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Colloid and Nanosize Catalysts in Organic Synthesis: VII.[1] Catalysis with Copper Colloid Particles in Leucart–Wallach Reaction

Yu. V. Popov, V. M. Mokhov, and I. I. Budko

Volgograd State Technical University, pr. Lenina 28, Volgograd, 400131 Russia
e-mail: tons@vstu.ru

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Abstract—Modification of Leucart–Wallach reaction using catalytic amounts of copper colloid particles was developed. Reductive amination of a series of cyclic ketones proceeds at 100°C under a small excess of formamide or of alkyl(aryl)ammonium formate.

Keywords: reductive amination, colloid copper, cyclic ketones, formamide, ammonium formate, formic acid

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The Leucart–Wallach reaction is widely used as the preparative method the preparation of amines from carbonyl compounds. In the classic protocol of this reaction besides the corresponding aldehyde or ketone a significant molar excess of formamide or the corresponding formylamino derivative (up to 20-fold) and of formic acid (up to 10-fold) is used. The temperature of the process (save with aldehydes and lower ketones) is above 160°C, most commonly 180–200°C. Despite of the rigid reaction conditions the yields of amines are as a rule considerably high (60–90%) [2]. But along with some advantages this reaction has also faults like considerable tarring of the reaction mixture arising from the prolonged heating, significant consumption of formamide and formic acid, prolonged reaction time (12–18 h), high demands to the absence of water in starting reagents. Besides, in the course of the reaction not the target amines, but the corresponding formamides are formed requiring prolonged hydrolysis and the subsequent isolation of products.

As the classic protocol requires considerably rigid conditions a series of works dealing with its modification by using the metal complex catalysis was carried out [3–5]. Since the platinum group metal compounds are expensive and difficultly available the application these modifications is significantly limited. Therefore the search for cheap and available catalyst of the hydroamination reaction is topical.

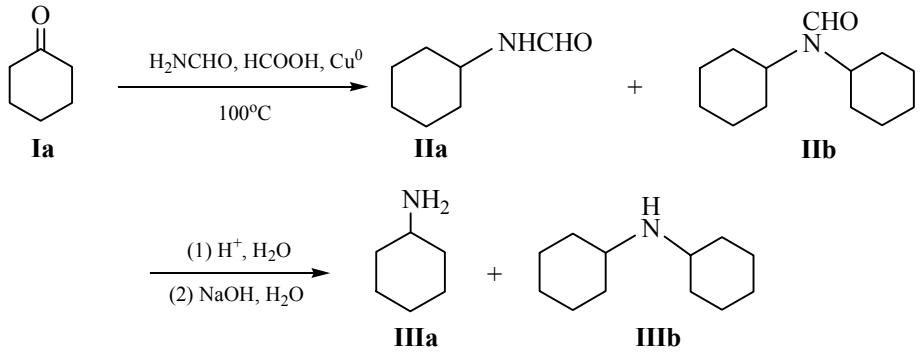
We have found that a series of cyclic ketones enters the Leucart–Wallach reaction under the significantly milder conditions while using the quasi homogeneous catalysis with ultra-disperse copper particles capable of formation of the clear homogeneous colloid solution in water or the reaction mixture corresponding to the particle size below 100 nm [6].

Synthesis of the colloid copper solution was carried out by the exchange between the copper(II) chloride and quickly rotating iron element of the magnetic stirrer in formamide or 4 : 1 formamide–water mixture. After supersaturation of the solution the separation of the colloid copper particles is possible by centrifugation or prolonged filtering through the paper filter with the subsequent washing with distilled water, acetone, and drying in a vacuum. Using of catalyst is possible in the form of ultra-disperse powder as well as of its formamide solution without isolation.

