ISSN 1070-4280, Russian Journal of Organic Chemistry, 2016, Vol. 52, No. 3, pp. 319–323. © Pleiades Publishing, Ltd., 2016.
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Hydrogenation of Alkenes over Nickel Nanoparticles under Atmospheric Pressure of Hydrogen

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Received May 5, 2015

Abstract—Nickel nanoparticles have been shown to be an accessible catalyst which allows hydrogenation of unsaturated compounds to be accomplished under atmospheric pressure of hydrogen at relatively low temperatures. Linear and cyclic alkenes, styrene and norbornene derivatives, as well as pinenes and camphene have been smoothly hydrogenated under these conditions. In some cases, selective hydrogenation of unsaturated carbon–carbon bond is possible with the other functional group remaining intact.

DOI: 10.1134/S1070428016030040

Hydrogen addition to an unsaturated carbon–carbon bond is among fundamental reactions in organic synthesis. It belongs to most comprehensively and extensively studied catalytic processes [1]. This is related to both practical importance of the hydrogenation process and the necessity of exploring a number of theoretical problems, such as activation of hydrogen and unsaturated substrate molecules and reaction mechanism. Industrial heterogeneous catalysts are stable, and they can be readily separated from the products; on the other hand, they are characterized by low activity and selectivity, and reactions in the presence of these catalysts generally require harsh conditions [2]. Homogeneous catalysts frequently used in laboratory practice feature high activity and selectivity due to great diversity of organic ligands. Their drawbacks include high cost, complexity of synthesis, low stability, and often impossibility of recycling [3]. Thus, an important problem is search for systems that would combine advantages of homogeneous and heterogeneous catalysts. Such systems could be catalysts in the form of nanoparticles or their colloidal solutions. Nanoparticles possess a high specific surface area, which makes the catalysis closer to homogeneous. A large number of atoms in nanoparticles reside on their surface, and the fraction of surface atoms increases as the particle size decreases. The chemical activity depends on the particle size since the properties of particular atoms, atomic clusters, and nanoparticles differ from the properties of the corresponding bulk material [4]. Furthermore, the term *nanocatalysis* has been introduced to describe a specific hybrid of heterogeneous and homogeneous catalysis [5].

Hydrogenation catalyzed by metal nanoparticles has been reported in a number of publications. In particular, Deghedi et al. [6] described hydrogenation of styrene and its derivatives over nickel nanoparticles at a temperature lower than 130°C under pressure (~30 atm). Palladium nanoparticles prepared by reduction of palladium(II) chloride with sodium tetrahydridoborate catalyzed hydrogenation of some unsaturated compounds and nitroarenes under atmospheric pressure of hydrogen [7]. Alonso et al. [8, 9] reported hydrogenation of alkenes with alcohols as hydrogen donor under very mild conditions. Here, the catalyst was nickel nanoparticles obtained by reduction of nickel chloride with lithium tetrahydridoaluminate in tetrahydrofuran in the presence of 4,4′-di-*tert*-butylbiphenyl. Iron nanoparticles prepared by reduction of iron salts with Grignard reagents were used to catalyze hydrogenation of alkenes under a hydrogen pressure of 10–20 atm [10].

We previously described liquid-phase hydrogenation of some unsaturated compounds in THF under catalysis by colloidal nickel; the catalyst was obtained using lithium tetrahydridoaluminate or hydrazine hydrate as reducing agent, and the hydrogenation of alkenes was carried out with aluminum hydride and hydrazine hydrate [11], as well as with hydrogen [12].

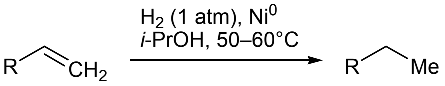
We studied the hydrogenation of some linear and cyclic alkenes with hydrogen under atmospheric pressure in the presence of nickel nanoparticles prepared by reduction of nickel(II) chloride with sodium tetrahydridoborate in propan-2-ol. The reduction of $NiCl_2$ gives a suspension of nickel nanoparticles [13, 14] which may contain some boron atoms [15], depending on the amount of $NaBH_4$ used. The size of nickel nanoparticles ranges from 14 to 20 nm. If oxygen is present in the reaction medium, small amounts of nickel oxide and boride are also formed [16]. The reduction with $NaBH_4$ in polar solvents affords monometallic nickel nanoparticles [17].

