ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 4, pp. 622–628. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © V.M. Mokhov, Yu.V. Popov, D.N. Nebykov, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 4, pp. 541–547.

Colloid and Nanodimensional Catalysts in Organic Synthesis: II.[1] The Hydrogenation of Alkenes with Hydrogen at Atmospheric Pressure

V. M. Mokhov, Yu. V. Popov, and D. N. Nebykov

Volgograd State Technical University, pr. Lenina 28, Volgograd, 400005 Russia
e-mail: tons@vstu.ru

Received May 14, 2013

Abstract—Colloid particles of metals of varying valence are found to be relatively cheap and easily prepared catalyst permitting the the hydrogenation under mild conditions. Procedure of reduction of unsaturated compounds with gaseous hydrogen at atmospheric pressure and low temperaturehas been developed. Colloid solutions of metals from the series iron, nickel, cobalt, chromium, manganese or their mixtures were prepared in situ directly in the reaction mixture. Selective the hydrogenation of multiple carbon–carbon bonds without the reduction of a series of functional groups was observed.

Keywords: catalyst, nanoparticles, alkenes, the hydrogenation
DOI: 10.1134/S1070363214040033

The hydrogenation of multiple carbon–carbon bonds is one of fundamental reactions in chemical industry as well as in organic synthesis. This process is usually carried out according to classical method of heterogenic catalytic the hydrogenation using nickel, platinum, rhodium or ruthenium as catalysts [2]. Nickel catalyst is most widely used, but for the successful hydrogenation high temperature and pressure are often necessary. For the hydrogenation under milder conditions good results were shown by platinum and palladium. Rhodium and ruthenium exhibiting high selectivity in the reduction of unsaturated alcohols, halides, and esters without the the hydrogenation of functional group are also used in the organic synthesis [3].

Nowadays more and more often the catalysts in a form of nanoparticles or their colloid solutions begin to be used. It opens many new possibilities in chemical synthesis. A series of works dealing with the search for the method of organic substrates the hydrogenation in the presence of metal nanoparticles was recently published. The reduction of some nitroarenes using nickel nanoparticles was carried out [4]. For the reduction of styrene and its derivatives on nickel nanoparticles temperature up to 130°C and pressure about 30 bar were used [5]. The the hydrogenation on nickel nanoparticles was carried out also under milder conditions [6]. The the hydrogenation of some unsaturated compounds and nitroarenes was carried out over palladium nanoparticles at atmospheric pressure of hydrogen [7]. Palladium nanoparticles were synthesized by reduction of palladium chloride with sodium borohydride.

The hydrogenation of alkenes with nickel nanoparticles using alcohols as hydrogen donors was performed [8]. The reaction proceeded under very mild conditions. Nickel nanoparticles were synthesized by the reduction of nickel chloride with lithium in the presence of 4,4'-bis(*tert*-butyl)biphenyl in THF. The attempts of hydrogenation of some olefins on this catalyst at milligram loadings of starting reagents and the significant excess of catalyst with respect to hydrogenated substrate were reported [9]. Iron nanoparticles prepared by reduction of iron salts with Grignard reagents were used for the hydrogenation of alkenes with hydrogen at 10–20 atm [10].

Performing of the hydrogenation with gaseous hydrogen in the laboratory conditions using cheap and available catalysts as Raney nickel is complicated due to the necessity of using high pressures and temperatures. Using of highly active and selective rhodium, ruthenium, or palladium complexes is often too expen-

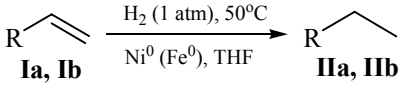
[1] For communication I, see [1].

sive. By the same reason it is inconvenient to use nanodimensional catalysts of palladium and platinum group.

The aim of this study is the search for comparatively cheap easily manufactured catalysts permitting to carry out the hydrogenation of olefins under relatively mild conditions. For the achievement of this goal a procedure of liquid phase hydrogenation of unsaturated compounds while bubbling gaseous hydrogen at atmospheric pressure was developed. Nanoparticles of transition metals like nickel, cobalt, iron, manganese, chromium or their mixtures which were prepared directly in the reaction mixture were used as catalysts. Some alkenes of normal structure, cyclohexene, derivatives of styrene and norbornene-5, α-pinene, β-pinene, and camphene were used as substrates.

