ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 9, pp. 1656–1661. © Pleiades Publishing, Ltd., 2014.
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Colloid and Nanodimensional Catalysts in Organic Synthesis: VI.[1] Hydrogenation and Hydrogenolysis of Carbonyl Compounds

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Received April 7, 2014

Abstract—Aldehydes and ketones are found to be hydrogenated to alcohols with hydrogen at atmospheric pressure under the catalysis with nickel nanoparticles. The reaction under study may be used as technologically available and cheap method for hydrogenation of carbonyl groups. It is found that in the case of aromatic ketones hydrogenolysis of C=O bond with partial hydrogenation of aromatic groups takes place.

Keywords: catalysis, nickel nanoparticles, hydrogenation, carbonyl bond, hydrogenolysis

DOI: 10.1134/S1070363214090023

Hydrogenation processes are widely used in organic chemistry and chemical technology. Reduction (hydrogenation) of carbonyl group is one of the widely used methods for preparation of compounds containing a hydroxy group. A series of methods of laboratory and industrial reduction of carbonyl group is known. It includes using of metal complex hydrides [2], hydrogen in the presence of catalysts [3], transfer hydrogenation with lower alcohols [4–6]. Most technologically convenient and suitable for industry are methods, using gaseous hydrogen as the most cheap and available hydrogenating agent. But use of hydrogen requires the presence of catalysts, the reactions proceed as a rule at the elevated hydrogen pressure. For example, synthesis of secondary alcohols by hydrogenation of ketones with hydrogen at 11 bar pressure using the Raney nickel and nickel applied on the magnesium oxide [7] and hydrogenation of ketones with isopropanol in the presence of ruthenium complexes and potassium *tert*-butylate [6] are described.

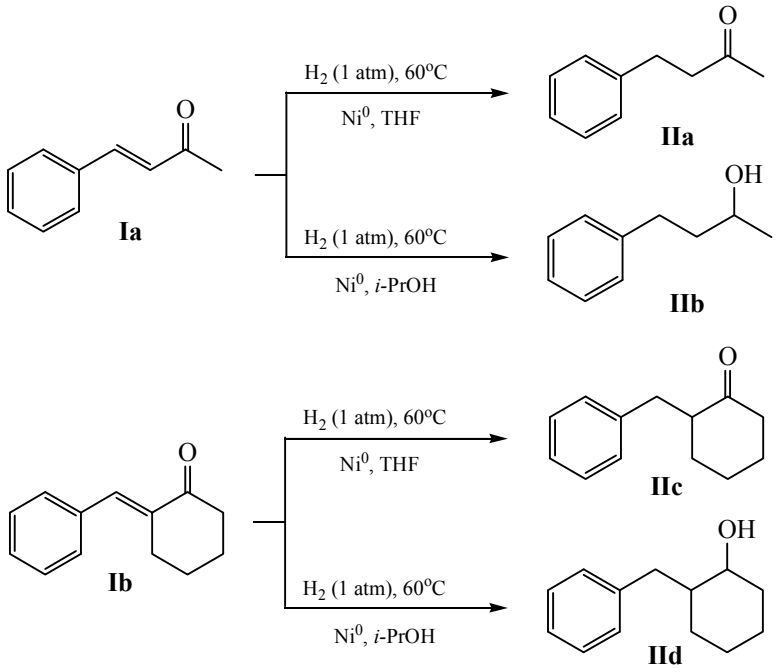
In a number of works the application of nanoparticles and nanoclusters as catalysts for hydrogenation of carbonyl compounds is reported. The synthesis of isopropanol by catalytic hydrogenation of acetone with hydrogen in the presence of iridium nanoclusters, synthetic procedure for preparing secondary alcohols by hydrogenation of ketones with hydrogen at 48 bar on the chiral ruthenium complexes applied on the magnetite nanoparticles [9], and also hydrogenation of ketones with hydrogen at 4 bar and 75°C in the presence of iridium nanoparticles [10] are described. The drawback of the above-mentioned methods is the use of expensive and difficultly availabile catalysts.

Hence, the investigation of possibility of carbonyl group hydrogenation using available highly disperse catalytic systems is topical.