Thus, analysis of published data shows that nickel nanoparticles may contain nickel oxide and boride as impurities. We have found that overheating of walls of the reaction vessel leads to deposition of nanoparticles onto the glass surface to form a metal mirror. This indicates formation of pure nickel nanoparticles or the presence of an insignificant amount of nickel boride in the resulting colloidal system.

The average size of nickel particles was estimated at 105 nm by photon correlation spectroscopy after keeping a colloidal nickel solution in propan-2-ol for 1 h. The substrates were alkenes with different positions of the C=C double bond: cyclohexene, derivatives of styrene and norbornene, α-pinene, β-pinene, and camphene. Colloidal nickel solution was prepared just before the hydrogenation. Alkene was added to a catalytic solution (containing 5–7 wt % of nickel with respect to the substrate), and gaseous hydrogen was passed through the solution over a period of 3–6 h under atmospheric pressure at a temperature below 70°C. There was no additional stabilization of colloidal nickel particles.

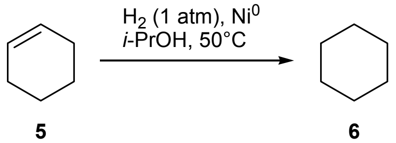
In the hydrogenation of oct-1-ene (**1**) and dec-1-ene (**3**), hydrogen was passed through a homogeneous mixture of the substrate and nickel nanoparticles in propan-2-ol for 6 h at at 40–50°C under stirring. After separation of the catalyst, alkanes **2** and **4** were isolated by distillation in 72 and 82% yield, respectively; according to the GC/MS data, the conversion of alkenes **1** and **3** was almost complete. Under analogous conditions, the conversion of cyclohexene (**5**) into cyclohexane (**6**) was also nearly quantitative (Scheme 1).

Scheme 1.



1, **3** **2**, **4**

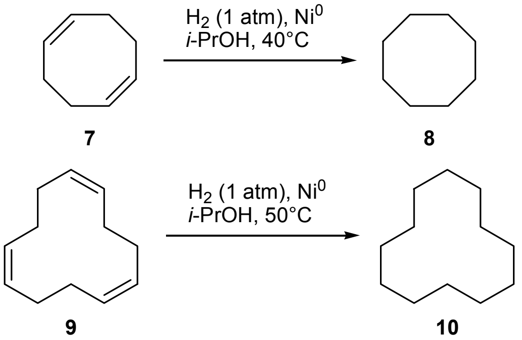
1, **2**, R = C_6H_{13}; **3**, **4**, R = C_8H_{17}.



5 **6**

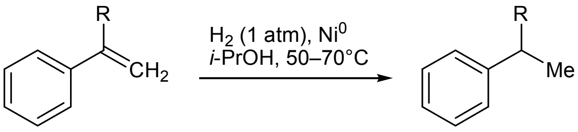
The hydrogenation of cycloocta-1,5-diene (**7**) and cyclododeca-1,5,9-triene (**9**) afforded the corresponding saturated cycloalkanes **8** and **10**. In these cases, no selective hydrogenation of one double bond was observed (Scheme 2).

Scheme 2.



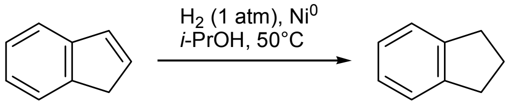
The given catalytic system was successfully used to hydrogenate styrene (**11**) and its homologs **13** and **15**. Polshettiwar et al. [18] reported hydrogenation of styrene derivatives over nickel-coated nano-ferrite at room temperature under a pressure of 7 atm. The colloidal nickel catalyst ensured hydrogenation of **11**, **13**, and **15** to the corresponding alkylbenzenes at 50–70°C under atmospheric pressure, while the aromatic ring was not involved (Scheme 3).

Scheme 3.



11, **13** **12**, **14**

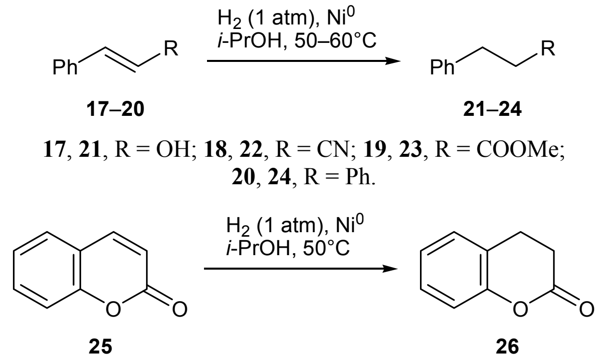
11, **12**, R = H; **13**, **14**, R = Me.



