Copper-catalyzed amination of alkenes and ketones by phenylhydroxylamine

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The catalytic activity of a number of copper complexes and salts toward allylic amination of alkenes using phenylhydroxylamine as the nitrogen fragment donor has been investigated. The best catalyst is $CuCl_2 \cdot 2H_2O$, which produces moderate yields of allylamines with high regioselectivity resulting from double bond transposition. A mechanism similar to that for the molybdenum and the FePc systems is proposed. The first step in the catalytic cycle is the formation of nitrosobenzene from the oxidation of phenylhydroxylamine by Cu(II). The next step is an ene reaction of the alkene with PhNO to produce an allylhydroxylamine, which is then reduced to the allylamine product by Cu(I), thus regenerating Cu(II). The same system can also transfer the nitrogen fragment to the α-carbon of cyclic ketones; this is accompanied by dehydrogenation in some cases to produce α-aminated, α,β-unsaturated ketones.

The search for simple and selective methods for the nitrogenation of hydrocarbons remains a challenge to chemists. A number of important methods have been reported, including metal-catalyzed aziridination of alkenes with PhI=NTs,[1,2] stoichiometric aziridination of alkenes with manganese nitrido species,[3] and metal-catalyzed allylic amination of alkenes with phenylhydroxylamine.[4] The latter method is particularly interesting due to the highly regioselective migration of the C–C double bond. The development of this method was stimulated by earlier reports by Sharpless *et al.* and by Mares and coworkers of stoichiometric allylic amination of alkenes by $L_nMoO(\eta^2\text{-RNO})$[5,6] and $X(=NTs)_2$ (X = S, Se).[7] Subsequently, Nicholas *et al.* and Jørgensen and colleagues have found that dioxomolybdenum(VI) complexes,[8] iron phthalocyanine[9] and Fe(II,III) salts[10] catalyze the allylic amination of alkenes with phenylhydroxylamine. Recently, it was reported that allylic amination can also be carried out with nitrobenzene as the N-donor under high CO pressures using ruthenium catalysts.[11] We report here that simple copper salts can also catalyze the allylic amination of alkenes with phenylhydroxylamine. Although copper(I,II) complexes and salts are good catalysts for the aziridination of alkenes with PhINTs,[2a,b] this is the first report on their use in catalytic allylic amination by PhNHOH. Moreover, this system is also able to perform catalytic amination of ketones, which has not been reported for the iron and the molybdenum systems.

Experimental

Materials

Solvents and alkenes were of reagent grade and were purified by standard methods.[12] 1,4-Dioxane was of HPLC grade and was used as received. *para*-Substituted α-methylstyrenes were prepared from the corresponding *para*-substituted acetophenone.[13] Cu(salen),[14] $[Cu(MeCN)_4](ClO_4)_2$,[15] $[Cu(tren)(H_2O)](ClO_4)_2$,[16] $[Cu(bpy)_2](ClO_4)_2$,[17] *o*-(hydroxyamino)biphenyl,[18] PhNHOH[19] and *N*-phenyl-*N*-(1,1,2-trimethylprop-2-enyl)hydroxyamino[9b] were prepared according to literature methods. All other chemicals were of reagent grade and were used as received.

Instrumentation

^{1}H NMR spectra were measured in $CDCl_3$ on a Varian VNMR 300 spectrometer with TMS used as an internal standard. Infrared spectra were recorded on a Perkin Elmer IR-1000 FT-IR spectrometer. Gas chromatographic analyses were performed on a Hewlett–Packard 5890 gas chromatograph with an HP Ultra 2 capillary column (25 m × 0.2 mm i.d.). GC-MS measurements were carried out on a HP 5890 gas chromatograph interfaced to an HP 5970 mass selective detector.

Catalytic allylic amination of alkenes

All reactions were carried out under argon. The alkene (7.0 mmol) and $CuCl_2 \cdot 2H_2O$ (0.1 mmol) were added to a mixture of 1,4-dioxane (9 ml) and dichloromethane (1 ml) and heated to reflux (*ca.* 100 °C). PhNHOH (1.0 mmol) dissolved in 1,4-dioxane (9 ml) and dichloromethane (1 ml) was then slowly added over a period of 30 min and the resulting mixture was further refluxed for 2 h. The reaction mixture was analyzed by GC and GC-MS using naphthalene as the internal standard. The allylamine products were identified by comparing with authentic samples prepared and characterized according to published methods.[8–10]

For competitive experiments a mixture of α-methylstyrene (1.0 mmol) and *para*-substituted α-methylstyrene (1.0 mmol) were used as substrates. The relative reactivities were determined using the equation: $k_X/k_Y = [\log(Y_f/Y_i)]/[\log(X_f/X_i)]$, where Y_i and Y_f are the initial and final concentrations of substituted α-methylstyrene, and X_i and X_f are the initial and final concentrations of α-methylstyrene.

