

# Catalytic oxidative carbonylation of aliphatic secondary amines to tetrasubstituted ureas

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## Abstract

Secondary amines can be catalytically carbonylated to symmetrical tetrasubstituted ureas using  $W(CO)_6$  as the catalyst,  $I_2$  as the oxidant, and CO as the carbonyl source. Preparation of the corresponding tetrasubstituted ureas from the aliphatic secondary amines  $HNR_2$  ( $R = C_2H_5$ , *n*-Bu, *i*-Pr,  $PhCH_2$ ) and  $HNRR'$  ( $R, R' = -(CH_2)_4-$ ;  $-(CH_2)_5-$ ;  $PhCH_2$ ,  $CH_3$ ) was achieved in moderate yields. Aromatic secondary amines are unreactive. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Oxidative carbonylation; Tetrasubstituted urea; Amine; Tungsten; Metal carbonyl

## 1. Introduction

Substituted ureas have found widespread use as agricultural chemicals, pharmaceuticals, resin precursors, dyes, and additives to petroleum compounds and polymers [1]. Among the numerous methods for synthesis of *N,N*-disubstituted ureas are the reactions of primary amines with isocyanates, phosgene, or phosgene derivatives [2]. While reports describing the synthesis of disubstituted ureas are prevalent, methods for the synthesis of tetrasubstituted ureas are less common, due to the difficulty of converting secondary amines directly to tetrasubstituted ureas [3]. The best known method involves the reaction of a carbamoyl chloride with a secondary amine [4]. However, both experimental

[3] and safety [2] problems with this method have been noted. Tetrasubstituted ureas can also be obtained in good yields from the reaction of lithium amides with carbon monoxide, followed by oxidation [5]. In addition, tetrasubstituted ureas have more recently been produced from reaction of phosgene derivatives, such as 1,1-carbonylbisbenzotriazole [3] and *N,N'*-carbonyldiimidazole, [6] with secondary amines.

Since phosgene is highly toxic and corrosive, and phosgene derivatives can be expensive to use on a large scale, there is continuing interest in the development of alternative systems for the synthesis of substituted ureas. This interest has led to exploration of the metal-catalyzed carbonylation of amines [7–9]. Transition metal complexes of Ni [10], Co [11], Mn [12,13], Ru [14], and most commonly, Pd [15–17], have been demonstrated to catalyze oxidative carbonylation of primary amines to disubstituted ureas. However, these metal-catalyzed reactions generally require high temperatures and pres-

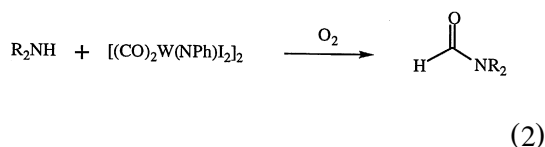
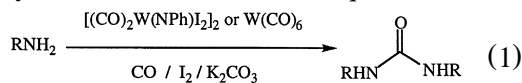
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tures. In addition, yields for aliphatic amines are usually lower than those for aromatic cases. Main group elements such as sulfur [18,19] and selenium [20–22] can also serve as catalysts.

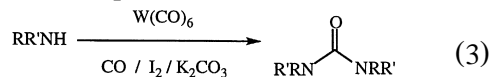
While transition metal-catalyzed carbonylation of aliphatic and aromatic primary amines to 1,3-disubstituted ureas is well known, the direct carbonylation of secondary amines to tetrasubstituted ureas is less well explored. More commonly, transition metal-catalyzed carbonylation of secondary amines selectively produces formamides [23–26]. However, there is one example of direct conversion of secondary amines and CO to tetrasubstituted ureas, which involves Pd(OAc)<sub>2</sub> as the catalyst and I<sub>2</sub> as an oxidant [15]. Using this system, Alper converted several secondary amines to the corresponding tetrasubstituted ureas in yields that range from 67% for 1,3-dibenzyl-1,3-dimethylurea to 2% for 1,1,3,3-tetrabutylurea. Among the main group elements, selenium also serves as a catalyst [27] or stoichiometric promoter [28] for the conversion of secondary amines to tetrasubstituted ureas.

