14
		CDI	49	30
		DMDTC	34	47
5	 **18**	$W(CO)_6$/CO	60	5
		CDI	55	28
		DMDTC	32	29
6	 **26**	$W(CO)_6$/CO	78	10
		CDI	18	22
		DMDTC	72	trace
7	 **29**	$W(CO)_6$/CO	79	14
		CDI	30	52
		DMDTC	73	trace

The selectivity of the $W(CO)_6$-catalyzed carbonylation of 5-aminopentanol is comparable to the selectivity when phosgene derivatives are used as the carbonylation agents. Carbonylation of amino alcohol **1** with CDI afforded urea **2** in 80% yield, while just trace amounts of the cyclic carbamate **3** and none of the acyclic carbamate **4** were observed. The other phosgene derivative, DMDTC, produced urea **2** from amino alcohol **1** in 45% yield with no evidence of the formation of **3** or **4** (Table 1, entry 1).

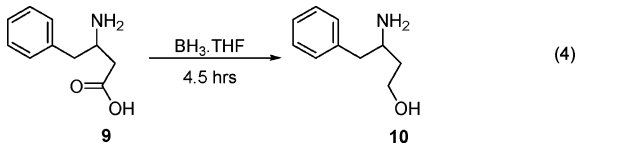
Carbonylation of 4-Amino-2-methylbutan-1-ol. The selectivity between conversion of a 1,4-amino alcohol to a seven-membered cyclic carbamate, an acyclic carbamate, or the corresponding urea was investigated with use of 4-amino-2-methylbutan-1-ol (**5**) as a representative substrate. The optimal reaction conditions were found to be the same as for 5-aminopentanol; with a substrate concentration of 4 M, 40 °C, and a reaction time of 18 h producing urea **6** in 93% yield. Compounds **7** and **8** were not detected in the reaction mixtures by NMR or IR.

To compare the carbonylation of **5** to results by using phosgene derivatives, 4-amino-2-methylbutanol was treated with CDI at a concentration of 4 M or DMDTC at a concentration of 4.5 M. All three carbonylation methods produced similar selectivity for the formation of urea **6** over products **7** and **8**. When CDI was used as the carbonylating agent, compound **6** was formed in 70% yield as the major component of the product mixture while **7** was detected in trace amounts (eq 3). There was no evidence for the formation of **8**. Likewise, in the case

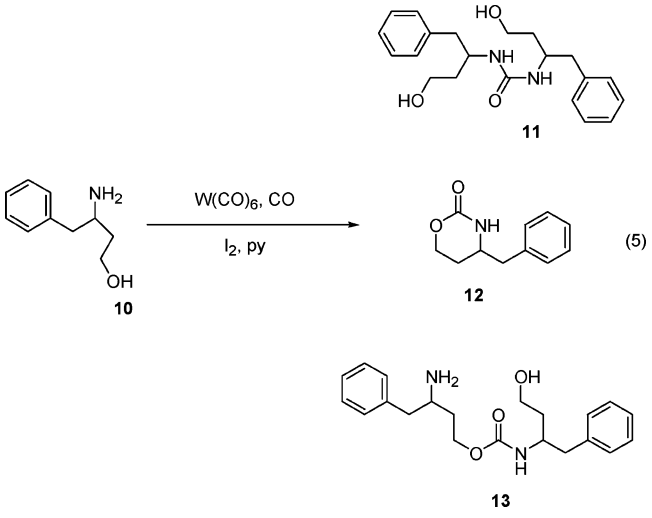
of DMDTC, urea **6** was produced in 93% yield as the only product (Table 1, entry 2).



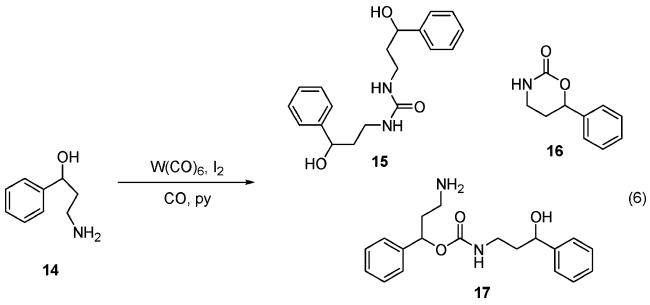
Carbonylation of 1,3-Amino Alcohols. The carbonylation of a 1,3-amino alcohol to a six-membered cyclic carbamate or an acyclic carbamate vs formation of the corresponding urea was first investigated with use of 3-amino-4-phenylbutanol (**10**)- as a representative substrate. Substrate **10** was synthesized by reduction of DL-β-homophenylalanine **(9)** with BH_3•THF at 0 °C (eq 4).[17]