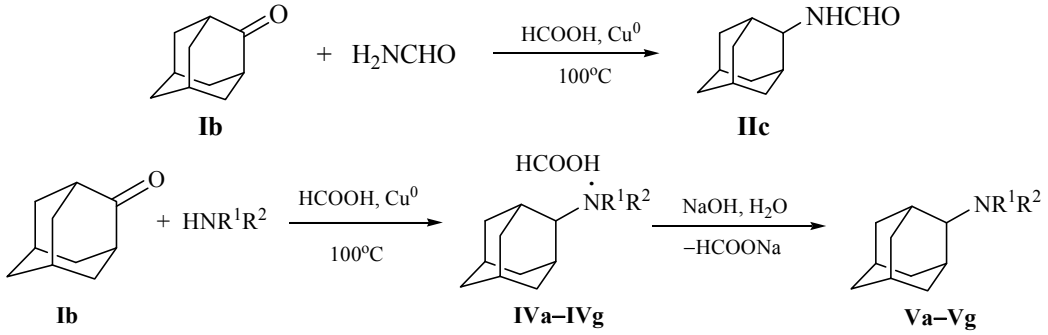
Methyl *n*-butyl ketone, methyl isobutyl ketone, cyclopentanone, cyclohexanone, racemic camphor, and adamantan-2-one were used as starting ketones. It was found that cyclohexanone in the presence of ultra-disperse copper enters the reaction with formamide and formic acid at 100°C. A significant (60–70%) conversion of ketone is achieved in 3 h (Scheme 1).

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

Scheme 1.



Scheme 2.



R^1 = H, R^2 = Bu (**IVa, Va**), $(CH_2)_2OH$ (**IVb, Vb**), Ph (**IVc, Vc**), Cy (**IVd, Vd**), or R^1R^2 = $–(CH_2)_5–$ (**IVe, Ve**), $–(CH_2)_2O(CH_2)_2–$ (**IVf, Vf**), $–(CH_2)_2NH(CH_2)_2–$ (**IVg, Vg**).

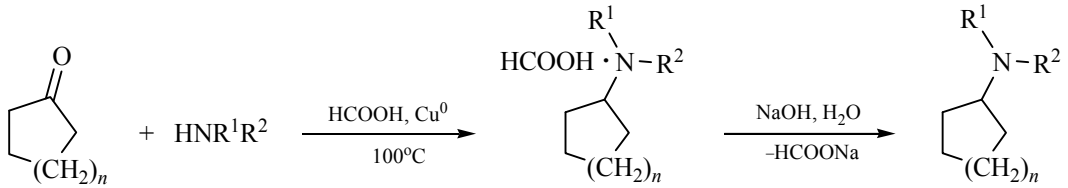
It was found that proceeding of the reaction under these conditions does not depend strongly on the absence of water. In presence of up to 10% of water it proceeds with the satisfactory rate. It was shown that under the excess of formamine lower than the 3-fold the formation of the formyldicyclohexyl derivative **IIb** together with the formylaminocyclohexane **IIa** takes place. At the equimolar ratio of ketone **Ia** and formamide these substances are obtained in the nearly equal ratio. The optimum ratio of ketone **Ia**, formamide, and formic acid is 1 : 3 : 3–3.5. Under these conditions the consumption of reagents is the lowest, complete conversion of cyclohexanone at 100°C is achieved in 4–5 h, and the yield of amines **IIIa, IIb** after the hydrolysis of the derivatives **IIa, IIb** reaches 85%.

Ketones of the scaffold structure are interesting as the substrates in the Leucart–Wallach reaction with secondary amines because in this case enolization is complicated or impossible. Adamantanone-2 **Ib** is the absolutely non-enolizable ketone, but it successfully reacts with formamide under the conditions analogous to the above-described to give formylaminoadamantane. It was found that ketone **Ib** at 100°C is considerably less reactive than cyclohexanone because of its partial sublimation under the reaction conditions. The increase in the reaction time to 6–7 h and the use of a small amount of inert solvent (2–3 mL of benzene) returning ketone **Ib** in the reaction mixture permitted to obtain the target product in 82% preparative yield.

One of the faults of the Leucart–Wallach reaction is the formation not of the free amines, but of the corresponding amides requiring the hydrolysis which is often prolonged and proceeds under rigid conditions. Therefore we have used not formamides, but primary and secondary amine formates as reagents. The reaction was carried out at the ketone : amine : formic acid molar ratio 1 : 3 : 5–6 at 100°C in the presence of catalytic amounts of ultra-disperse copper in the course of 3–8 h (Scheme 2).