Catalytic α-amination of ketones

The procedure is similar to that for the allylic amination of alkenes. The cyclic α-ketoenamine products were also isolated by precipitating the copper complex using hexane, followed by silica column chromatography using hexane–ethyl acetate as eluent. The products were characterized by ^{1}H NMR, IR and GC-MS. The spectral data of some of the cyclic α-ketoenamines are given below.

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2-(Phenylamino)cyclopent-2-enone. TLC: R_f 0.27 (hexane–EtOAc 10 : 1). IR (neat): 3327, 3056, 2922, 1693, 1631, 1598, 1537, 1502 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.30–6.95 (m, 5H), 6.75 (t, 1H, $J = 3.2$ Hz), 6.24 (br s, 1H), 2.68–2.63 (m, 2H), 2.49–2.46 (m, 2H). EI-MS (*m*/*z*): 173 (100), 144 (95), 130 (20), 117 (20), 90 (21), 77 (27%).

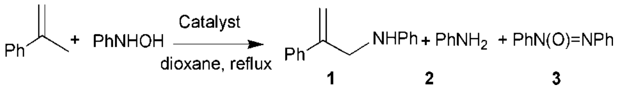
2-(Phenylamino)cyclohex-2-enone. TLC: R_f 0.50 (hexane–EtOAc 8 : 1). IR (neat): 3364, 3053, 2926, 1674, 1630, 1597, 1514, 1495 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.30–6.88 (m, 5H), 6.43 (t, 1H, $J = 4.8$ Hz), 6.36 (br s, 1H), 2.58–2.54 (m, 2H), 2.48–2.42 (m, 2H), 2.06–1.98 (m, 2H). EI-MS (*m*/*z*): 187 (100), 158 (48), 130 (70), 104 (22), 93 (21), 77 (42%).

2-Methyl-2-(phenylamino)cyclohexanone. TLC: R_f 0.5 (hexane–EtOAc 1 : 8). IR (neat): 3384, 3050, 2928, 2858, 1711, 1601, 1503, 1288 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.16–6.52 (m, 5H), 4.25 (br s, 1H), 2.85–2.75 (m, 1H), 2.37–2.21 (m, 1H), 2.08–1.75 (m, 6H), 1.41 (s, 3H). EI-MS (*m*/*z*): 203 (37), 175 (30), 160 (23), 146 (100), 134 (76), 118 (42), 93 (70), 77 (52%).

Results and discussion

Allylic amination of alkenes

Investigations of the catalytic activity of a number of copper(I) and copper(II) complexes and salts were carried out by slow addition (approx. 30 min) of a solution of PhNHOH (1.0 mmol) in dioxane (10 ml) to a refluxing solution of the copper catalyst (0.1 mmol) and α-methylstyrene (7 mmol) in dioxane (10 ml). After 2 h, analysis by GC and GC-MS reviewed the formation of products shown by the following equation:



(1)

As observed for the molybdenum and iron-catalyzed systems, the formation of the allylamine product **1** was accompanied by the side products **2** and **3**. The allylamine product **1** was also isolated and characterized by NMR. From the results shown in Table 1, it can be seen that copper complexes containing unidentate ligands are in general better catalysts than those containing multidentate ligands. The best catalyst is $CuCl_2 \cdot 2H_2O$, which gives a 32% yield of the desired product **1**. The yield is increased to 40% by using a dioxane–CH_2Cl_2 (9 : 1) mixed solvent system. The use of other solvents such as CH_3CN, THF or CH_2Cl_2, however, resulted in yields below 20%. 4-Fluorophenylhydroxylamine was also used as the nitrogen fragment donor, and a higher yield of 45% was obtained. Apart from molybdenum and iron, this is the third metal system that catalyzes this amination reaction with reasonable yields. The yields for the copper system are comparable to the molybdenum (42%)[8] and the $FeCl_2 + FeCl_3$ systems (41%),[10] but are lower than the FePc system (76%).[9]