Amino alcohol **10** was then subjected to oxidative carbonylation with use of the $W(CO)_6/I_2$ catalytic system under the previously determined optimal reaction conditions (eq 5, Table 1, entry 3). Urea **11** was isolated in 95% yield with carbamate **12** formed in trace amounts as a minor product. Acyclic carbamate **13** was not observed. To compare the carbonylation results to phosgene derivatives, **10** was treated with DMDTC and CDI, respectively. In contrast to the excellent yield of urea **11** from the $W(CO)_6$-catalyzed carbonylation, reaction of amine **10** with DMDTC afforded **11** and **12** in yields of 30% and 8%, respectively. Compound **13** was once again not detected. The reaction also produced a number of side products which were detected by TLC analysis. When CDI was used as the carbonylating agent, **11** and **12** were produced with **12** being the major product (60% yield) while **11** was formed in 36% yield. Once again, compound **13** was not observed (Table 1, entry 3).

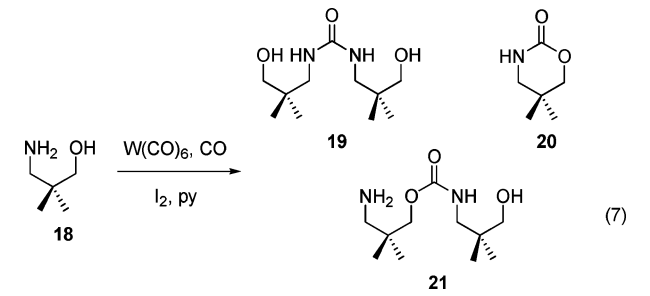


A second example of the preference for conversion of 1,3-amino alcohols to the urea vs the cyclic carbamate was obtained by carbonylation of 1-phenyl-3-aminopropanol (**14**). Amino alcohol **14** was synthesized by treating benzaldehyde with acetonitrile under basic conditions followed by reduction of the resulting cyanohydrin with borane dimethyl sulfide.[13] Carbonylation of **14** with use of the $W(CO)_6/I_2$ catalytic conditions provided the corresponding urea **15** in 72% yield, with the minor product being cyclic carbamate **16** in 14% yield after crystallization. The acyclic carbamate **17** was not formed in the reaction.



For comparison, 1-phenyl-3-aminopropanol was subjected to carbonylation with the phosgene derivatives CDI and DMDTC (Table 1, entry 4). When CDI was used as carbonylating agent, the urea **15** was formed in 49% yield, and the cyclic carbamate **16** in 30% yield. Once again, the acyclic carbamate was not observed in the product mixture. In contrast, when DMDTC was used as carbonylating agent, cyclic carbamate **16** was the major product (47% yield), while the urea was recovered in 34% yield.

Finally, 3-amino-2,2-dimethylpropanol (**18**) was studied under the optimal $W(CO)_6/I_2$ catalytic conditions (eq 7). Compound **18** was chosen to examine the effect of steric bulk at the position β to the nucleophilic nitrogen and the Thorpe−Ingold effect of the *gem*-dimethyl substituents at C3. Accordingly, the carbamate was expected to be favored by the presence of the *gem*-dimethyl



(13) Koenig, T. M.; Mitchell, D. *Tetrahedron Lett.* **1994**, *35*, 1339−1342.

(14) Hylton, K.-G.; Main, A. D.; McElwee-White, L. *J. Org. Chem.* **2003**, *68*, 1615−1617.

(15) Hylton, K.-G. Ph.D. Dissertation, Department of Chemistry, University of Florida, 2004.