The catalytic solution was prepared in the reaction volume directly before the hydrogenation. Lithium aluminum hydride was suspended in THF in a flat bottom flask, and anhydrous metal salts of the transition metals were added in a required ratio. After reduction of salts, black colloid solution of metal clear in thin layer was formed. The formation of metal nanoparticles of the size from 3 to 10 nm depending on the conditions of synthesis was reported [6, 7, 11]. The catalytic solution was mixed with hydrogenated alkene, and excess of gaseous hydrogen was bubbled at atmospheric pressure for 4–6 h at room or slightly increased temperature. In the course of the reaction the catalyst coagulated to give the particle agglomerates which could be removed by centrifugation or filtration. For the acceleration of coagulation several drops of water were added in the reaction mixture. The target product was isolated by distillation at atmospheric pressure or in a vacuum.

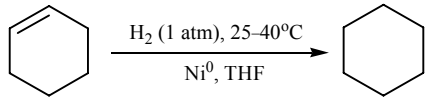
The hydrogenation of octene-1 **Ia** and decene-1 **Ib** was carried out at 40–50°C and bubbling of hydrogen through the stirred homogenic mixture of hydrocarbon **Ia, Ib** and a solution of nickel nanoparticles in THF for 6 h. Yields of the products **IIa, IIb** after removing the catalyst and distillation were 70 and 87% respectively. Chromatomass spectral analysis showed practically complete conversion of starting substances. Good catalytic activity was shown also by iron nanoparticles in the hydrogenation of compound **Ib**. Yield of product **IIb** was 83%.



Ia, Ib **IIa, IIb**

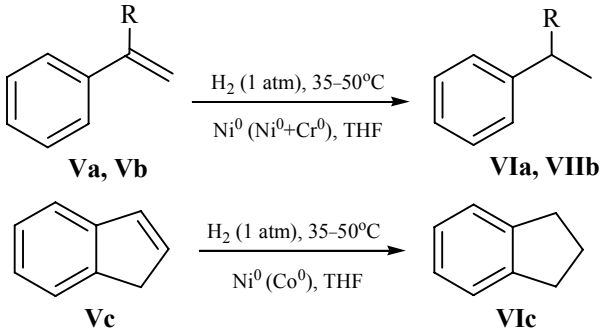
R = *n*-C_6H_{13} (**Ia, IIa**), *n*-C_8H_{17} (**Ib, IIb**).

It was shown that cycloalkenes enter this reaction still more easily. For example, cyclohexene **III** was hydrogenated on nickel nanoparticles to cyclohexane **IV** at 25–40°C within 3–4 h.



III **IV**

This method of the hydrogenation was applied to styrene **Va**, α-methylstyrene **Vb**, and indene **Vb**. Nickel and cobalt nanoparticles and a mixture of nanoparticles of nickel and chromium were used as catalysts. Yields of the products **VIa–VIc** were 76–82%. The hydrogenation of aromatic ring in the compounds **Va–Vc** was not observed.



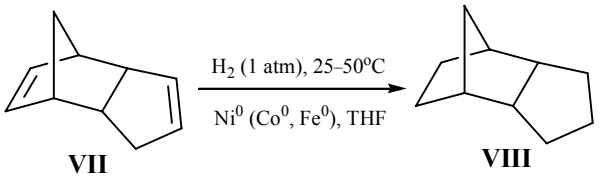
R = H (**Va, VIa**), Me (**Vb, VIb**).

It was found that the presence of aluminum chloride formed in the course of synthesis of colloid solutions of metals did not lead to significant polymerization of olefins evidently due to its complex formation with lithium chloride or solvent (THF). An insignificant still amount was found only in the case of the hydrogenation of styrene **Va** (5–7% from the mass of taken styrene).