As it was expected, the reaction products were not the formyl derivatives, but the ammonium formates **IVa–IVg**. It significantly facilitated the isolation of free bases. Ammonium formates are also used in the classic Wallach-Leucart protocol, but above 160°C the

Scheme 3.



Ia, Ic **IVh–IVl** **Vh–Vl**

n = 2 (**Ia**), n = 1 (**Ic**); n = 1, R^1R^2 = –$(CH_2)_5$– (**IVh, Vh**); n = 2, R^1R^2 = –$(CH_2)_5$– (**IVi, Vi**); n = 2, R^1 = H, R^2 = Cy (**IVj, Vj**), CH_2CH_2OH (**IVk, Vk**), $(CH_2)_7CH_3$ (**IVl, Vl**).

dehydration of these salts leads to the corresponding amides.

It was found that in the reaction of ketone **Ib** with piperidine under the above-mentioned conditions only 55% conversion of ketone is achieved. The increase in the reaction time to 6 h leads to 90% conversion, and the complete consumption of ketone is observed in 8 h. To confirm the catalytic action of copper nanoparticles in the reaction of ketone **Ib** with piperidine the syntheses in presence of roughly disperse copper, copper(I) chloride, copper(II) chloride, and also in the absence of catalyst were carried out. All of them were performed under the identical conditions, and no distinguishable amount of the target product was found in all cases. It proves that just the specific catalysis with the colloid copper particles takes place. Nowadays it is difficult to explain the effect of this catalysis, but it is presumable that formic acid under these conditions acts by an alternative mechanism.

As is known, the thermal decomposition of formic acid proceeds according to two pathways. One of them leads to the formation of hydrogen and carbon dioxide, while according to another one water and carbon monoxide are obtained. In the series of works it was shown that on the surface of nanoparticles of metals like silver, palladium, and gold the decomposition of formic acid proceeds under mild conditions exclusively with the liberation of hydrogen [7–10]. Hence, the intermediates obtained from ketone and amine are reduced to target amines with hydrogen on the surface of metal nanoparticles. It may explain the decrease in temperature of the beginning of the Leucart–Wallach reaction by 60–80°C under the catalysis with the colloid copper. The optimum temperature of synthesis is 100–105°C. At higher temperature the transformation of formates to formamides was observed, and below 100°C no reaction took place evidently due to the absence of generation of hydrogen from formic acid.

The reaction of the other cycloalcanones with amines was successfully carried out under the same conditions (Scheme 3).

It is interesting that the attempt to involve the ketones of linear structure in the reaction with piperidine under the above-mentioned conditions was unsuccessful. It may be due to the specific features of the catalysis used or sterical complications to the attack of linear ketones caused by the free rotation of the butyl or isobutyl group.

In contrast to adamantanone-2 D,L-camphor does not enter the reactions with piperidine formate and formamide under the conditions under study. It also can be attributed to the presence of methyl substituents sterically hindering the proceeding of this reaction.

The composition and structure of compounds synthesized were confirmed by the ^{1}H NMR spectroscopy. Properties of known compounds agree with the published data. The structure of adamantyl-containing amines is confirmed by the presence of 14-proton multiplet signal from the 2-substituted adamantyl group (1.3–2.0 ppm) and of the signal of proton in the position 2 of adamantane fragment at 2.0–2.7 ppm bound with nitrogen atom. Protons of cycloalkyl groups of amines often overlap with the signals of adamantyl group. Characteristic signals of the methylene group protons bound with nitrogen or oxygen appeared as triplets at 2.5 ppm and 3.5 ppm respectively.

Syntheses of 2-adamantylpiperazine and 2-adamantylmorpholine according to the classic version of the Leucart–Wallach reaction showed evident advantages of the procedure developed by us. For example, noncatalytic reaction of adamantan-2-one with piperazine and morpholine in the presence of formic acid proceeded at the temperature no lower than 180°C during 10–12 h. The target products were obtained in the yields 55% and 43% respectively. The formation of

the significant amount of tar was observed along with the incomplete conversion of adamantan-2-one.