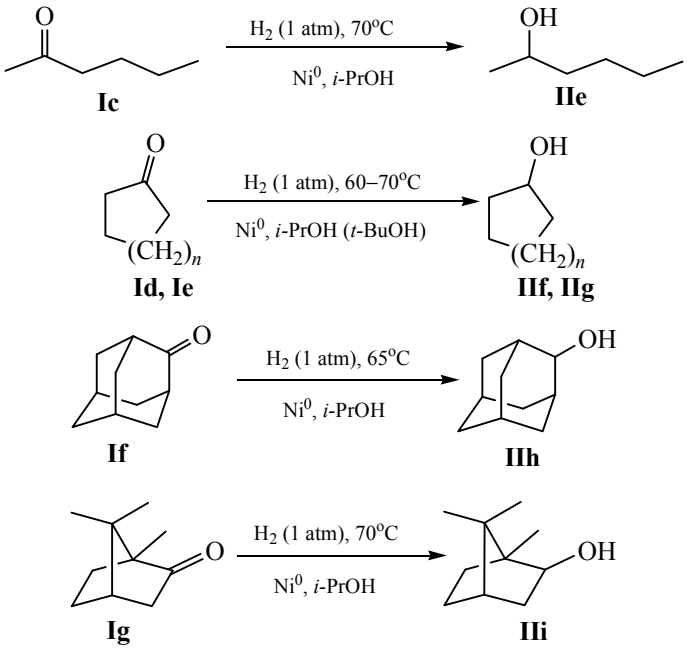
We have used nickel nanoparticles which were prepared by the reduction of anhydrous nickel(II) chloride with metal complex hydrides. Nickel nanoparticles were used as a colloid solution without their isolation or stabilization in the 5–10 mol % amounts with respect to the hydrogenated substrate. Use of nickel nanoparticles prepared in THF solution by the reduction of nickel chloride with lithium aluminum hydride proved to be inapplicable to the hydrogenation of carbonyl group because only the carbon–carbon multiple bonds of α,β-unsaturated ketones were involved in the reaction. On the other hand, use of ultradisperse nickel obtained by the reaction of nickel(II) chloride with sodium borohydride in isopropanol lead to formation of alcohols. Reaction proceeded at simple bubbling of hydrogen through the colloid solution of catalyst in isopropanol and ketone to be hydrogenated in the course of 6–8 h at 60–80°C. The difference in

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

Scheme 1.



Scheme 2.



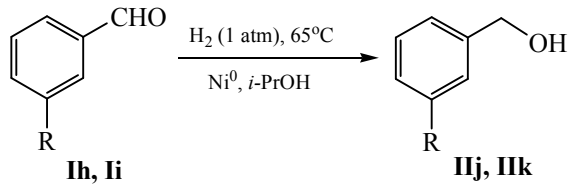
n = 1 (**Id, IIf**), 2 (**Ie, IIg**).

the hydrogenation chemoselectivity of α,β-unsaturated ketones **Ia, Ib** while using the above-mentioned catalytic systems is presented in the Scheme 1.

This difference in selectivity of the colloid nickel catalyst obtained in different ways may be used for the target hydrogenation either of the unsaturated bond or the C=C bond together with the carbonyl group.

It is found that nickel nanoparticles prepared by the reduction of nickel(II) chloride with sodium boro-hydride successively catalyze the hydrogenation of

Scheme 3.



Ih, Ii **IIj, IIk**

R = H (**Ih, IIj**), NO_2 (**Ii, IIk**).

acyclic **Ic** and cyclic **Id–If** ketones to the corresponding alcohols in 70–84% yields (Scheme 2).

As is known, metal nanoparticles catalyze the reaction of transfer hydrogenation [4] while using secondary alcohols as reagents. For the confirmation that just hydrogen and not isopropanol is the hydrogenation agent in the above-presented reactions we have used *tert*-butanol as a solvent for hydrogenation of cyclohexanone **Ie** because this alcohol cannot take part in transfer hydrogenation. It was shown that cyclohexanol is formed disregarding the alcohol used as a solvent. Hence, just hydrogen at atmospheric pressure is the hydrogenating agent. It was found that the ability of hydrogenation of the carbonyl group by means of this catalytic system is somewhat lower than the hydrogenation of the C=C bond.