Table 1 Allylic amination of α-methylstyrene by phenylhydroxylamine catalyzed by various copper complexes[a]

Catalyst[c]	Yield[b](%) 1	2	3
CuCl	6	46	11
$[Cu(MeCN)_4](ClO_4)$	14	42	2
$Cu(ClO_4)_2 \cdot 6H_2O$	9	35	9
$Cu(CH_3CO_2)_2 \cdot H_2O$	2	45	4
$Cu(OTf)_2$	14	40	2
$CuCl_2 \cdot 2H_2O$	32	38	1
Cu(salen)	3	41	12
$[Cu(tren)(H_2O)](ClO_4)_2$	7	50	18
$[Cu(bpy)_2](ClO_4)_2$	6	42	13
$[Cu(phen)Cl_2]$	7	50	6

[a] See experimental section for conditions. [b] Yields are based on phenylhydroxylamine and were determined by GC with naphthalene as the internal standard. Products were also characterized by IR, ^{1}H-NMR and GC-MS. [c] Abbreviations: salen = *N*,*N*′-bis(salicylidene)ethylenediamine dianion, tren = tris(2-aminoethyl)amine, bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline.

Experiments were also done with other alkenes using $CuCl_2 \cdot 2H_2O$ as the catalyst and the results are shown in Table 2. Similar to the iron and the molybdenum systems, higher yields were obtained with 1,1-disubstituted or trisubstituted alkenes; a single regioisomer was produced from double bond transposition and small or zero yields were obtained if product formation resulted in the lost of conjugation (*e.g.* no allylamine product could be detected with β-methylstyrene). The highest yield obtained was 72% (Table 2, entry 5).

Mechanistic considerations

A proposed mechanism similar to that for the molybdenum and the FePc systems is shown in Scheme 1. The first step in the catalytic cycle is the formation of PhNO from the oxidation of PhNHOH by Cu(II). The next step is an ene reaction of the alkene with PhNO to produce an allylhydroxylamine, which is then reduced to the allylamine product by Cu(I), thus regenerating Cu(II).

Formation of PhNO. When PhNHOH (1 mmol) was allowed to react with 2 mol equiv. of $CuCl_2 \cdot 2H_2O$ at room temperature in dioxane for 3 h, PhNO (70%), $PhNH_2$ (10%) and azoxybenzene (10%) were detected by HPLC. PhNO is most likely produced from the oxidation of PhNHOH by Cu(II):

$$PhNHOH + 2Cu^{2+} \rightarrow PhNO + 2Cu^{+} + 2H^{+} \quad (2)$$

On the other hand, $PhNH_2$ is probably formed from the deoxygenation of PhNHOH by Cu(I) according to eqn. (3):

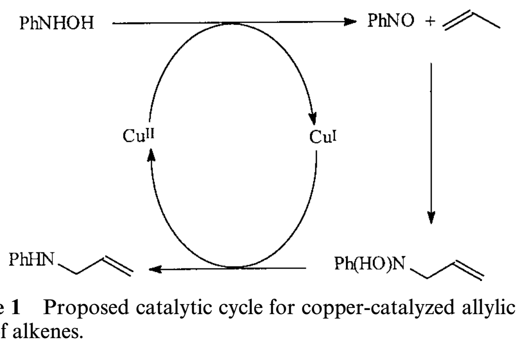
$$PhNHOH + 2Cu^{+} + 2H^{+} \rightarrow PhNH_2 + 2Cu^{2+} + H_2O \quad (3)$$

Combining eqn. (2) and (3) gives eqn. (4), which represents copper-catalyzed disproportionation of PhNHOH:

