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Colloid and Nano-Sized Catalysts in Organic Synthesis: X.[1] Synthesis of Carboxamides by Direct Amidation of Carboxylic Acids and Transamidation Catalyzed by Colloid Copper

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Abstract—It was found that in the presence of colloid copper the direct amidation of some carboxylic acids with primary and secondary amines in benzene with azeotropic distillation of water became possible. The catalyst was proven to be suitable also for transamidation reaction of a number of carboxylic acid amides under mild conditions in solvent-free conditions.

Keywords: catalysis, nanoparticles, copper colloid particles, direct amidation, transamidation, carboxylic acids, amides, amines

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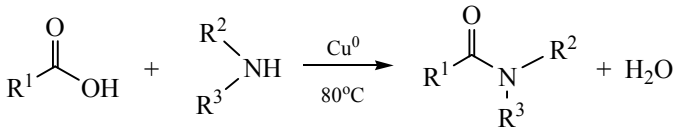
Preparation of carboxylic acid amides is one of the frequently used reactions of organic synthesis. Thus, the synthesis of amides can be performed by many methods, the most common among them being the conversion of carboxylic acid to acid chloride followed by its reaction with ammonia or an amine [2]. However multistage synthesis as well as use of compounds like phosgene, thionyl chloride, or phosphorus chlorides for preparation of acid chlorides is a significant drawback of this approach. Apparently, direct amidation of carboxylic acids without an acid chloride preparation is more promising method of amide synthesis. The preparation of unsubstituted carboxylic acid amides via pyrolysis of their ammonium salts has been described in [3, 4], but the requirement of high-temperature heating restricts the application of this method. The direct amidation with primary or secondary amines is possible only for the lowest specimen of carboxylic acids. For instance, at 70°C in the presence of zinc oxide or chloride and metallic indium formic acid underwent amidation with secondary amines affording the corresponding amides in 73–99% yield [5]. In the case of amidation of some benzoic acid derivatives with benzylamine or morpholine heteropoly acids are applied (8–10%) as catalysts [6]. Long-chain carboxylic acids and amines provided amides under catalysis with silica gel MSM-41 (20%) at high temperature [7].

Trialkoxy boranes have been also used for catalysis of direct amidation under microwave irradiation [8], as well as transition metal salts and zirconium complexes at 110°C in toluene [9], boric acid [10], or arylboric acids [11, 12], activated granules of aluminum oxide (10%, 140°C) [13], triphenylantimony oxide together with phosphorus sulfide [14], titanium tetraisopropoxide [15]. In the most cases the catalysts of amidation are common acids or Lewis acids. It is also known that catalysis-free synthesis of amides by the reaction of carboxylic acids with amines requires heating up to 160–180°C [16]. Impossibility to use compounds unstable at heating as starting substrates is a significant drawback of this method.

It is known that in the presence of barium hydroxide the polymer-supported palladium nanoparticles are capable to catalyze alkylation of ketones with alcohols [17]. Colloid nickel and cobalt particles have been applied to alkylation of amines with alcohols [18]. Earlier we used copper nanoparticles in the

[1] For communication IX, see [1].

Scheme 1.



Ia–Ic **IIa–IIc** **IIIa–IIId**

R^1 = Pr (**Ia**), Bu (**Ib**), *i*-Bu (**Ic**); R^2–R^3 = $(CH_2)_5$ (**IIa**), R^2–R^3 = $(CH_2)_2O(CH_2)_2$ (**IIb**); R^2 = H, R^3 = Cy (**IIc**); R^1 = Pr, R^2–R^3 = $(CH_2)_5$ (**IIIa**); R^1 = Pr, R^2 = H, R^3 = Cy (**IIIb**); R^1 = Bu, R^2–R^3 = $(CH_2)_2O(CH_2)_2$ (**IIIc**); R^1 = Bu, R^2–R^3 = $(CH_2)_5$ (**IIId**).

Leuckart–Wallach reaction [19] that proved promising to use copper as a catalyst of carbon-nitrogen bond formation.