As known, styrene derivatives were hydrogenated on a nickel applied on nanoferrite at room temperature and hydrogen pressure about 7 at [12]. Hence, while using our catalysts even compound **Vc** was hydrogenated under milder conditions because for its hydrogenation on the Raney nickel about 120 bar pressure was required.

The developed catalytic system underlain by the nickel colloid particles showed its effectiveness also in the reduction of norbornene derivatives. Hence, while the hydrogenation of dicyclopentadiene **VII** the product of exhaustive hydrogenation, tetrahydrodicyclopentadiene **VIII,** was formed. Note that the

reaction proceeded just at room temperature and was accompanied by noticeable heat evolution. The same reaction in the presence of cobalt or iron nanoparticles proceeded analogously readily at 25–50°C. For comparison, the industrial hydrogenation of compound **VII** on nickel catalyst proceeds at 3.5 bar [14].

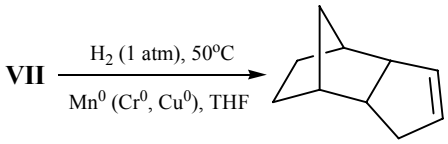


VII **VIII**

Chromatomass spectra of the reaction mixture obtained while hydrogenating dicyclopentadiene at 65–70°C show that significant increase in temperature lead to partial (5–10%) skeleton rearrangement of hydrogenated hydrocarbon **VIII** over the aluminum chloride complexes present in the reaction mixture.

It was found that for a successful hydrogenation of hydrocarbon **VII** 5–10 mol % of the catalyst is required. The relative cheapness of materials used for preparing the catalyst permits avoiding its regeneration in the laboratory.

Using colloid manganese solution led to selective partial hydrogenation of diene **VII** to 5,6-dihydrocyclopentadiene **IX** in about 80% yield.



IX (16–78%)

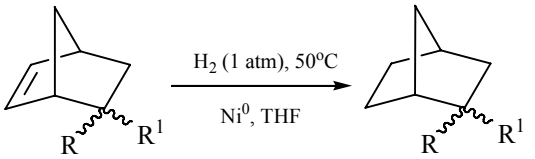
Using colloid chromium particles as the catalyst in this reaction led to low conversion of hydrocarbon **VII** and the formation of product **IX** in 28% yield. No formation of the product of the exhaustive hydrogenation of **VII** was observed. An attempt to use copper catalyst obtained analogously to the colloid solutions of metals of nickel group showed its low effectiveness even at higher duration of the reaction. Yield of product **IX** was only 16%. Non-effectiveness of this catalyst for the hydrogenation of compound **Va** was also demonstrated.

Hence, highest catalytic activity in the hydrogenation of alkenes was shown by nanoparticles of metals of VIII group what is not surprising considerating their wide use as the hydrogenation catalysts. On the other hand, the use of the other metals in some cases may be effective for performing of the selective hydrogenation of a single multiple bond.

The investigation of the possibility of recycling the catalyst by an example of nickel nanoparticles showed that even insignificant contact with air or water lead to a decrease in the activity of catalyst which in some cases may be used for performing selective hydrogenation. Hence, the use of regenerated nickel catalyst led to selective hydrogenation of only norbornene fragment of molecule **VII** and the formation of substance **IX**.

With the purpose of studying the possibility of the hydrogenation of functional groups and the investigation of selectivity of the competing reduction reactions of some norbornene derivatives like 2-cyanonorbornene-5 **Xa**, 2-carboxynorbornene-5 **Xb**, and methyl 2-methylnorborn-5-ene-2-carboxylate **Xc** were chosen.

The hydrogenation of compounds **Xa–Xc** was carried out at 25–50°C. Their lower reactivity as compared to substrate **VII** was marked. By means of ^{1}H NMR spectroscopy and chromatomass spectrometry the hydrogenation of unsaturated bonds and complete preservation of functional groups in the reaction products was shown.