Although many transition metal carbonylation systems have been examined, carbonylation of amines involving Group 6 metals [29] has remained rare. We recently reported the catalytic oxidative carbonylation of primary amines to ureas using either [(CO)<sub>2</sub>W(NPh)I<sub>2</sub>]<sub>2</sub> or W(CO)<sub>6</sub> as the catalyst and I<sub>2</sub> as the oxidizing agent (Eq. 1) [30,32]. In addition, [(CO)<sub>2</sub>W(NPh)I<sub>2</sub>]<sub>2</sub> was determined to be a stoichiometric reagent for the carbonylation of secondary amines to formamides (Eq. 2) [33].



Although [(CO)<sub>2</sub>W(NPh)I<sub>2</sub>]<sub>2</sub> and W(CO)<sub>6</sub>/I<sub>2</sub> both exhibit similar behavior with primary amines, the W(CO)<sub>6</sub>/I<sub>2</sub> carbonylation condi-

tions do not convert secondary amines to the expected formamides as does [(CO)<sub>2</sub>W(NPh)I<sub>2</sub>]<sub>2</sub>. We now report the catalytic oxidative carbonylation of cyclic and acyclic aliphatic secondary amines to *N,N,N',N'*-tetrasubstituted ureas in moderate yields using W(CO)<sub>6</sub> as the catalyst, I<sub>2</sub> as the oxidant and CO as the carbonyl source (Eq. 3).



## 2. Experimental

### 2.1. Materials and general methods

Tetrahydrofuran was distilled from sodium/benzophenone. Methylene chloride was distilled over calcium hydride. Acetonitrile was distilled from calcium hydride. Toluene was distilled over sodium. All other chemicals were purchased in reagent grade and used with no further purification unless stated otherwise. The tetrasubstituted urea products were identified by comparison to authentic samples purchased from Aldrich or by comparison of their spectral data to literature values.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Gemini 300 and VXR 300 spectrometers. IR spectra were recorded on a Perkin-Elmer 1600 FTIR. Gas chromatography for comparison of urea products to authentic samples was performed on an HP5890 chromatograph containing a 30 m × 0.75 mm column of SPB-20 on fused silica. High-resolution mass spectrometry was performed by the University of Florida analytical service.

### 2.2. General procedure for the catalytic carbonylation of secondary amines

The following procedure is typical: To a stirred solution of W(CO)<sub>6</sub> (100 mg, 0.28 mmol) in 40 ml of CH<sub>2</sub>Cl<sub>2</sub> in the glass liner of a Parr high-pressure vessel was added 50 eq of piperi-

dine (1.4 ml, 14 mmol),  $K_2CO_3$  (1.95 g, 14.2 mmol) and 25 eq of iodine (1.8 g, 7.1 mmol). The vessel was then charged with 80 atm of CO, and left to stir under pressure for 18 h. The pressure was released and the maroon solution was filtered and then rinsed with a  $Na_2SO_3$  solution and 1 M HCl. The resulting pale red solution was then dried with  $MgSO_4$  and filtered. The solution was concentrated to yield a red oil. The resulting red oil was dissolved in ethyl acetate and chromatographed on silica with ethyl acetate as eluent to obtain a white solid (0.47 g, 36% yield). The solid was identified as dipiperidylurea by comparison with an authentic sample purchased from Aldrich.

### 3. Results and discussion

Based on the similarity of the oxidation carbonylation chemistry of primary amines with  $[(CO)_2W(NPh)I_2]_2$  and with  $W(CO)_6/I_2$ , reaction of secondary amines with CO in the presence of  $W(CO)_6/I_2$  was expected to produce formamides. However, when  $W(CO)_6$ , 50 eq of piperidine, 25 eq of  $I_2$ , and 50 eq  $K_2CO_3$  are placed in a 125-ml Parr high-pressure vessel and pressurized with 80 atm CO, dipiperidylurea is produced in 36% yield based on amine. The expected piperidine formamide was found in the reaction mixture in trace quantities as a side product. The yield of dipiperidylurea from piperidine under these conditions was moderate. However, prior optimization of the oxidative carbonylation of primary amines to disubstituted ureas had resulted in yields that ranged up to 91% [31]. Based on the prior optimization of the primary amine cases, optimization studies were carried out using piperidine as a test case for secondary amines. Piperidine was chosen in part for comparison purposes because several literature carbonylation studies have utilized piperidine [15,23,26,27]. In addition, piperidine is a highly challenging substrate because its high basicity renders deprotonation of the byproduct amine salt problematic (vide infra).