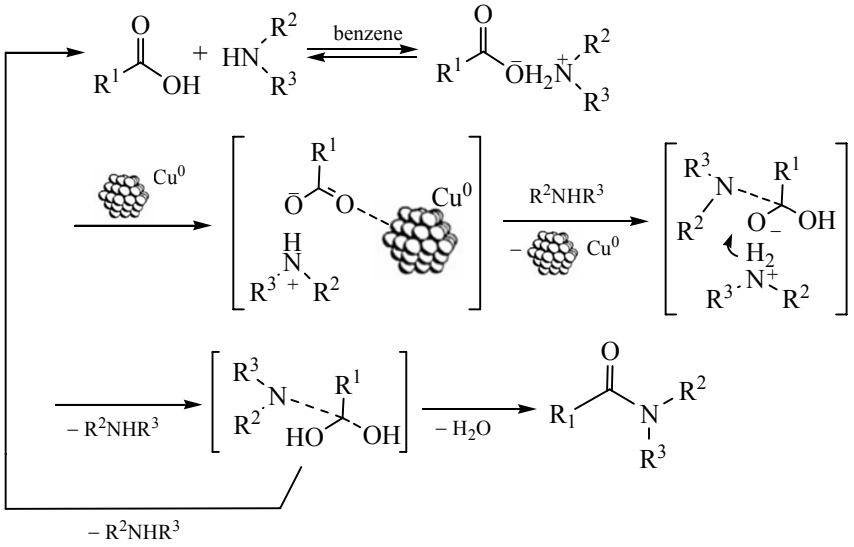
To confirm the nano-dimensionality of copper nanoparticles synthesized by the described procedure [19] we used reverse light-dispersion method. Isopropanol, formamide, and benzylamine were used as solvents. It was found that copper particles are well soluble in the amine and the amide with formation of light-blue and reddish-brown solutions respectively. The treatment of the correlated function with Dynals program allowed the determination of the average hydrodynamic radius of the particles. Thus, the average size of copper nanoparticles in formamide, benzylamine, and isopropanol was 70, 70.21, and 134.9 nm respectively. A large value of the particles size in the last case can be ascribed to the poor solvation of the copper particles in isopropanol with the possible formation of particles agglomerates. Interestingly, that the data on the particles size are the same as for the particles prepared before the measurements as a colloid solution and stored dry about one year, and finally dissolved in the amine or amide.

The synthesis of some amides by reaction of carboxylic acids with primary and secondary amines in the presence of the neutral colloid copper catalyst we successfully performed. Butyric **Ia**, valeric **Ib**, and 3-methylbutanoic **Ic** acids were used as starting carboxylic acids; piperidine **IIa**, morpholine **IIb**, and cyclohexylamine **IIc** were involved as starting amines. The amidation reaction was carried out in benzene at 80°C and molar ratio of acid : amine = 1 : (1–1.2) in the presence of copper nanoparticles; the formed water was removed by azeotropic distillation. The use of equimolar amount of the amine or its excess in the reaction ensured the absence of the acid catalysis. It was found that under the described conditions the amidation proceeded quantitatively to give amides **IIIa–IIId** in 78–90% (Scheme 1).

The addition of new portions of the catalyst to the reaction mixture accelerated water formation that confirmed catalytic effect of the colloid copper. In the absence of the catalyst the reaction proceeded with a low conversion of the starting reagents (only 12–15% after 6 h), and the water formation stopped. It was also found that amidation reaction rate was strongly affected by the basicity of the used amine. Thus, the reaction with piperidine and cyclohexylamine proceeded significantly faster (in 2–2.5 h) compared to the reaction with morpholine (6–8 h). The reaction with aniline proceeded with only 50% conversion (according to the amount of the formed water) and required 10–12 h. The structure of the carboxylic acid also affected the reaction rate: the acids of linear structure reacted with piperidine significantly faster. But the reaction of 1-adamantanecarboxylic acid resulted in the corresponding piperidide with only 30–40% conversion (according to the amount of the formed water) in 12 h. The structure of amides **IIIa–IIId** was confirmed by ^{1}H NMR spectroscopy.