The composition and structure of alkanols **IIe–IIi** was confirmed by the ^{1}H NMR spectroscopy. Properties of the known compounds agree with the reported data.

Hence, the procedure for hydrogenation of aliphatic and alicyclic carbonyl compounds with hydrogen at atmospheric pressure and 69–70°C on the available catalyst is developed. It may be used in the laboratory as well (Scheme 3).

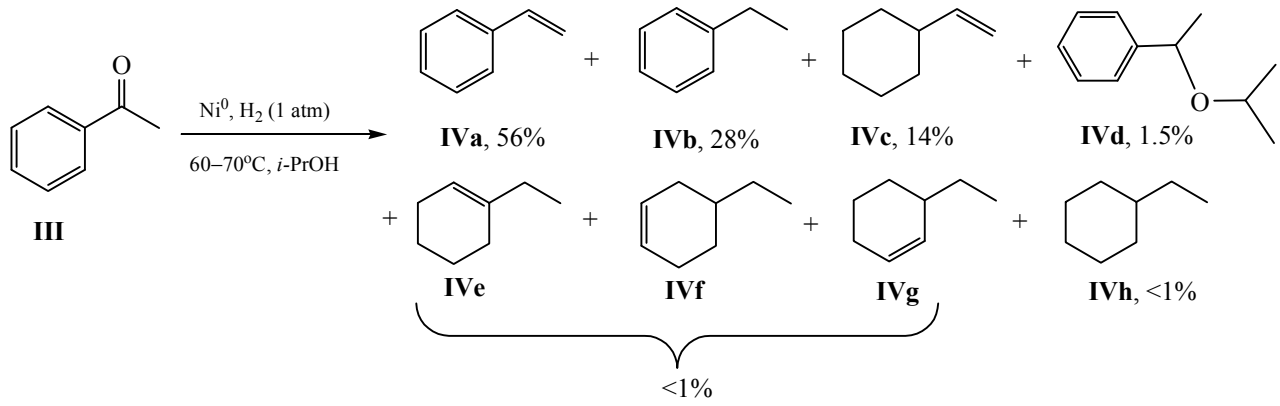
It was shown that the developed catalytic system is suitable also for hydrogenation of aromatic aldehydes. For example, unsubstituted benzaldehyde **Ij** within 6 h at 65–70°C forms benzyl alcohol **IIk** in about 80% yield. On the other hand, the hydrogenation of *m*-nitrobenzalhehyde under these conditions provided 3-nitrobenzyl alcohol **IIl** in a small amount (28%).

The hydrogenation of ketones containing the carbonyl group at the aromatic ring proceeds differently. It is established that in this case the main reaction pathway is hydrogenolysis of the C=O bond to the methylene group though the successful synthesis of secondary alcohols with aromatic substituent by means of catalytic hydrogenation of ketones with hydrogen at 5–8 bar in the presence of ruthenium complex and potassium isopropylate has been reported [11].

