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Colloid and Nanodimensional Catalysts in Organic Synthesis: I. Investigation of Hydrogenation Selectivity of Unsaturated Compounds with Hydrazine Hydrate and Aluminum Hydride

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Abstract—Results of investigation of selective hydrogenation of unsaturated carbon–carbon bonds with hydrazine hydrate or complex metal hydrides in the presence of metal nanoparticles are reported. Conditions of exhaustive and partial hydrogenation of some derivatives of norbornene, styrene, and unsaturated carboxylic acids are developed.

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Hydrogenation of multiple carbon–carbon bonds is widely used both in chemical industry and in laboratory practice [1]. Nickel, platinum, palladium, rhodium, and ruthenium are most widely used as catalysts in the form of metals or metal complex compounds. Hydrogenation is successfully performed also using sodium borohydride–boron trifluoride complex [2]. Alkenes with isolated double bonds under mild conditions do not react with metal hydrides, for example lithium aluminum hydride [3], but the presence of electron-acceptor functional groups conjugated with the double bond may lead to their hydrogenation [4].

The catalytic hydrogenation in the laboratory conditions is connected with some complications, in particular, with the use of expensive catalysts, of gaseous hydrogen, and of complicated laboratory equipment. Therefore the search for convenient methods of hydrogenation of unsaturated carbon–carbon bonds is urgent and possesses a practical interest.

Nowadays the chemistry of catalysis with colloid solutions of metal nanoparticles rapidly develops. It is connected with their high specific surface which at approaches the catalysis to the homogenic type, and also the surface of nanoparticle contains considerably larger part of metal atoms than the usual heterogenic catalyst. Besides, because of the small size of particles a considerable part of atoms is located out of the flat surface and exhibits higher catalytic activity. For example, the hydrogenation of alkenes with nickel nanoparticles using alcohols as hydrogen donors [5] permits carrying out the reaction under very mild conditions. The preparation of colloid metal solutions is well developed. For example, the nickel nanoparticles are known to be obtained by the reduction of its salt with hydrazine hydrate in water-ethanol medium [6, 7]. Palladium nanoparticles are prepared by treating its anhydrous salts with complex hydrides of metals [8]. Reduction of nickel or cobalt salts with lithium aluminum hydride also gives the corresponding metal nanoparticles [9, 10]. The shape, dimensions, and stabilization of metal nanoparticles is extensively investigated. The aim of this work is the study of the possibility to use colloid metal solutions prepared by known methods without their stabilization as hydrogenation catalysts of multiple carbon–carbon bonds.

Alkenes with isolated multiple bonds do not react with lithium aluminum hydride under usual conditions [3]. Non-catalytic hydroalumination of heptene-1, styrene, and dihydromyrcene was carried out in a pressure reactor under hydrogen pressure of 40 at and at heating to 100–110°C [11]. It was shown that the presence of zirconium, titanium, or nickel complexes catalyzed the reaction of hydroalumination of alkenes [12]. We suggested to use one of the methods of metal nanoparticles preparation by means of lithium aluminum hydride [8–10] also for hydrogenation of alkenes with the formation of the hydrogenating agent (AlH_3) and catalyst (nickel colloid) in situ according to the following reaction.

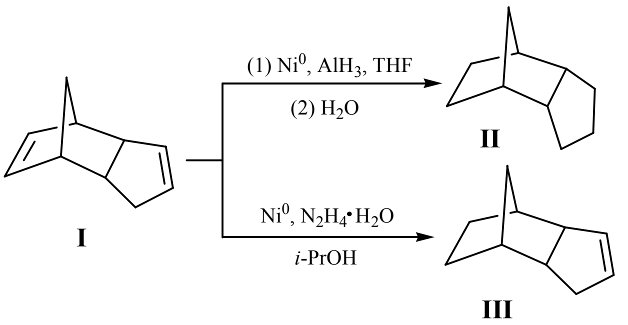
$$NiCl_2 + 2LiAlH_4 \rightarrow Ni^0 + 2LiCl + 2AlH_3 + H_2.$$

As known, nickel complexes catalyze the hydrogenation, in particular, the hydroalumination [13, 14]. It was suggested that nickel nanoparticles would also promote this reaction. Recent studies showed also that nickel nanoparticles are not only synthesized using metal hydrides, but are also stabilized by them in solution, simultaneously increasing their reactivity as reducing agents [9].