Hence, new modification of the Leucart–Wallach reaction developed by us permits to carry out hydroamination of ketones under mild conditions and in good yields. Ketones exhibiting moderate reactivity in this process can be used as well. The catalyst used is sufficiently available and in some cases can be obtained in situ directly in the reaction mixture. This method requires lower excess of other reagents and permits to obtain amines in the form of formates and not the amides facilitating the isolation of products.

EXPERIMENTAL

^{1}H NMR spectra were taken on a Varian Mercury-300 (300 MHz) spectrometer in carbon tetrachloride, internal reference HMDS. Chromatomass spectra were obtained on the Varian Saturn 2100 T/GC3900 spectrometer.

Cyclohexylamine (IIIa). Formamide, 22.5 g (0.5 mol), intensely stirred with the iron (steel) magnetic element of the magnetic stirrer without a cover was treated with 1.34 g (0.008 mol) of $CuCl_2 \cdot 2H_2O$ and heated to 80–100°C for 30 min until the formation of red-brown colloid solution. After that 16.3 g (0.167 mol) of cyclohexanone **Ia** and 38.4 g (0.84 mol) of formic acid were added. The reaction mixture was stirred for 4 h at 100°C. During this period of time its complete homogenization was achieved. Water, 100 mL, and 150 mL of 33% hydrochloric acid were added, and cyclohexylamine derivatives **IIa** and **IIb** were hydrolysed by boiling for 1–1.5 h. After that sodium hydroxide was added with shaking until the weakly basic reaction of the medium, and the mechanical admixtures were filtered off. Free base was twice extracted from the filtrate with diethyl ether (2 × 20 mL). Ether was removed, and the residue was distilled at atmospheric pressure to give 11.4 g (0.117 mol, 70%) of amine **IIIa**, bp 132–134°C, n_D^{20} 1.4314 (bp 134°C, n_D^{20} 1.4318 [11]). Distillation of the still gave 2.2 g (0.012 mol) of dicyclohexylamine **IIIb**, bp 269–272°C, n_D^{20} 1.4844 (bp 279°C, n_D^{20} 1.4842 [11]).

2-Formylaminoadamantane (IIc). To a mixture of 32 mL of formamide and 8 mL of water intensely stirred with an iron magnetic element of the magnetic stirrer 15.4 g of $CuCl_2 \cdot 2H_2O$ was added and the resulting mixture was heated at 80–100°C for 4 h. After super-saturation of the solution colloid nanoparticles were removed by multiple filtration through a paper filter. The precipitate formed was twice washed with 30 mL of water, then with 30 mL of acetone, and dried in a vacuum. A mixture of 4.5 g (0.1 mol) of formamide and 0.3 g of the colloid copper prepared as described above was heated to 100°C. After that 5 g (0.033 mol) of adamantanone-2 **Ib,** 3 mL of benzene**,** and 9.1 g (0.2 mol) of formic acid were added. The reaction mixture was stirred for 8 h at 100°C. Then the solvent was removed, 100 mL of water was added, white precipitate was filtered off, washed with water, and dried. Compound **IIc**, 5 g (0.026 mol, 79%) was obtained, mp 139–140°C (mp 140–141°C [12]). ^{1}H NMR spectrum, δ, ppm: 1.57–2.03 m (14H, 2-Ad), 4.00 s (1H, CH–N, 2-Ad), 6.44 br.s (1H, NHCO), 7.99 s (1H, CHO).

***N*-2-Adamantylbutylamine (Va)**. Analogously to **IIc** from 5 g (0.033 mol) of ketone **Ib,** 7.3 g (0.1 mol) of 1-butylamine**,** 9.2 g (0.2 mol) of formic acid, and 0.2 g of colloid copper after decomposition of salt **IVa** with sodium hydroxide solution, extraction with diethyl ether, removing of solvent, and distillation in a vacuum 5.6 g (0.027 mol, 81%) of amine **Va** was obtained, bp 187–188°C (20 mmHg), n_D^{20} 1.5026 (n_D^{20} 1.5020 [13]). ^{1}H NMR spectrum, δ, ppm: 0.56 s (1H, NH), 0.853 t (3H, CH_3, J = 13.8 Hz), 1.32–1.75 m (12H, 2-Ad, 4H, $2CH_2$), 1.81 d (2H, 2-Ad, J = 12.9 Hz), 2.47 q (2H, CH_2N, J = 12.6 Hz), 2.61 s (1H, CH–N, 2-Ad). Mass spectrum (electron impact, 70 eV), *m/e* (I_{rel}, %): 208.2 (100) [M + 1], 164.0 (81), 135.1 (71) [Ad^+], 107.1 (10), 79.2 (5).