The interesting problem in the formation of acid amides under pH-neutral conditions at low temperature consists in the possible reaction mechanism. Most probably the mechanism of catalysis of amidation reaction may be explained by the properties of crystalline particles. In the particles containing a low amount (100–10000) of metal atoms (M^0) some atoms on the particle surface are located on edges or apices of the crystal and have low coordination number. It leads to increased capability of these atoms to coordination with polar groups of organic molecules. Probably the coordination of the catalyst occurred with the oxygen of the carbonyl group of an acid salt. In the course of our investigations we found that little excess of an amine (5–10 mol%) increased the water formation showing that the process of amide synthesis proceeded not as a thermal dehydration of carboxylic acid salt but as an addition of an amine at the carbonyl group of the salt (Scheme 2).

Scheme 2.



The formation of the coordination bond between metallic copper and the oxygen of carbonyl or ester groups has been suggested earlier in [20].

The direct dependence of water formation intensity on basicity of an amine served as the indirect confirmation of an attack of the carbonyl group by an amine. Similarly, low rate of amidation of sterically hindered acids like 1-adamantanecarboxylic acid can be due to the fact that metal nanoparticles cannot effectively coordinate sterically shielded carbonyl group of the acid ammonium salt.

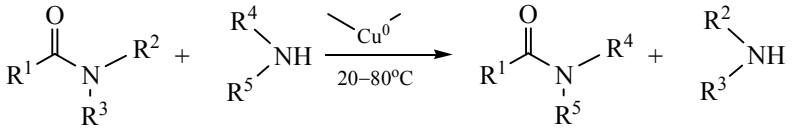
Along with the direct amidation, one of the convenient methods of preparation of *N*-substituted carboxylic acid amides is the transamidation of carboxamides with amines. The carboxamides transamidation can be performed by various procedures: as a rule, the process requires rigid conditions for the cleavage of the chemically strong amide bond. Noncatalytic transamidation requires heating up to 180°C [21]. The drawback of this method is the impossibility of using thermally unstable compounds as starting substrates. During last two decades for transamidation of carboxylic acid amides with amines a number of metal-contained compounds were used like $AlCl_3$ [22], $Sc(OTf)_3$, and $Ti(NMe_2)_4$ [23]. Along with them complex $Al_2(NMe_2)_6$ in toluene at 90°C was applied for catalysis of transamidation of the secondary carboxamides with primary alkylamines [24]. Secondary or tertiary amides can be synthesized by reaction of primary carboxamides with primary or secondary amines in the presence of catalytic amount of hydroxylamine hydrochloride [25]. Boric acid can also be used as a catalyst for transamidation [26]; when L-proline was used as a catalyst the reaction preceded for 36 h [27]; this method can be applied for a wide range of amines. The transamidation of dimethylformamide catalyzed by $B(OCH_2CF_3)_3$ has been also described in [28]; however application of such catalyst restricted choice of primary amides.

The transamidation of primary amides can be carried out also in cyclohexane at 80°C for 5–24 h in the presence of catalytic amounts of zirconocene dichloride. In the case of lower amides the reaction was performed at temperature below 30°C [29]. An effective catalyst for primary amides transamidation occurred to be mesoporous spheres of niobium oxide [30]. Reaction of various primary amides with wide range of amines was effectively catalyzed by cerium oxide at 160°C with the formation of the corresponding *N*-alkylamides in solvent-free conditions [31]. Therefore to achieve transamidation Lewis acids as the catalysts or high-temperature heating are required.

Successfully performed reaction of direct amidation of carboxylic acids catalyzed by colloid copper particles opened the possibility of the neutral metallic catalyst application for transamidation reaction of carboxamides with amines.