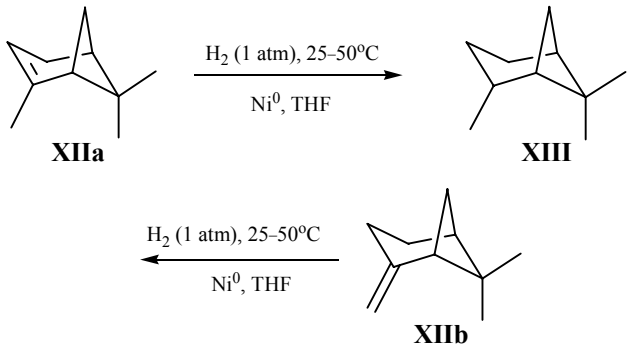
Xa–Xc **XIa–XIc**

R = H, R^1 = CN (**Xa, XIa**), COOH (**Xb, XIb**), R = Me, R^1 = C(O)OMe (**Xc, XIc**).

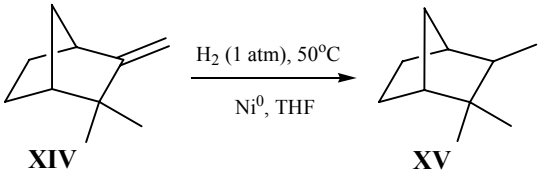
Note that the hydrogenation of **Xb** was accompanied by its reaction with the colloid nickel catalyst and the formation of the corresponding nickel salt. For the successful hydrogenation of carboxylic acids gradual addition of catalytic solution and subsequent treatment of the reaction mixture with mineral acid for complete isolation of hydrogenated product are required.

Hence, the developed method of the hydrogenation does not permit to reduce functional groups under the used reaction conditions, but it is promising for selective hydrogenation of multiple bonds with the preservation of functional substituents and may be used in fine organic synthesis.

Results of the hydrogenation of α- and β-pinenes **XIIa, XIIb** occurred to be unexpected. Chromatomass spectrometry and ^{1}H NMR spectra of the reaction mixture showed that the conversion of these compounds was low (45–50%), and it does not alter at the increase in temperature from 20 to 50°C and the prolongation of the process. Nevertheless it was shown that *exo*- as well as *endo*-cyclic double bond were subjected to hydrogenation.



Analogous results were obtained also in the hydrogenation of camphene **XIV**. Its conversion was only 55%.



This fact can be explained not only by steric features of pinene and camphene structure, but also by possible reversibility of the hydrogenation-dehydrogenation of these olefins on the catalyst under study, which requires the use of high pressure of hydrogen for successful performing the process.

Structures of the compounds synthesized were proved by ^{1}H NMR spectroscopy and also in some cases by chromatomass spectrometry. Physicochemical properties of compounds were in agreement with the published data.

Performed studies showed the prospect of further studies in the field of development of convenient and selective methods of hydrogenation of multiple carbon–carbon bonds with hydrogen under the laboratory conditions needing no high pressures and temperatures and expensive catalysts and equipment.

EXPERIMENTAL

^{1}H NMR spectra of obtained compounds were taken on a Varian Mercury-300 spectrometer (300 MHz) in carbon tetrachloride, internal reference HMDS or TMS. Chromatomass spectra were obtained on a Varian Saturn 2100T/GC 3900 instrument, ionizing energy 70 eV.

For the hydrogenation of alkenes gaseous hydrogen was used obtained with IVEL-80 hydrogen generator and dried by passing through the layer of concentrated sulfuric acid.

***n*-Octane (IIa).** A suspension of 0.3 g (0.008 mol) of lithium aluminum hydride in 50 mL of dry THF was placed in a flat bottom flask equipped with a magnetic stirrer, a bubbler, and an effective reflux condenser, and 1.75 g (0.01 mol) of anhydrous $NiCl_2$ was added in portions under the intense stirring. The formation of black colloid solution was observed. After that bubbling hydrogen was started at a rate that does not permit carrying off the reaction mixture, and 26.9 g (0.24 vol) of octane-1 was added. The reaction was carried out with stirring at 50°C for 8 h. After completion of the hydrogenation the reaction mixture was cooled, and 5 mL of water was added for acceleration of coagulation of catalyst. The obtained precipitate was filtered off, the organic layer of filtrate was separated, and the filtrate was distilled at atmospheric pressure to give 22.5 g (82%) of *n*-octane **IIa**, colorless liquid, bp 124–126°C (published data 124–126°C [14]). Mass spectrum, *m*/*e* (I_{rel}, %): 114 [M^+] (5), 85 (25), 71 (20), 57 (33), 43 (100).