On the other hand, hydrazine hydrate is a well-known and available hydrogen donor in redox reactions. It was used to reduce nitro groups under the catalysis with Raney nickel [15]. It is also known that under certain conditions hydrazine can form diimine which is capable of hydrogenation of isolated double and triple bonds [3, 16]. There is also a method for the preparation of colloid nickel solutions using hydrazine hydrate [6, 7]. It was reported that the mean size of metal particles under these conditions is 4–16 nm. Hence, the combination of these two processes (synthesis of catalyst and hydrogenation of organic substrate) leads to a promising one-stage method of olefin hydrogenation.

The hydrogenation of dicyclopentadiene **I** was carried out by both methods. The hydrogenation with aluminum hydride was carried out in THF for 6 h under the intense stirring. The product of exhaustive hydrogenation, tetrahydrodicyclopentadiene **II**, was isolated. In the ^1H NMR spectrum of the product signals of protons of unsaturated bonds in the region 5–7 ppm were absent. According to the properties of obtained product (mp 73–75°C) the reaction proceeded with the preferred formation of *endo*-isomer which was due to the mechanism of hydroalumination. We have carried out an attempt of hydrogenation of compound **I** in the absence of nickel colloid. Aluminum hydride was synthesized by slow addition of equivalent amount of sulfuric acid to the suspension of lithium aluminum hydride [17]. It was found that in the absence of catalyst the hydrogenation of this substrate does not take place indicating the important role of metal particles in this reaction.

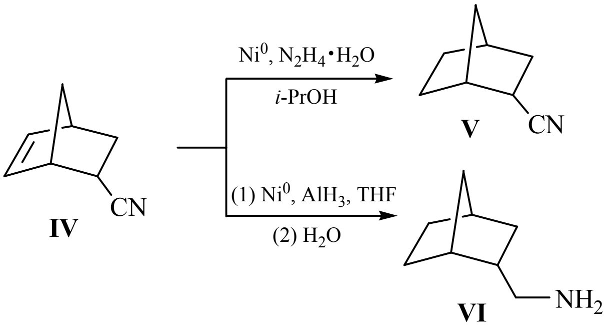
The hydrogenation of alkene **I** with hydrazine hydrate was carried out in presence of nickel nanoparticles in 2-propanol under reflux and intense stirring. Nickel nanoparticles were obtained in situ in the reaction mixture. According to ^1H NMR data the product of monohydrogenation, 5,6-dihydrodicyclopentadiene **III** was formed.



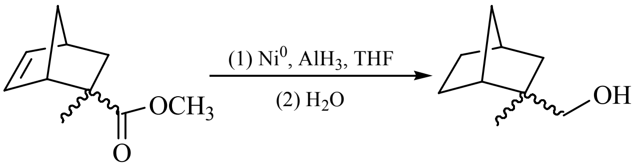
Hence, it was found that using one or another hydrogenation method permits the preparation of completely or partially hydrogenated cyclopentadiene dimer.

Successful reduction of strained double bond with hydrazine hydrate in compound **I** permitted using this method for hydrogenation of easily available norbornene derivatives. 2-Cyanonorbornene-5 **IV** was used as a starting substance. The hydrogenation was carried out on nickel nanoparticles either with hydrazine hydrate or with AlH_3.

It was found that the reaction with aluminum hydride leads both to hydrogenation of the unsaturated bond and to reduction of cyano group. On the other hand, hydrazine hydrate in 2-propanol solution hydrogenates only the double bond does not touching the cyano group.

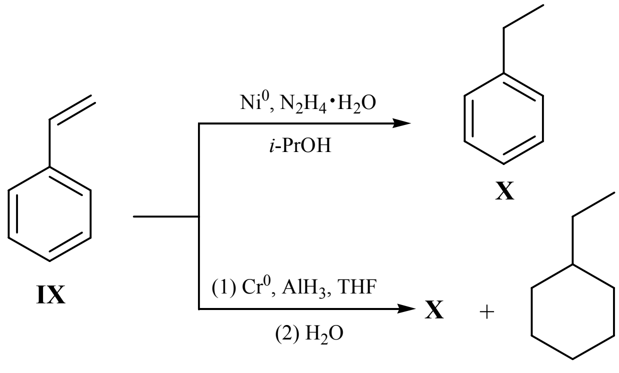


The reduction of adduct of cyclopentadiene with methyl metacrylate **VII** with aluminum hydride in the presence of nickel nanoparticles also leads to the formation of completely hydrogenated product, 2-methyl-2-hydroxymethylnorbornane **VIII**.