It was found that mixing colloid copper solution in formamide with aliphatic amines even at room temperature resulted in ammonium formation. We used formamide **IVa**, acetamide **IVb**, dimethyl-

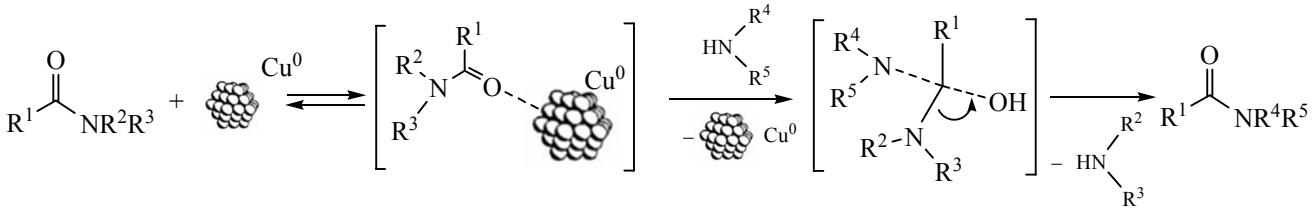
Scheme 3.



IVa–IVd **Va–Vd** **IIId, VIa–VIe**

$R^1 = R^2 = R^3 = H$ (**IVa**); $R^1 = CH_3$, $R^2 = R^3 = H$ (**IVb**); $R^1 = H$, $R^2 = R^3 = CH_3$ (**IVc**); $R^1 = i$-Bu, $R^2 = R^3 = H$ (**IVd**); $R^4 = H$, $R^5 = Cy$ (**Va**); $R^4 = H$, $R^5 = CH_2CH_2OH$ (**Vb**); $R^4–R^5 = (CH_2)_5$ (**Vc**); $R^4–R^5 = (CH_2)_2O(CH_2)_2$ (**Vd**); $R^1 = H$, $R^4 = H$, $R^5 = Cy$ (**VIa**); $R^1 = H$, $R^4 = H$, $R^5 = CH_2CH_2OH$ (**VIb**); $R^1 = H$, $R^4–R^5 = (CH_2)_5$ (**VIc**); $R^1 = H$, $R^4–R^5 = (CH_2)_2O(CH_2)_2$ (**VId**); $R^1 = CH_3$, $R^4 = H$, $R^5 = Cy$ (**VIe**).

Scheme 4.



formamide **IVc**, and 3-methylbutanoic acid amide **IVd** as starting carboxamides; cyclohexylamine **Va**, 2-aminoethanol **Vb**, piperidine **Vc**, and morpholine **Vd** were used as amines. The transamidation was performed in the presence of catalytic amounts of copper nanoparticles which were added to the reaction mixture or synthesized *in situ* (Scheme 3).

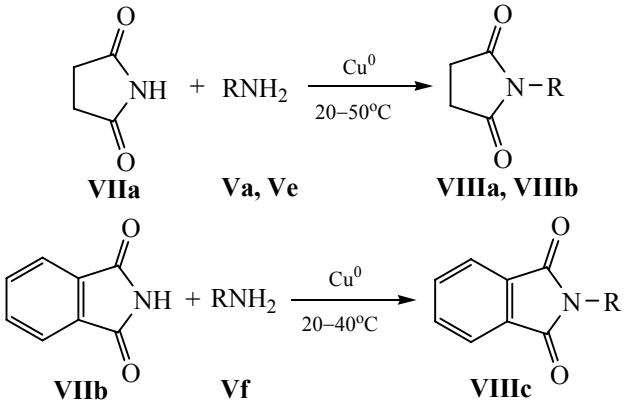
In the case of formamide the reaction began already at 20°C; an intensive release of ammonium happened at 40°C. Transamidation of acetamide and other substituted amides occurred at 40–80°C.

The reaction of dimethylacetamide and formamide with aniline did not succeed even at heating above 100°C. Therefore in this method basicity of the used amine strongly affected the rate of transamidation reaction. The dependence of the reaction rate on the amine basicity indirectly indicated the mechanism of transamidation which probably involved an attack of the carbonyl group by an amine. The process activation occurred via the formation of the complex between the terminal metal atoms of the nanoparticle and the oxygen of the amide carbonyl group (Scheme 4).

It was also found that the reaction of succinimide **VIIa** and phthalimide **VIIb** with primary amines catalyzed by colloid copper particles led to the formation of transamidation products **VIIIa–VIIIc** in high yields.