15 **16**

The developed procedure is also applicable to 3-phenylprop-2-en-1-ol (**17**, cinnamyl alcohol) **17**, 3-phenylprop-2-enenitrile (**18**, cinnamonitrile) and methyl ester **19**, (*E*)-1,2-diphenylethene (**20**), and coumarin (**25**) (Scheme 4). No appreciable hydrogena-

Scheme 4.

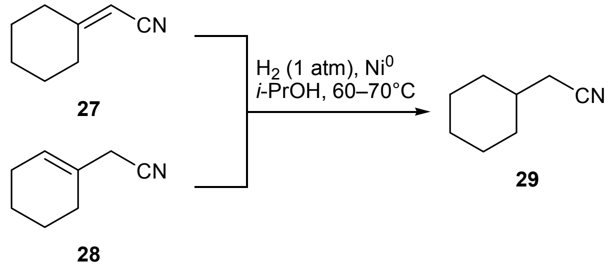


17, **21**, R = OH; **18**, **22**, R = CN; **19**, **23**, R = COOMe;
20, **24**, R = Ph.

tion of the cyano group in **18** was observed in 6–8 h, and the ester group in **19** also remained intact. Thus, the proposed method can be used for the hydrogenation of C=C bond in α,β-unsaturated compounds. The conversion of **20** was 50%, presumably due to lower reactivity of *trans*-configured double C=C bond in the hydrogenation.

Condensation products of cyclohexanone with acetonitrile, cyclohexylideneacetonitrile (**27**) and cyclohex-1-en-1-ylacetonitrile (**28**) were also used as substrates. The hydrogenation involved both α,β- and β,γ-unsaturated double bonds to give cyclohexylacetonitrile (**29**), while the nitrile functionality remained unchanged (Scheme 5).

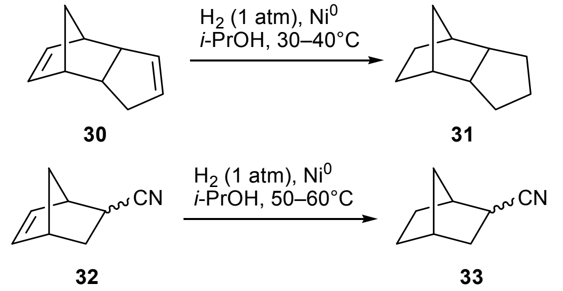
Scheme 5.



Thus, introduction of sterically unhindered functional groups into alkene molecules does not lead to appreciable reduction of their reactivity in the hydrogenation catalyzed by nickel nanoparticles. Therefore, the proposed procedure is promising from the viewpoint of selective hydrogenation of carbon–carbon double bonds with conservation of other functionalities, and it can find application in fine organic synthesis.

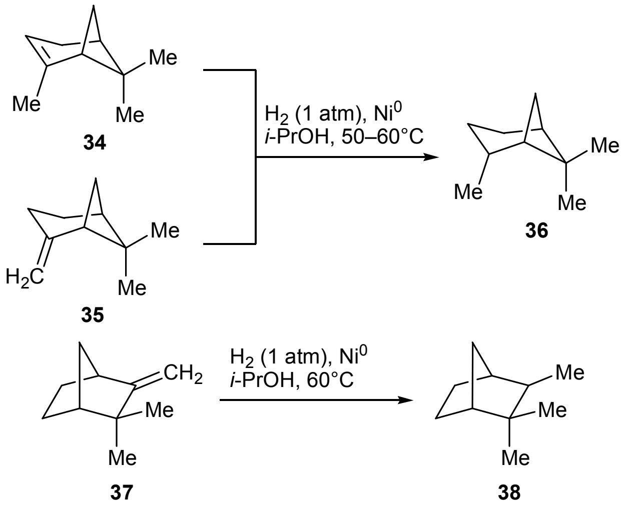
The colloidal nickel catalyst was also efficient in the reduction of norbornene derivatives. Exhaustive hydrogenation product, tricyclodecane **31**, was obtained from diene **30** (Scheme 6). The reaction occurred even at room temperature and was accompanied by appreciable heat evolution. The hydrogenation of dicyclopentadiene (**30**) over industrial nickel catalyst requires a temperature of 150°C and a pressure of 3.5 atm [19]. The hydrogenation of nitrile **32** was carried out at 50–60°C.