Table 1  
Oxidative carbonylation of piperidine with Group 6 metal carbonyls

Catalyst	Yield <sup>a,b</sup> (%)
$W(CO)_6$	36
$Mo(CO)_6$	19
$Cr(CO)_6$	16

<sup>a</sup> Isolated yield of dipiperidylurea calculated per equivalent of piperidine.

<sup>b</sup> Reaction conditions: piperidine (14.2 mmol),  $W(CO)_6$  (0.28 mmol),  $I_2$  (7.1 mmol),  $K_2CO_3$  (14.2 mmol), solvent (40 ml), room temperature, pressure 80 atm, 18 h.

Initial experiments involved comparison of  $W(CO)_6$  to other Group 6 metal carbonyl compounds (Table 1). Although first and second row transition metals are generally more reactive than their third row congeners,  $Mo(CO)_6$  and  $Cr(CO)_6$  produced the tetrasubstituted urea in lower yields than those obtained with  $W(CO)_6$ . As seen in Table 1, when  $Mo(CO)_6$  is used as the catalyst, dipiperidylurea was produced in a 19% yield, while with  $Cr(CO)_6$ , the urea yield was decreased further to 16%. Further optimization experiments were carried out only with  $W(CO)_6$ .

The results of variation of CO pressure are presented in Table 2. Although yields of disubstituted ureas from primary amines are dependent on the CO pressure [31], yields of dipiperidylurea vary little with CO pressure. At 40 atm, the yield of dipiperidylurea was 24%. As the total pressure varies from 40 to 90 atm, the yields only vary from 24% to 36%, with the maximum value obtained at 60 atm.

Oxidative carbonylation of piperidine is also surprisingly unresponsive to changes in solvent, as seen in Table 3. Trial solvents were limited to those that had worked well in the carbonylation of primary amines. Of the solvents examined, yields were highest in THF, but not significantly better than in toluene or  $CH_2Cl_2$ . The addition of water to the reaction does not affect the yield, as indicated when the reaction is run with a mixed solvent system of 35:5 ml  $CH_2Cl_2$ /water. While acetonitrile is the solvent of choice in the  $Pd(OAc)_2$ -catalyzed system [15],

Table 2  
Effects of CO pressure on the oxidative carbonylation of piperidine

Pressure (atm)	Yield <sup>a,b</sup> (%)
40	24
60	36
80	31
90	32

<sup>a</sup> Isolated yield of dipiperidylurea calculated per equivalent of piperidine.

<sup>b</sup> Reaction conditions: amine (14.2 mmol), W(CO)<sub>6</sub> (0.28 mmol), I<sub>2</sub> (7.1 mmol), K<sub>2</sub>CO<sub>3</sub> (21.3 mmol), CH<sub>2</sub>Cl<sub>2</sub> (40 ml), room temperature, 24 h.

with W(CO)<sub>6</sub>, the yield is decreased to 8%, most likely due to the high affinity of acetonitrile for coordination to tungsten compounds.

The stoichiometry of oxidative carbonylation of amines to ureas dictates that two equiv of the amine hydroiodide [R<sub>2</sub>NH<sub>2</sub>]<sup>+</sup>I<sup>-</sup> will be produced per equiv of urea (Eq. 4). Observation of piperidine hydroiodide in the reaction mixtures is consistent with this proton transfer. In the absence of added base, consumption of the amine substrate as a proton scavenger will thus limit the yields of urea. If the reaction is run in the presence of a sacrificial base, release of the free amine from the salt should increase the product yield.

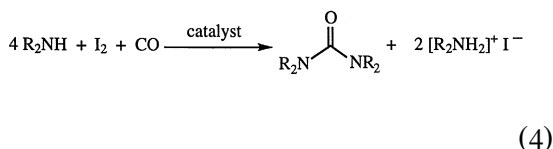


Table 3  
Solvent effects on the oxidative carbonylation of piperidine

Solvent	Yield <sup>a,b</sup> (%)
THF	37
Toluene	31
CH <sub>2</sub> Cl <sub>2</sub>	29
CH <sub>2</sub> Cl <sub>2</sub> / water <sup>c</sup>	29
CH <sub>3</sub> CN	6

<sup>a</sup> Isolated yield of dipiperidylurea calculated per equivalent of piperidine.

<sup>b</sup> Reaction conditions: amine (14.2 mmol), W(CO)<sub>6</sub> (0.28 mmol), I<sub>2</sub> (7.1 mmol), K<sub>2</sub>CO<sub>3</sub> (21.3 mmol), solvent (40 ml), room temperature, pressure 80 atm, 15 h.