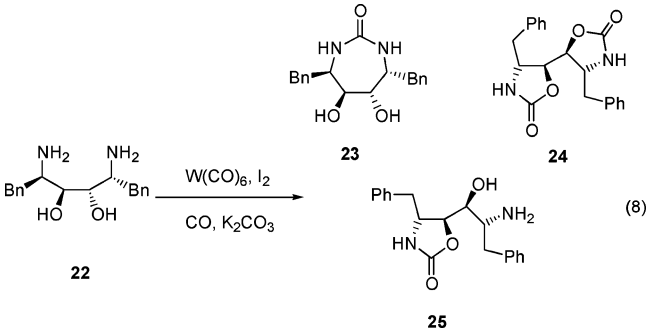
(16) Pierce, M. E.; Harris, G. D.; Islam, Q.; Radesca, L. A.; Storace, L.; Waltermire, R. E.; Wat, E.; Jadhav, P. K.; Emmett, G. C. *J. Org. Chem.* **1996**, *61*, 444−450.

(17) Ueno, K.; Ogawa, A.; Ohta, Y.; Nomoto, Y.; Takasaki, K.; Kusaka, H.; Yano, H.; Suzuki, C.; Nakanishi, S. WO Patent 2001047931, 2001.

substituents. However, when carried out under the $W(CO)_6/I_2$ carbonylation conditions, the reaction did not go to completion and 12% of the starting material was recovered. This may be due in part to steric bulk in the substrate. Nevertheless, urea **19** and carbamate **20** were obtained in 60% and 5% yield, respectively (Table 1, entry 5). There was no evidence for the formation of the acyclic carbamate **21**.

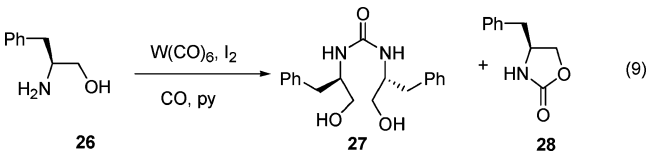
In contrast, when 3-amino-2,2-dimethylpropanol (**18**) was treated with CDI or DMDTC, much higher proportions of carbamate were generated than with the $W(CO)_6$-catalyzed carbonylation (Table 1, entry 5). Urea **19** was still the major product for both carbonylation reactions, being isolated in 55% yield and 32% yield, respectively. However, cyclic carbamate **20** was recovered in 28% yield from the reaction with CDI and in 29% yield when DMDTC was used in the carbonylation. Overall, there is a strong selectivity favoring formation of urea over carbamate in the $W(CO)_6$-catalyzed carbonylation for all three 1,3-amino alcohols that were investigated. In comparison, the selectivity for formation of the urea over formation of the carbamate is significantly lower when CDI or DMDTC is used as the carbonylating agent.

Carbonylation of 1,2-Amino Alcohols. Our interest in the carbonylation of 1,2-amino alcohols began with our preparation of the core structure of the HIV protease inhibitors DMP 323 and DMP 450 by $W(CO)_6$-catalyzed carbonylation of *O*-protected derivatives of diamine diol **22**.[14] As part of these investigations, it was determined that under the initially reported conditions, oxidative carbonylation of **22** afforded oxazolidinones **24** and **25** instead of the diol urea **23** (eq 8).[15] A similar preference had previously been reported for the reactions of **22** with CDI and phosgene.[16]



(8)

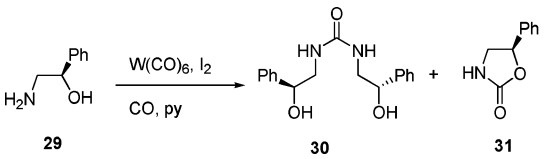
These prior results provided motivation for additional study of 1,2-amino alcohols. The initial substrate was β-amino alcohol **26** (eq 9), chosen for its structural similarity to half of **22**. To further investigate formation of the oxazolidinone ring vs coupling to the urea, oxidative carbonylation of β-amino alcohol **26** was carried out with use of the $W(CO)_6/I_2$ catalytic system (eq 9). The conditions were the same as described for the



(9)

previous amino alcohol substrates. Upon carbonylation of **26**, urea **27** and cyclic carbamate **28** were obtained in 78% and 10% yield, respectively, with urea formation once again strongly preferred (Table 1, entry 6). Although the phosgene derivative DMDTC afforded similar results, carbonylation of **26** with CDI produced only low yields of a roughly equal mixture of urea **27** and carbamate **28**.