The reaction started already at 20°C but in the absence of a solvent it was limited by low solubility of imines **VIIa** and **VIIb** in equimolar amount of amines. The reaction was found to successfully proceed in the presence of an excess of amines under gentle heating; the target imines **VIIIa–VIIIc** were isolated by distillation. However in contrast to transamidation, which did not proceed under mild conditions in the absence of a catalyst, in the case of transimidation of imides **VIIa** and **VIIb** the catalysis does not play such a significant role. Thus, transimidation of dichloromaleic acid imides with aliphatic amines has been performed at 60°C in ethanol [32]; the reaction of *N*-

Scheme 5.



VIIa **Va, Ve** **VIIIa, VIIIb**

VIIb **Vf** **VIIIc**

R = Cy (**Va, VIIIa**), $PhCH_2$ (**Ve, VIIIb**), Bu (**Vf, VIIIc**).

carbethoxyphthalimide with α-amino acids proceeded at 0–20°C with the formation of *N*-phthalyl-substituted amino acids [33]. We also found that the reaction of phthalimide with butylamine in the absence of the catalyst began at 40°C with ammonium release, but the addition of copper nanoparticles to the reaction mixture accelerated the reaction (Scheme 5).

Therefore a possibility of performance of the direct amidation of some carboxylic acids with amines was found, as well as the transamidation of primary, secondary, and tertiary amides with aliphatic amines which proceeded under mild conditions in the presence of ultra-dispersed copper particles. Non-reversibility of the latter reaction is explained by ease of the removal of the formed ammonium and low-boiled amines from the reaction medium. The discussed procedure can present an interest in the case when rigid conditions or acidic catalysts are not desirable or the latter are expensive. Since neutral amines are used as the starting reagents the procedure can be promising for selective acylation of amines without the use of carboxylic acid anhydrides or chlorides.

EXPERIMENTAL

^{1}H NMR spectra were registered on a Varian Mercury-300 (300 MHz) spectrometer. Carbon tetrachloride was used as a solvent, HMDS, as an internal standard. The size of copper nanoparticles was determined with the help of reverse light-dispersion using PhotoCor Compact Z analyzer at 25°C (angle 160°, laser of 15–30 mV).

1-Butyrylpiperidine (IIIa). A mixture of 10.5 g (0.139 mol) of acid **Ia**, 13.6 g (0.16 mol) of amine **IIa**, 15 mL of benzene, and 0.35 g (0.006 mol) of copper nanoparticles was heated for 2 h with azeotropic distillation of water. After distilling off 2.5 mL (0.139 mol) of water, the solvent was removed, and the residue was distilled in a vacuum. Yield 8.5 g (0.8 mol, 95%), bp 158–160°C (30 mmHg). ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, CH_3, *J* 7.2 Hz), 1.52–1.58 m (6H, $3CH_2$), 2.1–2.18 m (2H, CH_2CO), 3.37 d (2H, CH_2N, *J* 15 Hz).

***N*-Cyclohexylbutyramide (IIIb)** was prepared similarly from 9 g (0.1 mol) of acid **Ia**, 11.4 g (0.115 mol) of amine **IIc**, 15 mL of benzene, and 0.19 g (0.003 mol) of copper nanoparticles; reaction time 6 h. Yield 15 g (0.088 mol, 88%), bp 255–257°C. ^{1}H NMR spectrum, δ, ppm: 0.85 t (3H, CH_3, *J* 7.2 Hz), 0.98–1.39 m (4H, $2CH_2$), 1.5–1.67 m (6H, $3CH_2$), 1.83 d (2H, CH_2, *J* 12.9 Hz), 1.94 t (2H, CH_2, *J* 14.7 Hz), 3.57–3.62 m (1H, CHN), 5.39 br.s (1H, NHCO).