***n*-Decane (IIb)**. *a.* Analogously to the synthesis of *n*-octane **IIa** from the suspension of 0.25 g (0.0065 mol) of lithium aluminum hydride in 30 mL of THF and 1.75 g (0.014 mol) of $NiCl_2$ a solution of catalyst was prepared. Substrate **Ib**, 16.8 g (0.12 mol), was added, and after bubbling hydrogen at 50°C for 7 h 12.9 g (76%) of product **IIb** was obtained, colorless liquid, bp 174–175°C (published data 174–175°C [14]).

b. The catalytic solution was prepared from the suspension of 0.25 g (0.0065 mol) of lithium aluminum hydride in 20 mL of dry THF and 1.38 g (8.3 mol) of anhydrous iron(III) chloride. Decene-1, 30 g (0.214 mol), was added, and after bubbling hydrogen for 7 h at 50°C 21.9 g (72%) of product **IIb** was obtained. Colorless liquid, bp 174–175°C (published data 174–175°C [14]).

Cyclohexane (IV). Analogously to the synthesis of *n*-octane **IIa** from the suspension of 0.5 g (0.013 mol) of lithium aluminum hydride in 20 mL of THF and 2.7 g (0.021 mol) of anhydrous $NiCl_2$ the catalytic solution was prepared. After that 36.8 g (0.40 mol) of cyclohexene **III** was loaded, and hydrogen was bubbled through it at 30–40°C for 6 h. According to chromatomass spectrometry 28 g (85%) of cyclohexane was obtained. Mass spectrum *m*/*e* (I_{rel}, %): 85 (7), 84 [M^+] (100).

Ethylbenzene (VIa). Analogously to the synthesis of *n*-octane **IIa** from the suspension of 0.5 g (0.013 mol) of lithium aluminum hydride in 50 mL of THF and 3.5 g (0.028 mol) of $NiCl_2$ the catalytic solution was prepared. After that 50 g (0.48 mol) of styrene **Va** was added, and after bubbling of hydrogen for 6 h at 50°C 38.7 g (76%) of product **VIa** was obtained, bp 134–136°C (published data 135–136°C [14]). ^{1}H NMR spectrum, δ, ppm: 1.18 t (3H, CH_3), 2.56 q (2H, CH_2), 7.02–7.21 m (5H, C_6H_5).

Isopropylbenzene (VIb). Analogously to the synthesis of *n*-octane **IIa** from the suspension of 0.48 g (0.0125 mol) of lithium aluminum hydride in 30 mL of THF and a mixture of 0.5 g (0.003 mol) of anhydrous nickel(II) chloride and 0.5 g (0.002 mol) of anhydrous chromium(III) chloride the catalytic solution was prepared. After that 30 g (0.25 mol) of α-methylstyrene **Vb** was added, and hydrogen was bubbled through the solution obtained at 50°C for 6 h to give 23.4 g (78%) of isopropylbenzene. It is a colorless liquid with the characteristic odor, bp 152–155°C (published data 152–154°C [14]). ^{1}H NMR spectrum, δ, ppm: 1.17 t (6H, $2CH_3$), 2.79 m (1H, CH), 6.97–7.12 m (5H, C_6H_5).