$$2PhNHOH \rightarrow PhNO + PhNH_2 + H_2O \quad (4)$$

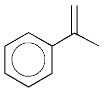
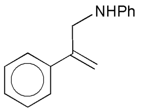
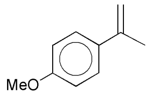
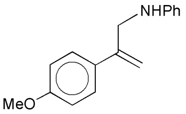
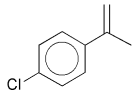
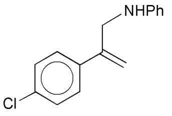
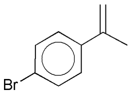
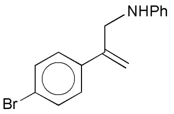
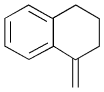
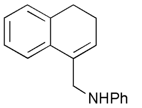
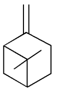
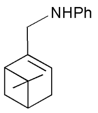
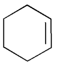
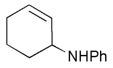
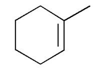
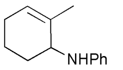
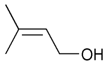
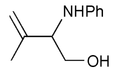
Although the disproportionation of PhNHOH can also occur thermally,[20] we found that it is much slower than the copper-catalyzed reaction. The third product, azoxybenzene, is believed to arise from the reaction of $PhNH_2$ and PhNO.[21] From the distribution of these three products, it can be estimated that 60% of PhNO arises from the oxidation pathway [eqn. (2)], while the remaining 40% comes from disproportionation.

To further test for the presence of PhNO in the catalytic system, a catalytic amount of $CuCl_2 \cdot 2H_2O$ (0.01 mmol) was mixed with PhNHOH (0.1 mmol) and 2,3-dimethylbutadiene, DMB (0.5 mmol), in dioxane at 75 °C for 3 h. DMB is known to react rapidly with aromatic nitroso compounds such as PhNO.[22] Analysis of the reaction mixture by GC indicated the formation of 21% of the hetero-Diels–Alder adduct, 7% of the allylamine of DMB and 33% of $PhNH_2$ [eqn. (5)]. Only a trace amount of the adduct was detected in the absence of the



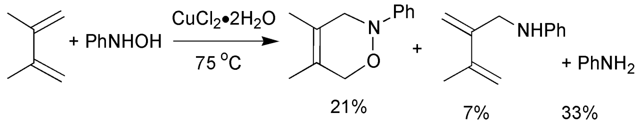
Scheme 1 Proposed catalytic cycle for copper-catalyzed allylic amination of alkenes.

Table 2 $CuCl_2 \cdot 2H_2O$ catalyzed allylic amination of alkenes by PhNHOH[a]

Entry	Substrate	Product	Yield[b](%)	N-selectivity[c](%)
1			40	52
2			22	36
3			22	31
4			9	15
5			72	70
6			6	12
7			2	5
8			9	13
9			21	39

[a] See experimental section for conditions. [b] Yields are based on phenylhydroxylamine. [c] N-selectivity = allylamine/(allylamine + aniline + azoxybenzene).

copper catalyst. This suggests that free PhNO is produced from Cu(II) and PhNHOH.



(5)

Ene reaction between PhNO and alkene. Alkenes are known to react with PhNO to produce allylhydroxylamines.[8b,9,23] The observed regioselectivity and relative alkene reactivity in the copper-catalyzed reactions are consistent with this ene-type reaction. The higher yield obtained when 4-fluorophenylhydroxylamine replaces phenylhydroxylamine is due to the formation of the stronger enophile F-PhNO. Since this step takes place in the presence of the copper catalyst, there is the possibility that the PhNO is coordinated to the metal during the ene reaction. Strong evidence for 'on-metal' transfer is found for the iron-salt-catalyzed reactions, where the active intermediate, an iron complex having a *C*-nitroso dimer ligand, has been isolated and structurally characterized.[10b] This compound can aminate alkenes to produce allylamine exclusively, even in the presence of DMB. In the case of the copper-catalyzed system, a hetero-Diels–Alder adduct is produced when DMB is added, suggesting an 'off-metal' mechanism involving free PhNO as the aminating agent.

In order to obtain more information on the nature of the transition state, competitive kinetic studies with a set of *para*-substituted α-methylstyrenes were carried out. A plot of $\log(k/k_0)$ *vs.* the Hammett constant σ gives a fairly linear relationship with $\rho = -1.1$ (Fig. 1). Such a small negative value indicates that a small positive charge was developed at the α-carbon in the transition state. This ρ value is comparable to that of the thermal ene reaction of *para*-substituted 1-arylcyclopentenes with diethyl oxomalonate ($\rho = -1.2$),[24] but is very different from that of iron-salt-catalyzed allylic aminations ($\rho = -3.9$).[10b] These results support free PhNO as the active aminating agent in the copper-catalyzed reaction.