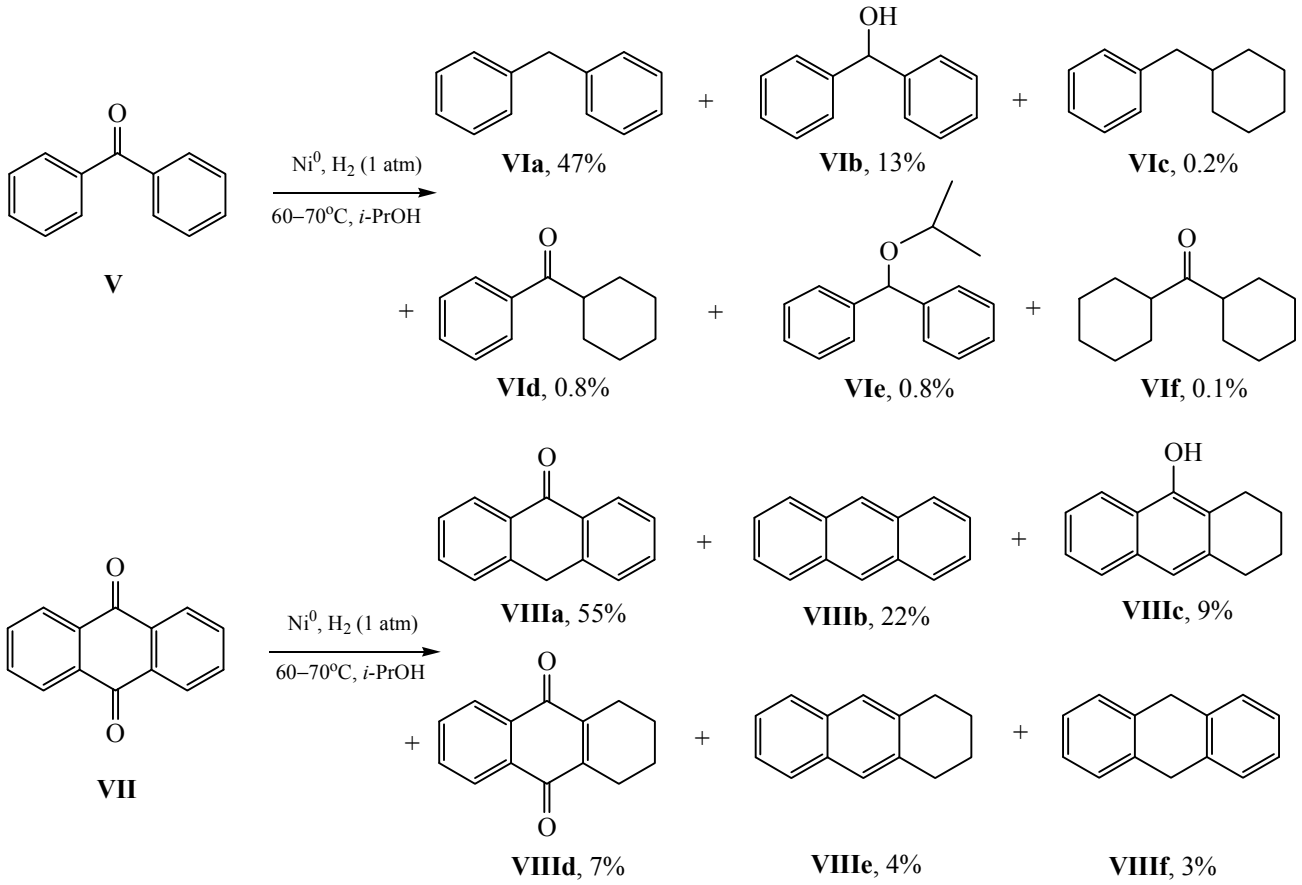
Results of hydrogenation of acetophenone **III** were unexpected. The reaction was carried out in the presence of nickel nanoparticles obtained by the reduction of anhydrous nickel chloride with sodium borohydride in isopropanol. The hydrogenation temperature was 60–70°C, and hydrogen was bubbled through the reaction mixture for 8 h. But instead of the expected 1-hydroxyethylbenzene according to the chromatomass spectrometry a mixture of hydrocarbons was obtained. It consisted mainly of styrene **IVa** (56 wt %), and ethylbenzene **IVb** (28 wt %). Beside these substances vinylcyclohexane **IVc** (14 wt %), three isomeric ethylcyclohexenes **IVf–IVg**, and ethylcyclohexane **IVh** were found (Scheme 4).

Therefore acetophenone suffered not hydrogenation but hydrogenolysis of the carbonyl bond. Besides it was found that the presence of water formed in the reaction decreased the activity of catalyst towards

Scheme 4.



Scheme 5.



hydrogenation of the multiple carbon–carbon bond because significant amount of styrene was obtained. At the same time the hydrogenation of aromatic ring started, and the total amount of compounds with partially or completely hydrogenated benzene ring reached 16%. This fact requires further study due to the importance of establishing the conditions of aromatic compounds hydrohenation at mild conditions on available catalysts. Up till now only the hydrogenation of benzene with hydrogen at atmospheric pressure and room temperature on the ruthenium or rhodium nanoparticles was described [12, 13].