***N*-Morpholyl-3-methylbutyramide (IIIc)** was prepared similarly from 10 g (0.1 mol) of acid **Ic**, 9.6 g (0.11 mol) of amine **IIb**, 15 mL of benzene, and 0.13 g (0.002 mol) of copper nanoparticles; reaction time 4 h. Yield 9.3 g (0.056 mol, 60%), bp 120–122°C (30 mmHg). ^{1}H NMR spectrum, δ, ppm: 0.82–0.9 m (6H, $2CH_3$), d (2H, CH_2CO), 3.07 t (2H, $(CH_2)_2N$, *J* 9.3 Hz), 3.37 t (2H, $(CH_2)_2N$, *J* 6 Hz), 3.5 t (2H, $(CH_2)_2O$, *J* 10.8 Hz), 3.75 t (2H,$(CH_2)_2O$, *J* 9.6 Hz), 2.07–2.21 m (1H, CH).

***N*-Piperidylvaleramide (IIId)** was prepared similarly from 5 g (0.049 mol) of acid **Ib**, 4 g (0.059 mol) of amine **IIa**, 15 mL of benzene, and 0.19 g (0.003 mol) of copper nanoparticles; reaction time 8 h. Yield 6.3 g (0.036 mol, 75%), bp 142–145°C (30 mmHg). ^{1}H NMR spectrum, δ, ppm: 0.87 t (3H, CH_3, *J* 14.4 Hz), 1.24–1.31 m (2H, CH_2), 1.58 d (2H, CH_2, *J* 4.2 Hz), 2.15 t (2H, CH_2CO, *J* 15 Hz), 3.32–3.39 m [4H, $(CH_2)_2N$], 1.61–1.56 m [6H, $(CH_2)_3$].

***N*-Cyclohexylformamide (VIa)**. *a*. A mixture of 5 g (0.11 mol) of formamide and 0.9 g (0.005 mol) of $CuCl_2{\cdot}2H_2O$ was stirred with a magnetic stirrer with a steel magnetic element without coating for 30 min. Then 10.7 mL (0.11 mol) of amine **Va** was added at 20°C. After the ammonium release completed the reaction product was distilled, collecting the fraction with bp 135–136°C (30 mmHg). Yield 11.2 g (0.099 mol, 90%), mp 35–38°C (mp 36–41°C, bp 137–138°C (10 mmHg) [34]). ^{1}H NMR spectrum, δ, ppm: 1.11–1.81 m (10H, $5CH_2$), 3.60–3.69 m (1H, CHN), 7.67 d (1H, NH, *J* 6.6 Hz), 7.88 s (1H, CHO).

b. A mixture of 0.13 g (0.002 mol) of copper nanoparticles, 5 g (0.11 mol) of formamide, and 11.9 g (0.12 mol) of amine **Va** was stirred for 30 min at 20–40°C. An excess of the amine was distilled off, and the residue was distilled. Yield 11.3 g (0.1 mol, 91%).

***N*-(2-Hydroxyethyl)formamide (VIb)** was prepared similarly according to procedure *b* from 5 g (0.11 mol) of formamide, 0.25 g (0.004 mol) of copper nanoparticles, and 6.8 g (0.12 mol) of amine **Vb** at 20–40°C for 1 h. Yield 8.2 g (0.092 mol, 83%), bp 347–350°C (bp 349.5°C [37]).

***N*-Formylpiperidine (VIc)** was prepared similarly according to procedure *b* from 5 g (0.11 mol) of formamide, 0.25 g (0.004 mol) of copper nanoparticles, and 11 g (0.13 mol) of piperidine at 20–40°C.

Yield 11.5 g (0.1 mol, 94%), bp 220–222°C (bp 222°C [35]). ^{1}H NMR spectrum, δ, ppm: 1.46–1.66 m (6H, $3CH_2$), 3.31 d. t (4H, $2CH_2N$, *J* 11, 26 Hz), 7.80 s (1H, CHO).