Scheme 6.



According to the GC/MS data, the conversion of α- and β-pinenes **34** and **35** over nickel nanoparticles was incomplete (48–56%; Scheme 7). Nevertheless, both exo- and endocyclic double bonds were saturated under the given conditions. Analogous result was obtained in the hydrogenation of camphene (**37**); its conversion was 55%.

Scheme 7.



To conclude, we have shown that readily accessible colloidal solution of nickel nanoparticles is a convenient catalyst for the hydrogenation of carbon–carbon double bonds in laboratory practice without high pressure or temperature.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Varian Mercury-300 instrument at 300 MHz using carbon tetrachloride as solvent and hexamethyldisiloxane as internal standard. Gas chromatographic–mass spectrometric data were obtained on a Varian Saturn 2100 T/GC3900 instrument (electron impact, 70 eV). The size of nickel nanoparticles was determined at 25°C by photon correlation spectroscopy (dynamic light scattering, DLS) on a PhotoCor Compact Z instrument at a single scattering angle of 160° (laser power 15–30 mW).

Gaseous hydrogen was generated by an IVEL-80 generator and was dried by passing through a layer of concentrated sulfuric acid.

Reduction of oct-1-ene (1). Anhydrous nickel(II) chloride, 1.75 g (14 mmol), was added to a suspension of 1.1 g (30 mmol) of $NaBH_4$ in 20 mL of propan-2-ol to obtain a black colloidal solution. Hydrogen was passed through the solution at a flow rate of 15–20 mL/min, 34 g (0.3 mol) of oct-1-ene (**1**) was added, and the mixture was stirred for 6 h at 50–60°C. The mixture was cooled, 1 mL of water was added to accelerate coagulation of the catalyst, the precipitate was filtered off, the solvent was removed from the filtrate by distillation through a column, and the residue was distilled. Yield 28 g (0.246 mol, 82%), bp 124–127°C [20]. Mass spectrum, *m/z* (I_{rel}, %): 114 (5) $[M]^+$, 85 (25), 71 (20), 57 (33), 43 (100).

The hydrogenation of compounds **3**, **5**, **7**, **9**, **11**, **13**, **15**, **17**–**20**, **25**, **27**, **28**, **30**, **32**, **34**, **35**, and **37** was carried out in a similar way.

Decane (4) was obtained from 35 g (0.25 mol) of dec-1-ene using 1.1 g (30 mmol) of $NaBH_4$, 20 mL of propan-2-ol, and 1.75 g (14 mmol) of $NiCl_2$; 8 h, 50°C. Yield 25.2 g (72%), bp 171–173°C [21].

Cyclohexane (6) was obtained from 36.8 g (0.40 mol) of cyclohexene (**5**) using 0.5 g (14 mmol) $NaBH_4$, 15 mL of propan-2-ol, and 0.9 g (7 mmol) of $NiCl_2$; 6 h, 50°C. According to the GC/MS data, the resulting solution contained alkane **6**, while initial alkene **5** was absent. Mass spectrum, *m/z* (I_{rel}, %): 85 (7), 84 (100) $[M]^+$.

Cyclooctane (8) was obtained from 35 g (0.32 mol) of cycloocta-1,5-diene (**7**) using 0.5 g (14 mmol) of $NaBH_4$, 20 mL of propan-2-ol, and 0.9 g (7 mmol) of $NiCl_2$; 6 h, 50°C. Yield 27.6 g (77%), bp 148–149°C [20].

Cyclododecane (10) was obtained from 38 g (0.23 mol) of cyclododeca-1,5,9-triene (**9**) using 0.5 g (14 mmol) of $NaBH_4$, 15 mL of propan-2-ol, and 0.9 g (7 mmol) of $NiCl_2$; 6 h, 50°C. Yield 25.2 g (68%), bp 241–244°C [21].

Ethylbenzene (12) was obtained from 25 g (0.24 mol) of styrene (**11**) using 0.5 g (14 mmol) of $NaBH_4$, 15 mL of propan-2-ol, and 0.9 g (7 mmol) of $NiCl_2$; 6 h, 50°C. Yield 19.5 g (78%), bp 134–136°C [21]. ^1H NMR spectrum, δ, ppm: 1.18 t (3H, CH_3), 2.56 q (2H, CH_2), 7.02–7.21 m (5H, H_{arom}).