VII **VIII**

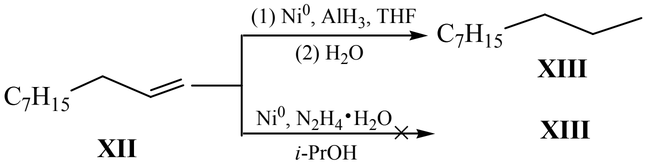
The catalytic hydrogenation of styrene **IX** with hydrazine hydrate on nickel nanoparticles leads to the formation of ethylbenzene **X** in 62% yield.



IX **X** **XI**

On the other hand, the hydrogenation of styrene on chromium particles prepared by reduction in the reaction mixture of CrCl$_3$ with lithium aluminum hydride led to formation according to chromatomass spectrometry along with the expected ethylbenzene (97.5 wt % in the reaction products) of some amount the product of exhaustive hydrogenation of the aromatic ring, ethylcyclohexane **XI** (1.86 wt %).

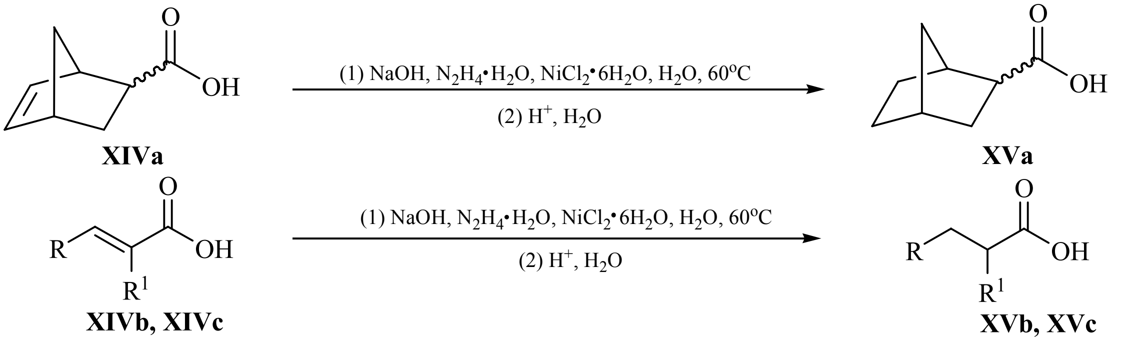
It was shown also that using aluminum hydride led to hydrogenation of decene-1 **XII**, but under the action of hydrazine hydrate no reaction was observed. This fact shows the high sensitivity of this method to the structure of alkene subjected to hydrogenation.



XII **XIII** **XIII**

A special preparative importance may possess the developed method of double bonds hydrogenation of unsaturated carboxylic acids carried out in alkaline water medium using hydrazine hydrate as hydrogen donor. The corresponding alkenecarboxylic acid that may contain a conjugated or isolated double bond is dissolved in aqueous sodium hydroxide solution, and the necessary amount of hydrazine hydrate is added. After that the obtained mixture is treated with nickel salt solution at 50–60°C with the formation in situ of catalyst and resulting in the hydrogenation of substrate. The use of sodium carboxylate permits avoiding the unwanted interaction of acid with hydrazine and requires no organic solvent.

Norborn-2-ene-5-carboxylic acid **XIVa**, metacrylic acid **XIVb**, and *trans*-cinnamic acid **XIVc** were used as substrates. After precipitation of acids **XVa–XVc** from the reaction mixture with mineral acid their purification was carried out by distillation. Reaction products were obtained in 67–75% yield.



XIVa **XVa** **XIVb, XIVc** **XVb, XVc**

R = H, R^1 = Me (**XIVb, XVb**), R = Ph, R^1 = H (**XIVc, XVc**).

Hence, this method may be used for hydrogenation of unsaturated acids with diverse location of multiple carbon–carbon bond, among them *trans*-isomers. The structure of compounds synthesized was proved by ^{1}H NMR spectroscopy, and in some cases by IR spectroscopy and chromatomass spectrometry. The characteristics of known compounds were in agreement with the published data.

This research showed that further studies in the field of development of convenient laboratory methods for hydrogenation of multiple bonds excluding gaseous hydrogen, expensive catalysts and equipment are quite promising.