<sup>c</sup> CH<sub>2</sub>Cl<sub>2</sub> (40 ml), water (5 ml).

The effects of different bases on the carbonylation of piperidine are presented in Table 4. When the reaction is run in the absence of a base the yield of urea is 33%, corresponding to nine turnovers of the catalyst. However, the addition of 50, 75, or 100 eq of K<sub>2</sub>CO<sub>3</sub> to the I<sub>2</sub>-oxidized reaction had virtually no effect on the yields. The similar yields of urea when the reaction is conducted in the absence or presence of base indicated that the K<sub>2</sub>CO<sub>3</sub> was not deprotonating the amine salt, as does the detection of piperidine hydroiodide in the reaction mixtures. The possibility that the deprotonation was not occurring due to the insolubility of K<sub>2</sub>CO<sub>3</sub> in methylene chloride was eliminated when the reaction was run in a 35:5 ml mixture of methylene chloride/water and the yield remained the same (29%).

Since accurate pK<sub>a</sub>s in organic solvents are difficult to obtain, an empirical study of several other bases was carried out. When Na<sub>3</sub>PO<sub>4</sub> was used as the base with CH<sub>2</sub>Cl<sub>2</sub> as solvent, the dipiperidylurea was produced in a 36% yield, while in the CH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub>O solvent mixture, only a 4% yield of the urea was obtained. This indicates that Na<sub>3</sub>PO<sub>4</sub> was also not deprotonating the amine hydroiodide salt in CH<sub>2</sub>Cl<sub>2</sub>. In

Table 4  
The effects of base on the oxidative carbonylation of piperidine

Base	Equiv <sup>a</sup>	Solvent <sup>b</sup>	Yield <sup>c,d</sup> (%)
K <sub>2</sub> CO <sub>3</sub>	0.0	CH <sub>2</sub> Cl <sub>2</sub>	33
K <sub>2</sub> CO <sub>3</sub>	1.0	CH <sub>2</sub> Cl <sub>2</sub>	36
K <sub>2</sub> CO <sub>3</sub>	1.0	CH <sub>2</sub> Cl <sub>2</sub> / H <sub>2</sub> O	29
K <sub>2</sub> CO <sub>3</sub>	1.5	CH <sub>2</sub> Cl <sub>2</sub>	29
K <sub>2</sub> CO <sub>3</sub>	2.0	CH <sub>2</sub> Cl <sub>2</sub>	32
KOH	1.0	CH <sub>2</sub> Cl <sub>2</sub>	8
KOH	1.0	CH <sub>2</sub> Cl <sub>2</sub> / H <sub>2</sub> O	3
Na <sub>3</sub> PO <sub>4</sub>	1.0	CH <sub>2</sub> Cl <sub>2</sub>	36
Na <sub>3</sub> PO <sub>4</sub>	1.0	CH <sub>2</sub> Cl <sub>2</sub> / H <sub>2</sub> O	4
Pyridine	1.0	CH <sub>2</sub> Cl <sub>2</sub>	29
NEt <sub>3</sub>	1.0	CH <sub>2</sub> Cl <sub>2</sub>	0
DBU	1.0	CH <sub>2</sub> Cl <sub>2</sub>	0

<sup>a</sup> Equivalents of base with respect to piperidine.

<sup>b</sup> CH<sub>2</sub>Cl<sub>2</sub> (40 ml) or CH<sub>2</sub>Cl<sub>2</sub> (40 ml) + water (5 ml).


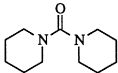

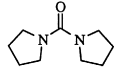

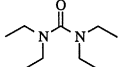

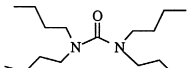

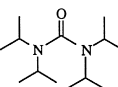

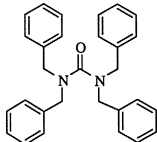

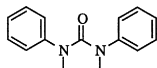
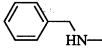
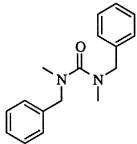
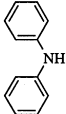
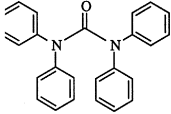
<sup>c</sup> Isolated yield of dipiperidylurea calculated per equivalent of piperidine.