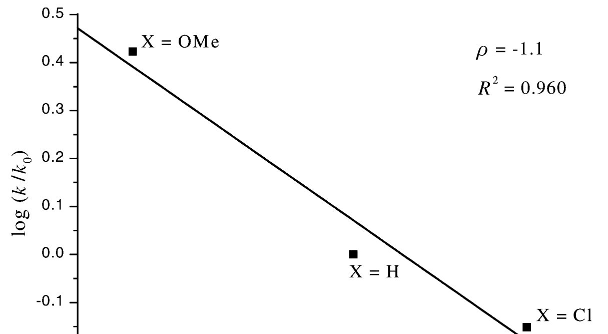
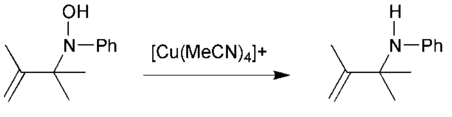


Fig. 1 Hammett plot for copper-catalyzed allylic amination of *para*-substituted α-methylstyrenes.

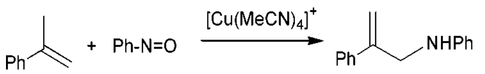
Deoxygenation of hydroxylamines by Cu(I). When *N*-phenyl-*N*-(1,1,2-trimethylprop-2-enyl)hydroxylamine (**4a**, 1 mmol) was treated with $[Cu(MeCN)_4]^+$ (0.1 mmol) under refluxing conditions in dioxane (10 ml), 2,3-dimethyl-3-(phenylamino)but-1-pene (**4b**) was formed in 10% yield:



4a **4b**

(6)

This shows that Cu(I) is capable of deoxygenating an allylhydroxyamine to give an allylamine. Although attempts to isolate the allylhydroxylamine formed from nitrosobenzene and α-methylstyrene were not successful, the reaction of α-methylstyrene (1 mmol) and nitrosobenzene (5 mmol) in the presence of $[Cu(MeCN)_4]^+$ (0.1 mmol) produced the deoxygenated product 2-phenyl-3-(phenylamino)propene in 11% yield. No allylamine product was observed in the absence of Cu(I).



(7)

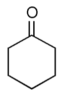
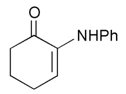
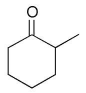
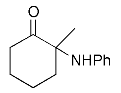
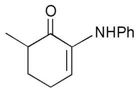
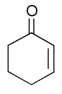
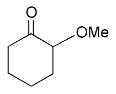
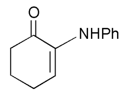
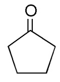
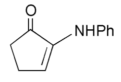
Relative reactivities of the copper catalysts. Since this mechanism requires the copper catalyst to shuttle between Cu(II) and Cu(I), the rates and the yields are expected to be very sensitive to the redox potential of the copper catalyst. Copper catalysts with relatively high Cu(II)/Cu(I) redox potentials are expected to be efficient in the oxidation of PhNHOH to PhNO, the first step of the catalytic process. However, the last step of the process, the deoxygenation of allylhydroxylamine, should be rather sluggish with these catalysts. The reverse situation should occur with catalysts of relatively low Cu(II)/Cu(I) redox potentials. Presumably, among the various copper catalysts, $CuCl_2 \cdot 2H_2O$ has the most appropriate redox potential in dioxane so that the first and the last steps occur with reasonable efficiencies, thus giving the highest yield.

Detection of aryl nitrene intermediate. In the Mo-catalyzed reaction, aryl nitrene was found to be one of the intermediates through the detection of carbazole when *o*-(hydroxyamino)biphenyl was used as the aminating agent. The carbazole product arises from intramolecular C–H insertion of a biphenylnitrene.[25] We have performed similar experiments; *o*-(hydroxyamino)biphenyl (1mmol) in dioxane (10 ml) was slowly added to a refluxing solution of $CuCl_2 \cdot 2H_2O$ (0.1 mmol) in dioxane (10 ml) and the mixture was further refluxed for 20 h. No carbazole was detected by GC, suggesting that a free arylnitrene intermediate is rather unlikely in the copper-catalyzed reaction.