2-(2-Adamantyl)aminoethanol (Vb). Analogously to **IIa** from 5 g (0.033 mol) of ketone **Ib,** 6.1 g (0.1 mol) of monoethanolamine, 8.8 g (0.19 mol) of formic acid and 0.25 g of colloid copper 5.1 g (0.026 mol, 78%) of aminoalcohol **Vb** was obtained, mp 118–120°C (mp 111.5–113°C [14]). ^{1}H NMR spectrum, δ, ppm: 0.82 br.s (1H, NH), 1.43–2.01 m (14H, 2-Ad), 2.63 s (1H, CH–N, 2-Ad), 2.75 q (2H, CH_2N, J = 10.3 Hz), 2.87 br.s (1H, OH), 3.61 t (2H, OCH_2, J = 10.2 Hz).

***N*-2-Adamantylaniline (Vc)**. Analogously to **Va** from 3 g (0.02 mol) of ketone **Ib,** 4.6 g (0.05 mol) of aniline, 4.6 g (0.1 mol) of formic acid and 0.2 g of colloid copper 3.5 g (0.015 mol, 77%) of amine **Vc** was obtained, bp 214–216°C (20 mmHg), mp 150–152°C (mp 150–153°C [15]). ^{1}H NMR spectrum, δ, ppm: 1.50–1.97 m (14H, 2-Ad), 3.43 s (1H, CH–N), 3.50 br.s (1H, NH), 6.37-6.98 m (5H, Ph).

***N*-2-Adamantylcyclohexylamine (Vd)**. Analogously to **Va** from 3 g (0.02 mol) of ketone **Ib,** 6 g (0.06 mol)

of cyclohexylamine, 4.6 g (0.1 mol) of formic acid and 0.25 g of colloid copper 3.3 g (0.014 mol, 71%) of the amine **Vd** was obtained, bp 205–207°C (18 mmHg). ^{1}H NMR spectrum, δ, ppm: 0.60 br.s (1H, NH), 0.94–1.99 m [14H, 2-Ad, 10H, $(CH_2)_5$], 2.38 m (1H, CH–N, Cy), 2.75 s (1H, CH–N, 2-Ad). Found, %: C 82.29; H 11.64, N 6.07. $C_{16}H_{27}N$. Calculated, %: C 82.34; H 11.66, N 6.00.

***N*-2-Adamantylpiperidine (Ve)**. Analogously to **Va** from 5 g (0.033 mol) of ketone **Ib,** 10 g (0.12 mol) of piperidine, 8.8 g (0.19 mol) of formic acid and 0.25 g of colloid copper 5.55 g (0.025 mol, 76%) of amine **Ve** was obtained, bp 166–168°C (10 mmHg), n_D^{20} 1.5281 (n_D^{20} 1.5250 [13]). ^{1}H NMR spectrum, δ, ppm: 1.27–1.76 m [10H, 2-Ad, 6H $(CH_2)_3$],1.92 s (1H, CH–N, 2-Ad), 2.00 s (4H, 2-Ad), 2.28 br.s [4H, $N(CH_2)_2$].

***N*-2-Adamantylmorpholine (Vf)**. Analogously to **Va** from 5 g (0.033 mol) of ketone **Ib,** 10 g (0.12 mol) of morpholine, 8.8 g (0.19 mol) of formic acid and 0.3 g of colloid copper 5.2 g (0.024 mol, 70%) of amine **Ve** was obtained, bp 223–225°C (20 mmHg), mp 39–42°C (mp 38–40°C [13]). ^{1}H NMR spectrum, δ, ppm: 1.25–1.78 m (10H, 2-Ad), 1.92 s (4H, 2-Ad), 1.99 s (1H, CH–N, 2-Ad), 2.26 br.s [4H, $N(CH_2)_2$], 3.51 t [4H, $O(CH_2)_2$, J = 9.6 Hz].