To further investigate the carbonylation of 1,2-amino alcohol substrates, catalytic carbonylation of (*R*)-(−)-2-amino-1-phenylethanol (**29**) was also subjected to the $W(CO)_6$-catalyzed carbonylation (eq 10). Urea **30** and cyclic carbamate **31** were obtained in 79% and 14% yield, respectively. As observed for 1,2-amino alcohol **26**, there was a high selectivity for conversion of **29** to the urea in preference to the oxazolidinone.



(10)

The phosgene derivatives CDI and DMDTC were also used in the carbonylation of **29** for comparison. In the former reaction, the cyclic carbamate **31** was the major product (52% yield) while the urea **30** was recovered in 30% yield from the mixture. On the other hand, when DMDTC was used as the carbonylating agent, urea **30** was the major product of the reaction (73% yield) while oxazolidinone **31** was isolated in just trace amounts (Table 1, entry 7). Note that for 1,2-amino alcohols **26** and **29**, both the $W(CO)_6$-catalyzed carbonylation and DMDTC afforded the hydroxyalkyl ureas as the major products but carbonylation with CDI favored the cyclic carbamate.

Conclusions

In summary, the $W(CO)_6/I_2$ methodology can be applied to carbonylation of amino alcohols to the ureas without protection of the hydroxyl group. The $W(CO)_6$-catalyzed oxidative carbonylation is consistently selective for the urea over the cyclic carbamate in all cases studied. Acyclic carbamates are not detected in the reaction mixtures. In contrast, reactions of the phosgene derivatives CDI and DMDTC with 1,3- and 1,2-amino alcohol substrates exhibit variable selectivities between ureas and cyclic carbamates.

Experimental Section

General. All experimental procedures described were carried out under nitrogen and in oven-dried glassware unless stated otherwise. Solvents used for carbonylation reactions were passed through a solvent purification system[18] prior to use. Most of the amino alcohol substrates were commercially available and were used without further purification. The amino alcohols 3-amino-4-phenylbutanol[17] and 3-amino-1-phenylpropanol[13] were prepared as described in the literature.

Procedure A for Carbonylation of Amino Alcohols with CDI. The amino alcohol (2 equiv) was dissolved in dry THF and placed into the flask under a flow of N_2. One equivalent of CDI was then added. The reaction was left to stir for 18 h, then the solvent was evaporated under a flow of N_2. The residue was dissolved in a 1:1 mixture of CH_2Cl_2:H_2O. The mixture was placed in a separatory funnel. After the layers were separated, the aqueous layer was washed with CH_2Cl_2, then with a 2:1 solution of chloroform/ethanol. The combined organic layers were dried and filtered, then the solvent was removed. The crude product was purified by flash chromatography on silica gel with 5% MeOH/CH_2Cl_2 as eluent for the carbamate and 30% MeOH/CH_2Cl_2 for the urea.

(18) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.

Procedure B for Carbonylation of Amino Alcohols with DMDTC. The amino alcohol (2 equiv) was dissolved in dry methanol and placed into the flask under a flow of N_2. DMDTC (1 equiv) was then added and the reaction was left to stir for 18 h under N_2. The solvent was then evaporated under N_2 and the product was immediately chromatographed on silica gel with use of a mixture of 5% to 30% MeOH/CH_2Cl_2 as eluent to recover the carbamate and urea, depending on the substrate.