Indane (VIc). *a.* From the suspension of 1 g (0.026 mol) of lithium aluminum hydride in 20 mL of THF and 4 g (0.031 mol) of $NiCl_2$ the catalytic solution was prepared. After that 24.2 g (0.21 mol) of indene **Vc** was added, and hydrogen was bubbled through the solution obtained at 50°C for 6 h to give 20.3 g (82%) of product **VIc** as a colorless liquid with bp 176–177°C (published data bp 178°C [14]). ^{1}H NMR spectrum, δ, ppm: 1.90 m (2H, CH_2), 2.74 t (4H, $2CH_2$), 6.90–7.01 m (4H, C_6H_4).

b. From the suspension of 1 g (0.026 mol) of lithium aluminum hydride in 20 mL of THF and 5.16 g (0.04 mol) of anhydrous $CoCl_2$ the catalytic solution was prepared. After that 18.6 g (0.16 mol) of indene **Vc** was added, and hydrogen was bubbled through the solution obtained at 50°C for 6 h to give 15.1 g (80%) of product **VIc** as a colorless liquid with bp 176–177°C (published data bp 178°C [15]). ^{1}H NMR spectrum, δ, ppm: 1.90 m (2H, CH_2), 2.74 t (4H, $2CH_2$), 6.90–7.01 m (4H, C_6H_4).

Tricyclo[5.2.1.0^{2,6}]decane (VIII). *a.* Analogously to the synthesis of *n*-octane **IIa** from the suspension of 1.0 g (0.026 mol) of lithium aluminum hydride in 50 mL of THF and 5 g (0.038 mol) of $NiCl_2$ the catalytic solution was prepared. Then 42 g (0.32 mol) of dicyclopentadiene **VII** was added and after bubbling hydrogen at 25–50°C for 6 h 41.7 g (96%) of product **VII** was obtained as colorless crystals with bp 192–193°C (bp 193°C [13]). ^{1}H NMR spectrum, δ, ppm: 1.20 t (2H, CH_2), 1.25–1.58 m (10H, $5CH_2$), 2.02 s (2H, 2CH), 2.27 s (2H, 2CH).

b. Analogously to the synthesis of *n*-octane **IIa** from the suspension of 1 g (0.026 mol) of lithium aluminum hydride in 50 mL of THF and 4.9 g (0.038 mol) of anhydrous $CoCl_2$ the catalytic solution was prepared. From 42 g (0.32 mol) of dicyclopentadiene **VII** after 6 h of bubbling hydrogen at 50°C 40.5 g (93%) of product **VIII** was obtained as colorless crystals with bp 192–193°C.

c. The catalytic solution was prepared from the suspension of 1 g (0.026 mol) of lithium aluminum hydride in 50 mL of THF and 5.36 g (0.033 mol) of anhydrous $FeCl_3$. From 42 g (0.32 mol) of dicyclopentadiene **VII** after 6 h of bubbling hydrogen at 50°C 38.7 g (89%) of product **VIII** was obtained as colorless crystals with bp 192–193°C.

Tricyclo[5.2.1.0^{2,6}}dec-3-ene (IX). *a.* Through the suspension of 2 g (0.033 mol) of recycled nickel catalyst in THF and 30 g (0.227 mol) of dicyclopentadiene **VII** hydrogen was bubbled at 50–60°C for 10 h. After the isolation analogous to the procedure for *n*-octane 24 g (79%)of the product **IX** was obtained as colorless liquid crystallizing on storage, bp 184–187°C (published data bp 184–187°C [16]). ^{1}H NMR spectrum, δ, ppm: 1.11–1.23 m (4H, $2CH_2$), 1.35 q (2H, CH_2), 2.03–2.18 m (4H, CH_2, 2CH), 2.39–2.47 m (1H, CH), 2.87–2.92 m (1H, CH), 5.40–5.44 m (1H, CH=), 5.51–5.55 m (1H, CH=).

b. The catalytic solution was prepared from the suspension of 0.27 g (0.007 mol) of lithium aluminum hydride in 20 mL of anhydrous THF and 1.7 g (0.0136 mol) of anhydrous $MnCl_2$. Then 30.0 g

(0.227 mol) of dicyclopentadiene **VII** was added, and after bubbling hydrogen at 50–60°C for 10 h 27.7 g (78%) of compound **IX** was obtained, bp 184–186°C.