For the confirmation of established rules we have carried out hydrogenation of two other aromatic ketones, benzophenone **V** and anthraquinone **VII** under the same conditions (Scheme 5).

After the completion of the reactions and separation of catalyst and solvent the reaction mixtures were analyzed by the chromatomass spectrometry. The majority of products were identified by coincidence of their spectra with the database of spectrometer. It was found that in this case alcohols also were not the main reaction products. The conversion of benzophenone was 65%. The main reaction product was diphenylmethane **VIa**. Its amount permitted to isolate it pure by fractional distillation. Similarly to the reduction of acetophenone the products of partial hydrogenation of aromatic rings **VIc, VId, VIf** were found. In the case of anthraquinone the product of partial hydrogenolysis, anthrone **VIIIa,** was formed. It is interesting that the preferred hydrogenation of the side ring of anthraxquinone takes place (conversion 82%). Quinone **VIIId**, phenol **VIIIc**, and hydrocarbon **VIIIe** are mainly formed. It shows the independence of pathways of hydrogenation of the carbonyl group and aromatic rings.

If in the hydrogenation of acetophenone **III** the mechanism of formation of the mixture obtained through the stage of dehydration leading to phenylacetylene which is completely hydrogenated to styrene and the other products is possible, for compounds **V, VII** dehydration as well as hydrogenation of the enol form is impossible. Hence, the mechanism of the

above-presented reactions should be specially studies. The reactions described are not only interesting from the theoretical point of view, but after optimization of conditions may have certain preparative use. Besides the fact of the change in selectivity of the catalytic system under investigation in the presence of water it is interesting because it may probably permit a development of a convenient procedure for hydrogenation of aromatic compounds under relatively mild conditions.

EXPERIMENTAL

^{1}H NMR spectra were taken on a Varian Mercury-300 (300 MHz) spectrometer in carbon tetrachloride, internal references HMDS or TMS. Chromatomass spectral analysis was carried out on a Saturn 2100T/GC3900 instrument.

Benzylacetone (IIa). To a suspension of 0.5 g (0.014 mol) of lithium aluminum hydride in 20 mL of anhydrous THF 3.6 g (0.028 mol) of anhydrous $NiCl_2$ was added in portions under bubbling of hydrogen. After the formation of black colloid solution 22 g (0.151 mol) of ketone **Ia** was added. The reaction mixture was maintained under stirring and bubbling of hydrogen (30–35 mL/min) for 6 h at 60°C. After that the mixture was cooled and 1 mL of water was added for coagulation of catalyst. The mixture was filtered, and THF was distilled off from the filtrate. The residue was distilled to give 13.2 g (0.116 mol, 77%) of ketone **IIa**, bp 233–236°C, n_D^{20} 1.5121 (bp 234°C, n_D^{20} 1.5124 [14]). ^{1}H NMR spectrum, δ, ppm: 1.90 s (3H, CH_3), 2.53 t [2H, $CH_2C(O)$, *J* 14.4 Hz], 2.70 t (2H, CH_2, *J* 14.2 Hz), 6.92–7.08 m (5H, C_6H_5).

4-Phenylbutanol-2 (IIb). Analogously to **IIa** from 0.5 g (0.014 mol) of $NaBH_4$ in 20 mL of isopropanol, 0.9 g (0.007 mol) of $NiCl_2$ and 14.6 g (0.1 mol) of ketone **Ia** after bubbling of hydrogen at 60°C for 8 h 10.4 g (0.071 mol, 71%) of ketone **IIb** was obtained, bp 155–157°C (25 mmHg), n_D^{20} 1.5153 {bp 124°C (12 mmHg), n_D^{20} 1.5159 [14]}. ^{1}H NMR spectrum, δ, ppm: 1.09 t (3H, CH_3, *J* 10 Hz), 1.59 m (2H, CH_2CO), 2.52 m (2H, CH_2-Ar), 3.62 m (1H, CH–O), 4.36 s (1H, OH), 6.91–7.12 m (5H, C_6H_5).