***N*-Formylmorpholine (VId)**. *a*. Synthesis was performed similarly according to procedure *a* from 5 g (0.11 mol) of formamide, 0.9 g (0.005 mol) of $CuCl_2·2H_2O$, and 9.6 g (0.11 mol) of amine **Vd**. Yield 10.7 g (0.093 mol, 85%), bp 238–241°C (bp 239–241°C, mp 20–23°C [36]). ^{1}H NMR spectrum, δ, ppm: 3.34 d.t (4H, $2CH_2N$, *J* 9.3, 15.6 Hz), 3.51 d. t (4H, $2CH_2O$, *J* 9.3, 15.8 Hz), 7.89 s (1H, CHO).

b. Synthesis was performed similarly to compound **VIa** according to procedure *a* from 5 g (0.067 mol) of dimethylformamide, 0.51 g (0.003 mol) of $CuCl_2·2H_2O$, and 5.8 g (0.067 mol) of morpholine at 60°C for 1 h. Yield 6.6 g (0.057 mol, 85%), bp 239–241°C.

***N*-Cyclohexylacetamide (VIe)** was prepared similarly to compound **VIa** according to procedure *a* from 5 g (0.085 mol) of acetamide, 0.51 g (0.003 mol) of $CuCl_2·2H_2O$, and 8.2 g (0.085 mol) of amine **Va** at 60°C; reaction time 1 h. Yield 10.3 g (0.073 mol, 86%), bp 289–292°C (bp 291–293°C [32]).

1-(3-Methylbutanoyl)piperidine (VIf) was prepared similarly to compound **VIa** according to procedure *b* from 5 g (0.05 mol) of compound **IVd**, 0.06 g (0.001 mol) of copper nanoparticles, and 4.2 g (0.05 mol) of amine **Vc** at 80–100°C for 3 h. Yield 7.2 g (0.043 mol, 85%), bp 142–145°C (20 mmHg). ^{1}H NMR spectrum, δ, ppm: 0.87 m (6H, $2CH_3$), 1.59 s (2H, CH_2), 1.58 d (2H, CH_2, *J* 4.2 Hz), 2.06 m (2H, CH_2CO), 3.38 d. t [4H, $(CH_2)_2N$, *J* 27.2, 9.6 Hz].

***N*-(Cyclohexyl)succinimide (VIIIa)** was prepared similarly to compound **VIa** according to procedure *b* from 5 g (0.05 mol) of imide **VIIa**, 0.06 g (0.001 mol) of copper nanoparticles, and 7.9 g (0.08 mol) of amine **Va** for 2 h. Yield 6.9 g (0.038 mol, 76%), mp 165–166°C, bp 139–142°C (20 mmHg) (mp 164–166°C, bp 322.7°C (760 mmHg) [36]). ^{1}H NMR spectrum, δ, ppm: 1.17–2.13 m (10H, $5CH_2$), 2.49 s [4H, $2CH_2C(O)$], 3.79 m (1H, CHN).

***N*-Benzylsuccinimide (VIIIb)** was prepared similarly to compound **VIa** according to procedure *b* from 5 g (0.05 mol) of imide **VIIa**, 0.06 g (0.001 mol) of copper nanoparticles, and 9.6 g (0.09 mol) of amine **Ve** at 50°C for 3 h. Yield 7 g (0.037 mol, 74%), mp 99–100°C (mp 98–99°C [37]). ^{1}H NMR spectrum, δ, ppm: 2.52 s [4H, $2CH_2C(O)$], 4.48 s (2H, CH_2N), 7.14–7.29 m (5H, C_6H_5).

***N*-Butylphthalimide (VIIIc)** was prepared similarly to compound **VIa** according to procedure *b* from 6 g (0.041 mol) of imide **VIIb**, 0.06 g (0.001 mol) of copper nanoparticles, and 7.3 g (0.1 mol) of amine **Vf** for 3 h. Yield 5.9 g (0.029 mol, 70%), mp 28–31°C (mp 29–33°C [38]). ^{1}H NMR spectrum, δ, ppm: 0.89 t (3H, CH_3, *J* 14.7 Hz), 1.23–1.34 m (2H, CH_2), 1.50–1.60 m (2H, CH_2), 3.51 t (2H, CH_2N, *J* 14.4 Hz), 7.60–7.69 m (4H, C_6H_4).

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