c. The catalytic solution was prepared from the suspension of 0.27 g (0.007 mol) of lithium aluminum hydride in 30 mL of anhydrous THF and 2.1 g (0.014 mol) of anhydrous $CrCl_3$. Then 30.0 g (0.227 mol) of dicyclopentadiene **VII** was added, and after bubbling hydrogen at 50–60°C for 10 h 8.5 g (28%) of compound **IX** was obtained, bp 183–186°C.

d. The catalytic solution was prepared from the suspension of 0.27 g (0.007 mol) of lithium aluminum hydride in 20 mL of anhydrous THF and 1.89 g (0.014 mol) of anhydrous $CuCl_2$. Then 30.0 g (0.227 mol) of dicyclopentadiene **VII** was added, and after bubbling hydrogen at 50–60°C for 10 h 8.5 g (28%) of compound **IX** was obtained, bp 183–186°C.

2-Cyanonorbornane (XIa). The catalytic solution was prepared from the suspension of 1 g (0.026 mol) of lithium aluminum hydride in 30 mL of THF and 4 g (0.031 mol) of anhydrous $NiCl_2$. Then 50 g (0.42 mol) of 2-cyanonorbornene **Xa** was added, and after bubbling hydrogen for 6 h at 50°C 36.8 g (73%) of compound **XIa** was obtained as colorless crystals, bp 191–193°C, mp 47–50°C (published data mp 48–51°C [16]). ^{1}H NMR spectrum, δ, ppm: 0.93–1.04 m (2H, CH_2), 1.17–1.53 m (6H, $3CH_2$), 2.24–2.37 m (2H, 2CH), 2.52–2.68 m (1H, CHCN).

2-Carboxynorbornane XIb. The catalytic solution was prepared from the suspension of 1 g (0.026 mol) of lithium aluminum hydride in 30 mL of THF and 4 g (0.031 mol) of $NiCl_2$. The obtained solution was added in portions to 50 g (0.36 mol) of compound **Xb** under bubbling hydrogen for 6 h at 25–50°C. After the completion of the reaction the mixture obtained was cooled and the solution of 7 g of concentrated sulfuric acid in 20 mL of water was added. From the organic layer THF was distilled off, and the residue was distilled in a vacuum to give 37.4 g (67%) of colorless crystals, bp 147–149°C (20 mmHg), mp 62–63°C (published data 63–65°C [17]). ^{1}H NMR spectrum, δ, ppm: 1.09–1.85 m (8H, $4CH_2$), 2.24 q (1H, CH), 2.53 s (1H, CH), 2.68–2.75 m [1H, CHC(O)O], 12.24 s (1H, COOH).

Methyl 2-methylnorbornan-2-carboxylate (XIc). The catalytic solution was prepared from the suspension of 0.25 g (0.065 mol) of lithium aluminum hydride in 30 mL of anhydrous THF and 2 g (0.016 mol) of $NiCl_2$. Then 42 g (0.25 mol) of ester **Xc** was added, and after bubbling hydrogen at 50°C for 6 h 31.7 g (75%) of product **XIc** was obtained as colorless liquid, bp 113–114°C (20 mmHg). ^{1}H NMR spectrum, δ, ppm: 1.09–1.14 m (3H, CH_3, 2H, CH_2), 1.25–1.59 m (4H, $2CH_2$), 2.02–2.90 m (2H, CH_2, 2H, CH), 3.53 s (1H, OCH_3).

Pinane (XIII). *a. The hydrogenation of α-pinene*. The catalytic solution was prepared from the suspension of 0.5 g (0.013 mol) of lithium aluminum hydride in 30 mL of anhydrous THF and 3.5 g (0.028 mol) of anhydrous $NiCl_2$. Then 34.4 g (0.25 mol) of pinene **XIIa** was added, and after bubbling hydrogen at 50°C for 5 h 16.9 g (49%) of compound **XIII** was obtained. Mass spectrum, *m*/*e* (I_{rel}, %): 138 (3, M^+), 95 (91), 81(93), 67 (100), 55 (58), 41 (34).

b. The hydrogenation of β-pinene. The catalytic solution was prepared from the suspension of 1 g (0.026 mol) of lithium aluminum hydride in 50 mL of THF and 4 g (0.031 mol) of $NiCl_2$. Then 30 g (0.22 mol) of pinene **XIIb** was added, and after bubbling hydrogen at 50°C for 5 h 14.2 g (47%) of pinane **XIII** was obtained. Mass spectrum, *m*/*e* (I_{rel}, %): 138 (8, M^+), 95 (88), 81 (100), 67 (47), 41 (34).