Procedure C for Catalytic Carbonylation of Amino Alcohols with $W(CO)_6/I_2$: 1,3-Bis(5-hydroxypentyl)urea (2). To a 15 mL glass vial in a multicompartment Parr high-pressure vessel containing 1.9 mL of CH_2Cl_2 were added **1** (800 mg, 7.7 mmol), $W(CO)_6$ (136 mg, 0.38 mmol), pyridine (0.93 mL, 12 mmol), and I_2 (977 mg, 3.8 mmol). The vessel was then charged with 80 atm of CO and heated at 40 °C for 18 h. The pressure was released and methylene chloride (5 mL) was added to the reaction mixture to further dissolve the crude product. The solution was washed successively with saturated sodium sulfite, then saturated sodium bicarbonate. Each of the collected aqueous layers was washed with 2:1 $CHCl_3$/EtOH (4 × 30 mL). The combined $CHCl_3$/EtOH layers were dried with $MgSO_4$ and the solvents removed by evaporation to afford urea **2** as a white solid in 64% yield. To recover the carbamate, the methylene chloride layer from the original extractions was washed with 0.1 M aqueous HCl, then dried with $MgSO_4$. The solvent was removed under vacuum to afford carbamate **3** in 2% yield. The urea was identified by comparison with literature data (elemental analysis and melting point).[19] Urea **2**: ^{1}H NMR (D_2O) δ 1.22 (m, 4H), 1.37 (m, 4H), 1.52 (m, 4H), 2.88 (m, 4H), 3.42 (m, 4H). MS (LSIMS) $[M + H]^+$calcd for $C_{11}H_{24}N_2O_3$ 232.18, found 232.18. IR ($CHCl_3$) υ_{CO} 1654 cm^{-1}. Anal. Calcd for $C_{11}H_{24}N_2O_3$: C 56.87, H 10.41, N 12.06. Found: C 56.96, H 10.80, N 11.89. Mp reported 106.6−108.5 °C (found 106.3−108.5 °C). Carbamate **3**: ^{1}H NMR ($CDCl_3$) δ 1.49 (m, 2H), 1.50 (m, 2H), 1.52 (m, 2H), 3.30 (m, 2H), 3.65 (t, 2H), 5.9 (br, 1H); ^{13}C NMR ($CDCl_3$) δ 22.9, 29.3, 32.1, 41.2, 62.6, 147.2; IR (CH_2Cl_2) υ_{CO} 1708 cm^{-1}; MS (LSIMS) $[M + H]^+$calcd for $C_6H_{11}NO_2$ 130.08, found 130.08.

1,3-Bis(4-hydroxy-3-methylbutyl)urea (6). Procedure C afforded **6** from **5** (0.20 mL, 1.8 mmol) in 93% yield. ^{1}H NMR ($CDCl_3$) δ 0.86 (d, 6H, J = 6.6 Hz), 1.22 (m, 2H), 1.59 (m, 4H), 3.07 (m, 4H), 3.38 (m, 4H), 6.08 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 16.4, 33.0, 33.4, 38.4, 67.4, 161.0; IR ($CHCl_3$) υ_{CO} 1648 cm^{-1}; MS (LSIMS) $[M + H]^+$ $C_{11}H_{24}N_2O_3$ calcd 233.1865, found 233.1913.

3-Amino-4-phenyl-1-butanol (10). DL-β-homophenylalanine (1000 mg, 5.57 mmol) was added to 2.2 mL of THF and the mixture was cooled to 0 °C. BH_3·THF (1 M, 8.36 mL, 8.36 mmol) was added dropwise to the suspension. The resulting mixture was stirred at room temperature for 4.5 h. The mixture was then cooled to 0 °C, 4 mL of 3 N sodium hydroxide was slowly added, and the mixture was stirred at room temperature overnight. The pH of the solution was adjusted to 11 by adding a few pellets of sodium hydroxide. The aqueous phase was saturated with potassium carbonate, the THF phase was separated, and the aqueous phase was extracted with (6 × 50 mL) diethyl ether. The combined organic layers were dried over magnesium sulfate. The solvents were evaporated and the product was obtained in 82% yield. The product was identified by comparison with literature data.[17]

***N,N′*-Bis(1-benzyl-3-hydroxypropyl)urea (11) and 4-Benzyl-1,3-oxazinan-2-one (12).** Procedure C afforded urea **11** from **10** (760 mg, 4.6 mmol) as a pale yellow oil in 95% yield. Carbamate **12** was recovered in trace amount. The products were identified by comparison with authentic samples prepared as described below.