EXPERIMENTAL

^{1}H NMR spectra were registered on a Varian Mercury-300 spectrometer (100 MHz) in carbon tetrachloride, internal references HMDS or TMS. Chromatomass spectra were measured on a Varian Saturn 2100T/GC 3900 spectrometer, ionizing electrons energy 70 eV. IR spectra of compounds synthesized were recorded on a SPECORD M 82 spectrophotometer, in pellets with KBr.

***endo*-Tricyclo[5.2.1.0^{2,6}]decane II**. A solution of 2.9 g (0.076 mol) of lithium aluminum hydride in 30 mL of anhydrous THF was placed in a flat-bottom flask equipped with a magnetic stirrer and a reflux condenser. After that 10 g (0.076 mol) of dicyclopentadiene was added, and to the mixture obtained 4.3 g (0.034 mol) of anhydrous nickel chloride was gradually added. A formation of black suspension was observed. The reaction mixture was refluxed with intense stirring for 6 h. After that it was cooled, 6 mL of water was added, and the resulting mixture was stirred for 1 h. Nickel precipitate was removed from the organic layer which was distilled at atmospheric pressure to give 6.5 g (65%) of compound **II**, colorless crystals, bp 192–193°C (bp 191–193°C [18]), mp 73–75°C. ^{1}H NMR spectrum, δ, ppm: 1.20 t (2H, CH_2); 1.25–1.58 m (10H, 5 CH_2); 2.02 s (2H, 2CH); 2.27 s (2H, 2CH).

Tricyclo[5.2.1.0^{2,6}]dec-2-ene III. A mixture of 3 g (0.075 mol) of sodium hydroxide, 20 mL of 2-propanol, and 5 mL (0.1 mol) of hydrazine hydrate was heated to 60°C, and under intense stirring a solution of 9 g (0.03 mol) of $Ni(NO_3)_2 \cdot 6H_2O$ in 20 mL of 2-propanol was added. After the formation of black suspension of nickel nanoparticles 10 g (0.076 mol) of dicyclopentadiene **I** and 15 g (0.3 mol) of hydrazine hydrate were added. The obtained mixture was refluxed with intense stirring for 8 h. After the reaction was complete, the nickel precipitate was filtered off, organic layer of the filtrate was separated and distilled under atmospheric pressure to give 7 g (70%) of product **III** as a colorless oil with bp 179–181°C {reported data bp 182°C (768 mm Hg [19])}. ^{1}H NMR spectrum, δ, ppm: 1.11–1.23 m (4H, 2CH_2); 1.32 q (2H, CH_2); 2.03–2.18 m (4H, CH_2, 2CH); 2.2.39–2.47 m (1H, CH); 2.88–2.92 m (1H, CH); 5.40–5.44 m (1H, CH=), 5.51–5.54 m (1H, CH=).

2-Cyanonorbornane V. Analogously to product **III** from 3 g (0.075 mol) of sodium hydroxide, 40 mL of 2-propanol, 5 mL (0.1 mol) of hydrazine hydrate, and 9 g (0.03 mol) of $Ni(NO_3)_2 \cdot 6H_2O$ after the addition of 6 g (0.05 mol) of compound **IV** and 15 mL (0.3 mol) of hydrazine hydrate and refluxing for 8 h 3.6 g (62%) of product **V** was obtained, bp 191–193°C, mp 47–50°C (reported data mp 48–51°C [20]). ^{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-Aminomethylnorbornane VI. Analogously to product **II** from the suspension of 4.5 g (0.117 mol) of lithium aluminum hydride in 30 mL of dry THF, 9.3 g (0.978 mol) of compound **IV**, and 4 g (0.031 mol) of anhydrous $NiCl_2$ 4.5 g (48%) of 2-aminomethylnorbornane, bp 68–70°C (20 mm Hg) {reported data 63–64°C (12–13 mm Hg [21])} was obtained. ^{1}H NMR spectrum, δ, ppm: 0.93–1.09 m (2H, CH_2); 1.10–1.47 m (6H, 3CH_2); 1.77 m (1H, CH); 2.13 s (2H, 2CH); 2.23–2.58 m (2H, CH_2N).