***N*-2-Adamantylpiperazine (Vg)**. Analogously to **Va** from 5 g (0.033 mol) of ketone **Ib,** 11 g (0.13 mol) of piperazine, 15 g (0.33 mol) of formic acid and 0.3 g of colloid copper 5.4 g (0.025 mol, 74%) of amine **Vg** was obtained, bp 235–237°C (20 mmHg), mp 68–70°C (mp 67–70°C [16]). ^{1}H NMR spectrum, δ, ppm: 0.82 br.s (1H, NH), 1.33–2.02 m (14H, 2-Ad), 1.99 s (1H, CH–N, 2-Ad), 2.36 m [4H, $N(CH_2)_2$], 2.75 s (1H, CH–N, 2-Ad), 3.36 d.t [4H, $N(CH_2)_2$, J_1 = 31.5 Hz, J_2 = 9.9 Hz].

***N*-Cyclopentylpiperidine (Vh)**. Analogously to **Va** from 11 g (0.13 mol) of ketone **Ic,** 33.4 g (0.4 mol) of piperidine, 30 g (0.65 mol) of formic acid and 0.75 g of colloid copper without the addition of benzene 16.5 g (0.108 mol, 83%) of amine **Vh** was obtained, bp 230–231°C, n_D^{20} 1.4840 (bp 230°C [14]).

***N*-Cyclohexylpiperidine (Vi)**. Analogously to **Vg** from 9.8 g (0.1 mol) of ketone **Ia,** 26 g (0.3 mol) of piperidine, 25 g (0.5 mol) of formic acid and 0.6 g of colloid copper 13.3 g (0.08 mol, 80%) of amine **Vi** was obtained, bp 232–234°C, n_D^{20} 1.4842 (bp 234°C [14]).

Dicyclohexylamine (Vj). Analogously to **Vg** from 9.9 g (0.1 mol) of cyclohexylamine**,** 7.6 g (0.165 mol) of formic acid, 0.3 g of colloid copper, and 3.3 g (0.033 mol) of ketone **Ia** 4.1 g (0.022 mol, 68%) of amine **Vi** was obtained, bp 269–270°C, n_D^{20} 1.4839 (bp 270°C, n_D^{20} 1.4842 [11]).

***N*-Cyclohexylaminoethanol (Vk)**. Analogously to **Vg** from 9.8 g (0.1 mol) of ketone **Ia,** 18 g (0.295 mol) of 2-aminoethanol, 20 g (0.435 mol) of formic acid and 0.4 g of colloid copper 11.2 g (0.078 mol, 78%) of amine **Vk** was obtained, n_D^{20} 1.4870 (n_D^{20} 1.4865 [17]). ^{1}H NMR spectrum, δ, ppm: 1.01-1.18 m (10H, Cy), 2.31–2.44 m (1H, CHN), 2.59 t (2H, CH_2–N, J = 9.4 Hz), 3.49 t (2H, OCH_2, J = 9.4 Hz), 3.75 br.s (2H, NH, OH).

***N*-Cyclohexyl-*N*-octylamine (Vl)**. Analogously to **Vg** from 9.8 g (0.1 mol) of ketone **Ia,** 32.3 g (0.25 mol) of 1-octylamine, 20 g (0.435 mol) of formic acid and 0.5 g of colloid copper 18.6 g (0.088 mol, 88%) of amine **Vl** was obtained, bp 159–160°C (20 mmHg). ^{1}H NMR spectrum, δ, ppm: 0.83 t (3H, CH_3, J = 12 Hz), 0.94–1.76 m (22H, $11CH_2$), 2.29 br.s (1H, NH), 2.48 t (2H, CH_2N, J = 13.5 Hz), 3.07–3.14 m (1H, CHN). Mass spectrum (electron impact, 70 eV), *m/e* (I_{rel}, %): 212.1 (100) [M + 1], 168.1 (35), 148.9 (18), 112.1 (45) [M – C_7H_{16}]. Found, %: C 79.51; H 13.88; N 6.61. $C_{14}H_{29}N$. Calculated, %: C 79.55, H 13.83, N 6.63, M 211.39.

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