2-Benzylcyclohexanone (IIc). Analogously to **IIa** from 0.5 g (0.014 mol) of $LiAlH_4$ in 20 mL of dry THF, 3.6 g (0.028 mol) of $NiCl_2$ and 20 g (0.11 mol) of ketone **Ib** after bubbling of hydrogen at 60°C for 7 h 15.7 g (0.082 mol, 75%) of ketone **IIc** was obtained, bp 185–187°C/20 mm, {bp 160°C (12 mmHg) [15]}. ^{1}H NMR spectrum, δ, ppm: 1.19–1.93 m (6H, $3CH_2$), 2.19–2.30 m (2H, CH_2–Ar), 2.34 t [2H, $CH_2C(O)$, *J* 13.2 Hz], 2.71 t [1H, CHC(O), *J* 12.6 Hz], 6.98–7.30 m (5H, C_6H_5).

2-Benzylcyclohexanol (IId). Analogously to **IIa** from 0.5 g (0.014 mol) of $NaBH_4$ in 20 mL of isopropanol, 0.9 g (0.007 mol) of $NiCl_2$ and 18.6 g (0.1 mol) of ketone **Ib** after bubbling of hydrogen at 60°C for 10 h 12.7 g (0.067 mol, 67%) of alkanol **IId** was obtained, bp 195–198°C (20 mmHg), {bp 90–93°C (0.15 mmHg) [16]}. ^{1}H NMR spectrum, δ, ppm: 0.93–1.57 m (8H, $4CH_2$), 2.19 t (1H, CH, *J* 22 Hz), 2.38–2.68 m (2H, CH_2-Ar), 3.15 m (1H, CH–O), 4.32 br.s (1H, OH), 6.99–7.08 m (5H, C_6H_5).

Hexan-2-ol (IIe). Analogously to **IIa** from the suspension of 0.72 g (0.02 mol) of $NaBH_4$ in 20 mL of isopropanol, 1.3 g (0.01 mol) of $NiCl_2$ and 20 g (0.2 mol) of ketone **Ib** after bubbling of hydrogen at 55°C for 8 h 14.9 g (0.146 mol, 73%) of alkanol **IIe** was obtained, bp 138–140°C, n_D^{20} 1.4140 (bp 140°C, n_D^{20} 1.4144 [14]).

Cyclopentanol (IIf). Analogously to **IIa** from the suspension of 0.5 g (0.014 mol) of $NaBH_4$ in 20 mL of isopropanol, 0.9 g (0.007 mol) of $NiCl_2$ and 15.8 g (0.2 mol) of cyclopentanone **Id** after bubbling of hydrogen at 60°C for 8 h 10.4 g (0.14 mol, 69%) of cyclopentanol **IIf** was obtained, bp 140–142°C, n_D^{20} 1.4532 (bp 139–141°C, n_D^{20} 1.4530 [14]).

Cyclohexanol (IIg). *a*. Analogously to **IIa** from the suspension of 0.58 g (0.016 mol) of $NaBH_4$ in 20 mL of isopropanol, 1 g (0.008 mol) of $NiCl_2$ and 19.6 g (0.2 mol) of cyclohexanone **Ie** after bubbling of hydrogen at 60°C for 8 h 15.8 g (0.158 mol, 79%) of cyclohexanol **IIg** was obtained, mp 23–25°C, bp 159–161°C, n_D^{20} 1.4639 (mp 25.2°C, bp 161.1°C, n_D^{20} 1.4641 [14]).

b. Analogously to **IIa** from the suspension of 0.4 g (0.011 mol) of $NaBH_4$ in 15 mL of *tert*-butanol, 0.65g (0.005 mol) of $NiCl_2$ and 14.7 g (0.15 mol) of ketone **Ie** after bubbling of hydrogen at 60°C for 9 h 11.7 g (0.117 mol, 78%) of cyclohexanol **IIg** was obtained.