2,2,3-Trimethylnorbornane (XV). The catalytic solution was prepared from the suspension of 0.5 g (0.013 mol) of lithium aluminum hydride in 50 mL of dry THF and 3.5 g (0.028 mol) of $NiCl_2$. Then 25 g (0.184 mol) of norbornene **XIV** was added, and after bubbling hydrogen at 50°C for 6 h 15.4 g (54%) of the product **XV** was obtained. Mass spectrum, *m*/*e* (I_{rel}, %): 138 (18, M^+), 109 (67), 95 (100), 82 (30), 67 (47), 41 (53).

REFERENCES

1. Popov, Yu.V., Mokhov, V.M., and Nebykov, D.N., *Russ. J. Gen. Chem.*, 2014, vol. 84, no. 3, p. 444.
2. Augustine, R.L., *Catalytic The hydrogenation*, New York: Marcel Dekker, 1965, ch. 4, pp. 38, 135.
3. Rylander, P.N., *Catalytic The hydrogenation over Platinum Metals*, New York: Academic Press, 1967, ch. 4, p. 71.
4. Kalbasi, R.J., Nourbakhsh, A.A., and Badaknezhad, F., *Catalysis Commun*., 2011, vol. 12, p. 955.
5. Deghedi, L., Basset, J.M., Candy, J.P., Dalmon, J.A., Dubreuil, A.C., and Fischer, L., *Chem. Ing. Trans*., 2009, vol. 17, p. 31.
6. Belykh, L.B., Titova, Yu.Yu., Rokhin, A.V., and Shmidt, F.K., *Russ. J. Appl. Chem*., 2010, vol. 83, no. 11, p. 1911.

7. Hosahalli, P., Hemantha, H.P., Vommina, V., and Sureshbabu, V.V., *Org. Biomol. Chem*., 2011, vol. 9, p. 2597.
8. Alonso, F., Osantey, I., and Yus, M., *Tetrahedron,* 2007, vol. 63, p. 93.
9. Alonso, F., Candela, P., Gomez, C., and Yus, M., *Adv. Synth. Catal*., 2003, vol. 345, nos. 1–2, p. 275.
10. Rangheard, C., de Julian Fernandez, C., Pim-Huat Phua, Hoorn, J., Lefort, L., and de Vries, J.G., *Dalton Trans*., 2010, vol. 39, p. 8464.
11. In Soo Park, Min Serk Rwon, Kyung Yeon Kang, Jae Sung Lee, and Jaiwook Park, *Adv. Synth. Catal*., 2007, vol. 349, p. 2039.
12. Polshettiwar, V., Baruwati, B., and Varma, R.S., *Green Chem*., 2009, vol. 11, p. 127.
13. Topchiev, A.V., Pokrovskaya, E.S., and Stepanyseva, T.G., *Russ. Chem. Bull*., 1958, vol. 8, no. 11, p. 1887.
14. Schleyer, P.R., Donaldson, M.M., Nicholas, R.D., and Cupas, C., *Org. Synth*., 1962, vol. 42, p. 9.
15. *Khimicheskaya entsiklopediya* (Chemical Encyclopedy), Knunyants, I.L., Ed., Moscow: Sovetskaya Entsiklopediya, 1988, vol. 2, p. 438.
16. Bruson, H.A. and Reiner, T.W., *J. Am. Chem. Soc*., 1948, vol. 70, no. 8, p. 2809.
17. Oldenziel, O.H., van Leusen, D., and van Leusen, A.M., *J. Org. Chem*., 1977, vol. 42, no. 19, p. 3114.
18. Bartlett, P.D. and Pincock, R.E., *J. Am. Chem. Soc*., 1962, vol. 84, no. 12, p. 2445.