α-Amination of ketones

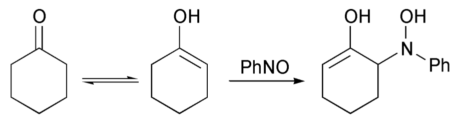
The same catalytic system can also transfer the nitrogen fragment to the α-carbon of cyclic ketones, accompanied by dehydrogenation in some cases to produce α-aminated, α,β-unsaturated ketones. Thus, reaction of cyclohexanone with PhNHOH in refluxing dioxane in the presence of a catalytic amount of $CuCl_2 \cdot 2H_2O$ produced 2-(phenylamino)-2-cyclohexenone in 25% yield (Table 3). In the case of 2-methylcyclohexanone, amination occurs at the tertiary C–H bond without dehydrogenation. However, cyclohex-2-enone gave diphenylamine as the product. No products were detected when linear ketones such as pentan-2-one were used as substrates. Acetophenone, which gives a higher equilibrium concentration of the enol form than cyclohexanone but lacks an allylic C–H bond, also gives no product. Mares *et al.* have communicated that the stoichiometric reaction of $Mo(O)L'L(\eta^2\text{-}PhNO)$ (L′ = pyridine-2,6-dicarboxylato; L = hexamethylphosphoric triamide) with cyclohexanone produced a mixture of 2-(*N*-phenyl)iminocyclohexanone and azobenzene;[6] however, the yield was not reported and apparently no dehydrogenation occurred. Although the yields of the copper-catalyzed reactions are not yet satisfactory, this is the first report of a catalytic system for the amination of ketones using phenylhydroxylamine.

Table 3 $CuCl_2 \cdot 2H_2O$ catalyzed allylic amination of ketones by PhNHOH[a]

Substrates	Products	Yield[b](%)	N-selectivity[c](%)
		25	34
		7	14
		2	
	Ph_2NH	38	80
		44	78
		6	13

[a] See experimental section for conditions. [b] Yields are based on phenylhydroxylamine. [c] N-selectivity = allylamine/(allylamine + aniline + azoxybenzene).

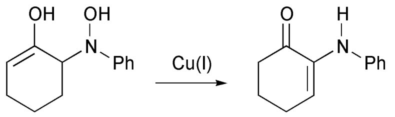
A mechanism similar to that for the amination of alkenes is proposed. The first step is the formation of PhNO from the oxidation of PhNHOH by Cu(II) and the copper-catalyzed disproportionation of PhNHOH [eqns. (2) and (4)]. The PhNO then undergoes an ene reaction with the enol form of the ketone:



5a

(8)

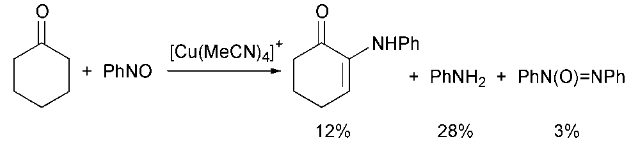
5a is then converted to the ketone product by Cu(I):



5a **5b**

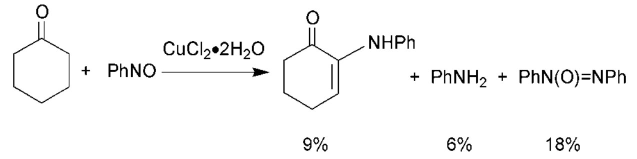
(9)

The involvement of free PhNO as the aminating agent in the reaction was demonstrated by the addition of DMB to the catalytic amination of cyclohexanone. It was found that the yield of α-ketoenamine was decreased to 5% but 8% of the hetero-Diels–Alder adduct of DMB was produced. The role of Cu(I) in the conversion of **5a** to **5b** is not clear, since this process involves only an overall loss of an H_2O molecule. However, no product was detected when PhNO was mixed with cyclohexanone in the absence of a copper catalyst. On the other hand, α-ketoenamine was readily detected in the presence of a Cu(I) species, such as $Cu(MeCN)_4{}^+$:



(10)

This process, however, can also be catalyzed by Cu(II):



(11)

Summary

In conclusion, $CuCl_2 \cdot 2H_2O$ catalyzes the amination of alkenes and ketones by phenylhydroxylamine. The catalyst appears to act as a redox reagent, oxidizing the starting hydroxylamine to the reactive nitrosobenzene and then reducing the resulting allylhydroxylamine. The major factor limiting the yields seems to be copper-catalyzed disproportionation of the starting phenylhydroxylamine. The α-amination of ketones, which is also accompanied by dehydrogenation, appears to have a more complicated mechanism, and this reaction will be further studied.

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