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Authentic Samples of *N,N′*-Bis(1-benzyl-3-hydroxypropyl)urea (11) and 4-Benzyl-1,3-oxazinan-2-one (12). Procedure B afforded compounds **11** and **12** from **10** (600 mg, 2.97 mmol) as white solids in 30% and 8% yield, respectively. For urea **11**: ^{1}H NMR ($CDCl_3$) δ 1.22 (m, 2H), 1.77 (m, 2H), 2.70 (m, 4H), 3.42 (m, 4H), 4.10 (s, 2H), 4.82 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 38.4, 42.0, 48.0, 58.6, 126.6, 128.6, 129.2, 138.2, 159.9; IR (CH_2Cl_2) υ_{CO} 1600 cm^{-1}; MS (LSIMS) $[M + H]^+$ calcd for $C_{21}H_{28}N_2O_3$ 257.2178, found 257.2161. For carbamate **12**: ^{1}H NMR ($CDCl_3$) δ 1.68 (m, 1H), 1.87 (m, 1H), 2.78 (m, 1H), 2.89 (m, 1H), 3.67 (m, 1H), 4.14 (m, 1H), 4.27 (m, 1H), 6.81 (s, 1H), 7.24 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 26.5, 42.3, 51.8, 65.4, 126.8, 128.6, 129.1, 136.2, 154.5; IR (CH_2Cl_2) υ_{CO} 1710 cm^{-1}; MS (LSIMS) $[M + H]^+$ calcd for $C_{11}H_{13}NO_2$ 192.1024, found 192.1020.

1,3-Bis(3-hydroxy-3-phenylpropyl)urea (15) and 6-Phenyl-1,3-oxazinan-2-one (16). Procedure C afforded urea **15** from **14** (320 mg, 2.12 mmol) in 72% yield. ^{1}H NMR ($CDCl_3$) δ 1.87 (m, 4H), 3.30 (m, 2H), 3.6 (m, 2H), 4.72 (t, 2H), 6.19 (s, 2H), 7.32 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 38.4, 38.7, 72.3, 125.8, 127.5, 128.4, 143.8, 160.1; IR ($CHCl_3$) υ_{CO} 1646 cm^{-1}. Cyclic carbamate **16** was recovered in 14% yield; it was identified by comparison with literature data.[20]

***N,N′*-Bis(3-hydroxy-2,2-dimethylpropyl)urea (19) and 5,5-Dimethyl-1,3-oxazinan-2-one (20).** Procedure C afforded urea **19** from **18** (600 mg, 5.81 mmol) as a white solid in 60% yield. ^{1}H NMR ($CDCl_3$) δ 0.73 (s, 12H), 2.85 (d, 4H, 6.3 Hz), 3.03 (d, 4H, 6 Hz), 4.61 (t, 2H, 6 Hz), 6.02 (t, 2H, 6.3 Hz); ^{13}C NMR ($CDCl_3$) δ 22.3, 36.6, 46.2, 67.6, 159.7; IR ($CHCl_3$) υ_{CO} 1666 cm^{-1}; MS (LSIMS) $[M + H]^+$calcd for $C_{11}H_{24}N_2O_3$ 233.1751, found 233.1750. Anal. Calcd for $C_{11}H_{24}N_2O_3$: C 56.89, H 10.41, N 12.06. Found: C 57.69, H 10.63, N 12.01. Carbamate **20**: yield 5%; ^{1}H NMR ($CDCl_3$) δ 0.96 (s, 6H), 2.88 (s, 2H), 3.80 (s, 2H), 7.12 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 22.1, 27.3, 50.6, 75.1, 152.4; IR ($CHCl_3$) υ_{CO} 1702 cm^{-1}; MS (LSIMS) $[M + H]^+$calcd for $C_6H_{11}NO_2$ 130.0868, found 130.0867.

1,3-Bis(1-benzyl-2-hydroxyethyl)urea (27) and 6-Phenyl-6-oxazolidin-2-one (28). Procedure C afforded urea **27** from **26** (800 mg, 5.3 mmol) in 78% yield. Carbamate **28** was recovered in 10% yield. The products were identified by comparison with literature data.[21]

1,3-Bis(3-hydroxy-2-phenylethyl)urea (30) and 5-Phenyloxazolidine-2-one (31). Procedure C afforded urea **30** from **29** (800 mg, 5.83 mmol) in 79% yield. ^{1}H NMR ($CDCl_3$) δ 2.85 (m, 2H), 3.08 (m, 2H), 4.78 (t, 2H), 5.64 (br, 2H), 7.38 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 49.2, 74.2, 125.8, 127.5, 128.4, 147.2, 159.5; IR ($CHCl_3$) υ_{CO} 1649 cm^{-1}. Cyclic carbamate **31** was isolated in 14% yield; it was identified by comparison with literature data.[22]

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Supporting Information Available: ^{1}H NMR spectra for compounds **3**, **6**, **11**, **12**, **15**, **20**, **30**, and **31**. This material is available free of charge via the Internet at http://pubs.acs.org.

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