Adamantan-2-ol (IIh). Analogously to **IIa** from the suspension of 0.25 g (0.007 mol) of $NaBH_4$ in 20 mL of isopropanol, 0.45 g (0.0035 mol) of $NiCl_2$ and 7.5 g (0.05 mol) of ketone **Ib** after bubbling of hydrogen at 65°C for 9 h 6.75 g (0.045 mol, 90%) of alkanol **IIh** was obtained, mp 260–262°C, (mp 258–262°C [16]). ^{1}H NMR spectrum, δ, ppm: 0.83–2.05 m (14H), 3.72 br.s (1H, OH), 3.86 m (1H, CH–O).

1,7,7-Trimethylbicyclo[2.2.1]heptan-2-ol (IIi). Analogously to **IIa** from the suspension of 0.25 g (0.007 mol) of $NaBH_4$ in 20 mL of isopropanol, 0.45 g (0.0035 mol) of $NiCl_2$ and 7.7 g (0.05 mol) of D,L-camphor **Ig** after bubbling of hydrogen at 70°C for 10 h 6.3 g (0.04 mol, 82%) of alkanol **IIi** was obtained, mp 209–210°C, (mp 208-209°C [16]). ^{1}H NMR spectrum, δ, ppm: 0.74–0.79 m (9H, $3CH_3$), 0.88–1.84 m (6H, $3CH_2$), 2.10 m (1H, CH) 3.45 br.s (1H, OH), 3.81–3.85 m (1H, CH).

Benzyl alcohol (IIj). Analogously to **IIa** from 0.5 g (0.014 mol) of $NaBH_4$ in 20 mL of isopropanol, 0.9 g (0.007 mol) of $NiCl_2$ and 10.6 g (0.1 mol) of benzaldehyde after bubbling of hydrogen at 60°C for 6 h 9.1 g (0.084 mol, 84%) of alkanol **IIj** was obtained, bp 204–206°C, n_D^{20} 1.5391 (bp 205°C, n_D^{20} 1.5396 [15]).

3-Nitrobenzyl alcohol (IIk). Analogously to **IIa** from 0.4 g (0.011 mol) of $NaBH_4$ in 20 mL of isopropanol, 0.65 g (0.005 mol) of $NiCl_2$ and 8 g (0.053 mol) of aldehyde **Ii** after bubbling of hydrogen at 60°C for 8 h a mixture, containing alkanol **IIk** was obtained. Alkanol **IIk** content according to chromato-mass spectral data 28%. Electron impact mass spectrum (70 eV), *m/e* (I_{rel}, %): 154 (4), 153 (38), 136 (40), 107 (35), 89 (64), 77 (100), 51 (53).

Hydrogenolysis of acetophenone (III). Analogously to **IIa** from 0.5 g (0.014 mol) of $NaBH_4$ in 20 mL of isopropanol, 0.9 g (0.007 mol) of $NiCl_2$ and 20 g (0.167 mol) of ketone **III** after bubbling of hydrogen at 60–70°C for 12 h, removing of isopropanol, and distillation of the residue 14.5 g of a mixture of hydrogenolysis products **IVa–IVh** was obtained.

Hydrogenolysis of benzophenone (V). Analogously to **IIa** from 0.5 g (0.014 mol) of $NaBH_4$ in 20 mL of isopropanol, 0.9 g (0.007 mol) of $NiCl_2$ and 18.2 g (0.1 mol) of ketone **V** after bubbling of hydrogen at 60–70°C for 10 h 13.4 g of a mixture of hydrogenolysis products **VIa–VIf** was obtained. Repeated distillation of a mixture of products gave 6.7 g (0.04 mol, 40%) of diphenylmethane **VIa**, bp 263–265°C, mp 23–25°C (bp 264.3°C, mp 25.2°C [13]). ^{1}H NMR spectrum, δ, ppm: 3.84 s (2H, CH_2), 7.021–7.32 m (10H, 2 C_6H_5).

Hydrogenolysis of anthraquinone VII. Analogously to **IIa** from 0.5 g (0.014 mol) of $NaBH_4$ in 20 mL of isopropanol, 0.9 g (0.007 mol) of $NiCl_2$ and 10.4 g (0.05 mol) of anthraquinone **VII** after bubbling of hydrogen at 60–70°C for 10 h 8.1 g of a mixture of hydrogenolysis products **VIIIa–VIIIg** was obtained.

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