2-Methyl-2-hydroxymethylnorbornane VIII. Analogously to product **II** from the suspension of 1 g (0.026 mol) of lithium aluminum hydride in 20 mL of THF, 4 g (0.024 mol) of 2-methylnorborn-5-en-2-methylcarboxylate **VII**, and 1.7 g (0.014 mol) of anhydrous $NiCl_2$ 2 g (59%) of product **VIII** was obtained, bp 113–114°C (20 mm Hg). IR spectrum, ν, cm^{-1}: 3370 (OH). ^{1}H NMR spectrum, δ, ppm: 0.94 s (3H, CH_3); 1.05–1.62 m (6H, 3 CH_2), 2.01–2.15 m (2H, CH_2, CH); 2.27 br.s (1H, CH); 3.55 d (2H, CH_2O), 3.99 br.s (1H, OH).

Ethylbenzene X. *a.* Analogously to product **III** from 20 mL (0.4 mol) of hydrazine hydrate, 1.89 g (0.047 mol) of NaOH, 20 mL of propan-2-ol, 3 g (0.013 mol) of $NiCl_2 \cdot 6H_2O$, and 17 g (0.163 mol) of compound **IX** 10.7 g (62%) of the product **X** was obtained, bp 133–135°C (reported data bp 136°C [22]). ^{1}H NMR spectrum, δ, ppm: 1.18 t (3H, CH_3); 2.56 q (2H, CH); 7.07–7.21 m (5H, C_6H_5).

b. Analogously to product **II** from 9 g (0.937 mol) of lithium aluminum hydride in 40 mL of anhydrous THF, 12 g (0.125 mol) of styrene, and 12 g (0.047 mol) of anhydrous $CrCl_3$ 7 g (58%) of ethylbenzene **X** was obtained, bp 133–134°C (reported data bp 136°C [22]). ^{1}H NMR spectrum, δ, ppm: 1.18 t (3H, CH_3); 2.56 q (2H, CH_2); 7.07–7.21 m (5H, C_6H_5).

***n*-Decane XIII**. Analogously to product **II** from the suspension of 4.5 g (0.12 mol) of lithium aluminum hydride in 40 mL of THF, 14 g (0.1 mol) of compound **XII**, and 8 g (0.063 mol) of anhydrous $NiCl_2$ 7 g (58%) of the product **XIII** was obtained, colorless liquid, bp 174–175°C (reported data 174°C [22]).

2-Carboxynorbornane XVa. The unsaturated acid **XIVa,** 20 g, was dissolved in a solution of 8 g (0.2 mol) of sodium hydroxide in 50 mL of water. After that 25 g (0.5 mol) of hydrazine hydrate was added, the obtained mixture was heated to 60°C, and a solution of 4 g (0.017 mol) of $NiCl_2 \cdot 6H_2O$ in 15 mL of water was added in portions. The obtained black solution was stirred for 4 h at 60°C. Then the reaction mixture was cooled, and a solution of 24.5 g (0.25 mol) of sulfuric acid in 20 mL of water was added. The product was extracted with diethyl ether, the solvent was distilled off, and the residue was distilled in a vacuum to give 15.2 g (75%) of acid **XVa**, colorless crystals, mp 60–61°C, bp 147–149°C (20 mm Hg) (reported data: *endo*-isomer mp 63–65°C, *exo*-isomer mp 54–56°C [23]). ^1H NMR spectrum, δ, ppm: 1.09–1.80 m (8H, $4CH_2$); 2.21–2.29 m (1H, CH), 2.53 s (1H, CH); 2.68–2.75 m (1H, CHCO), 12.2 s (1H, COOH).

Isobutyric acid XVb. Analogously to the synthesis of compound **XVa** from 20 g (0.233 mol) of acid **XIVb**, 12 g (0.3 mol) of sodium hydroxide, 25 g (0.5 mol) of hydrazine hydrate, and 3 g (0.013 mol) of $NiCl_2 \cdot 6H_2O$ in 60 ml of water 14.2 g (70%) of acid **XVb** was obtained as a colorless liquid, bp 152–155°C, n_D^{20} 1.3933 (reported data bp 154.4°C, n_D^{20} 1.3930 [22]).

3-Phenylpropionic acid XVc. Analogously to the synthesis of compound **XVa** from 15 g (0.1 mol) of unsaturated acid **XIVc**, 6 g (0.15 mol) of sodium hydroxide, 18 g (0.36 mol) of hydrazine hydrate, and 3 g (0.013 mol) of $NiCl_2 \cdot 6H_2O$ in 60 mL of water 10 g (67%) of hydrogenation product **XVc** was obtained as colorless crystals, mp 49°C, bp 279–281°C (reported data mp 48.6°C, bp 279.6°C [24]).

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