<sup>d</sup> Reaction conditions: amine (14.2 mmol), W(CO)<sub>6</sub> (0.28 mmol), I<sub>2</sub> (7.1 mmol), room temperature, 80 atm CO, 15 h.

the mixture with water, hydroxide generated by reaction with  $\text{Na}_3\text{PO}_4$  was probably interfering with the carbonylation chemistry. While hydroxide is a strong enough base to deprotonate

the amine salt, it is also nucleophilic and known to react with metal carbonyls [34]. Problems with hydroxide in this system were confirmed by experiments with added hydroxide bases. For

Table 5  
Oxidative carbonylation of secondary amines to ureas

Amine	Product	Yield <sup>a,b</sup> (%)
		36
		33
		40
		trace
		0
		55
		0
		49
		0

<sup>a</sup> Isolated yield of urea calculated per equivalent of amine

<sup>b</sup> Reaction conditions: amine (14.2 mmol),  $\text{W}(\text{CO})_6$  (0.28 mmol),  $\text{I}_2$  (7.1 mmol),  $\text{K}_2\text{CO}_3$  (21.3 mmol),  $\text{CH}_2\text{Cl}_2$  (40 mL), room temperature, pressure 80 atm, 15 h.

example, using KOH as the base, the urea was produced in only 8% yield in  $\text{CH}_2\text{Cl}_2$  and in 3% yield in the  $\text{CH}_2\text{Cl}_2$ /water solvent system.

Nitrogen bases which would not be substrates for the reaction, such as pyridine,  $\text{NEt}_3$ , and DBU, were also examined. When pyridine was used as the base, the urea was produced in a 29% yield. However, when  $\text{NEt}_3$  and DBU were used as bases, no urea was produced. Interestingly, addition of  $\text{NEt}_3$  caused a shift in the reaction chemistry. The only identifiable organic product from the  $\text{NEt}_3$  study was *N*-formylpiperidine, which was formed in trace quantities.

Even though several different bases were examined, the turnover number did not exceed nine, which corresponds to an approximately 33% yield of urea. This is consistent with the reaction stoichiometry of two deprotonations per urea product (Eq. 4) so that half of the amine is consumed as a base. Piperidine hydroiodide is also present in the reaction mixtures. The reaction thus appears to be limited by the inability of the bases to deprotonate the amine salt and return the amine to the substrate pool. The choice of base for this reaction is complicated by the fact that the metal carbonyl catalyst is vulnerable to nucleophilic attack. The base not only needs to be strong enough to deprotonate the HI salts of secondary amines, but it also needs to be non-nucleophilic. Unlike the reaction of primary amines, in which  $\text{K}_2\text{CO}_3$  is adequate as the base [31], a suitable choice for the reaction of secondary amines has yet to be found.

Further optimization experiments addressed other variables. Raising the temperature, which worked very well in the primary amine case, was ineffective. At  $90^\circ\text{C}$ , the yield of urea was lowered to 18%. Further increasing the catalyst concentration to 5 mol% gave a urea yield of 37%. The similar result with 2 mol% indicates that catalyst decomposition is not responsible for the low turnover numbers, consistent with the limiting factor being formation of the amine

salt. In addition, longer reaction times (30 h) also did not result in any increase in urea yield.

The best overall reactant ratios were determined from the piperidine optimization experiments to be 2 mol%  $\text{W}(\text{CO})_6$ , equimolar amounts of  $\text{K}_2\text{CO}_3$  and amine and 0.5 eq  $\text{I}_2$ . The reaction was best carried out at room temperature under 60–80 atm CO pressure in  $\text{CH}_2\text{Cl}_2$ . Several secondary amines were reacted to give the corresponding tetrasubstituted ureas, using the conditions described in Table 5. The ureas were formed in moderate to good yields, ranging up to 55% for tetrabenzylurea. The yields typically decrease with increasing steric bulk, with diisopropylamine failing as a substrate. In addition, as observed for the carbonylation of primary amines under these conditions, aromatic amines do not react.

In conclusion, we have developed a system for oxidative carbonylation of cyclic and acyclic aliphatic secondary amines to symmetrical tetrasubstituted ureas in moderate yields under mild conditions using  $\text{W}(\text{CO})_6$  as the catalyst,  $\text{I}_2$  as the oxidant, and CO as the carbonyl source. This reaction provides an alternative to the nucleophilic reaction of amines with phosgene derivatives. Further work on amine carbonylation reactions is currently underway.

## Acknowledgements

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