Isopropylbenzene (14) was obtained from 17.7 g (0.15 mol) of (prop-1-en-2-yl)benzene (**13**) using 1.1 g (30 mmol) of $NaBH_4$, 20 mL of propan-2-ol, and 1.75 g (14 mmol) of $NiCl_2$; 6 h, 50°C. Yield 14.4 g (80%), bp 152–155°C [21]. ^1H NMR spectrum, δ, ppm: 1.17 t (6H, CH_3, J = 6.9 Hz), 2.79–2.87 m (1H, CH), 6.97–7.12 m (5H, H_{arom}).

Indan (16) was obtained from 24.2 g (0.21 mol) of indene (**15**) using 1 g (28 mmol) of $NaBH_4$, 20 mL of propan-2-ol, and 1.7 g (13 mmol) of $NiCl_2$; 8 h, 50°C. Yield 20.5 g (83%), bp 176–177°C [21]. ^1H NMR spectrum, δ, ppm: 1.90 m (2H, CH_2), 2.74 t (4H, CH_2, J = 4.0 Hz), 6.90–7.01 m (4H, C_6H_4).

3-Phenylpropan-1-ol (21) was obtained from 24 g (0.18 mol) of (*E*)-3-phenylprop-2-en-1-ol (**17**) using 1 g (28 mmol) of $NaBH_4$, 20 mL of propan-2-ol, and 1.7 g (13 mmol) of $NiCl_2$; 8 h, 50°C. Yield 20.5 g (85%), bp 235–237°C [21]. Mass spectrum, *m/z* (I_{rel}, %): 132 (1), 131 (14), 91 (100), 67 (100), 65 (10).

3-Phenylpropanenitrile (22) was obtained from 12.9 g (0.1 mol) of (*E*)-3-phenylprop-2-enenitrile (**18**) using 1.1 g (0.03 mol) of $NaBH_4$, 20 mL of propan-2-ol, and 1.82 g (0.014 mol) of $NiCl_2$; 6 h, 60°C. Yield 8.5 g (65%), bp 115–117°C (10 mm). ^1H NMR spectrum, δ, ppm: 2.43 t (2H, CH_2CN, J = 7.6 Hz), 2.62 t (2H, CH_2, J = 7.6 Hz), 6.98–7.25 m (5H, H_{arom}). Mass spectrum, *m/z* (I_{rel}, %): 132 (1), 131 (14), 91 (100), 67 (100), 65 (10).

Methyl 3-phenylpropanoate (23) was obtained from 26.2 g (0.157 mol) of methyl (*E*)-3-phenylprop-2-enoate (**19**) using 1 g (28 mmol) of $NaBH_4$, 20 mL of propan-2-ol, and 1.7 g (13 mmol) of $NiCl_2$; 8 h, 50°C. Yield 22.8 g (87%), bp 91–92°C (4 mm). Mass spectrum, *m/z* (I_{rel}, %): 148 (77) $[M]^+$, 133 (15), 105 (92), 91 (71), 77 (24), 43 (100).

1,2-Diphenylethane (24) was obtained from 22 g (0.122 mol) of (*E*)-1,2-diphenylethene (**20**) using 1 g (28 mmol) of $NaBH_4$, 20 mL of propan-2-ol, and 1.8 g (14 mmol) of $NiCl_2$. After bubbling of hydrogen for 6 h at 40°C, the mixture contained (GC/MS) compounds **24** and **20** at a weight ratio of 56:44. Mass spectrum of **24**, *m/z* (I_{rel}, %): 182 (19), 104 (7), 91 (100), 65 (20).

Chroman-2-one (26) was obtained from 26.4 g (0.18 mol) of coumarin (**25**) using 1 g (28 mmol) of $NaBH_4$, 20 mL of propan-2-ol, and 1.8 g (14 mmol) of $NiCl_2$; 6 h, 40°C. Yield 24.9 g (94%). Mass spectrum, m/z (I_{rel}, %): 148 (100), 120 (60), 91 (43), 79 (12).

Cyclohexylacetonitrile (29) was obtained from 12.1 g (0.1 mol) of a mixture of nitriles **27** and **28**; 7 h, 65°C. Yield 8.4 g (0.068 mol, 68%), bp 110–112°C (20 mm). ^{1}H NMR spectrum, δ, ppm: 1.15–1.75 m (10H, CH_2), 1.97 m (1H, CH), 2.38 d (2H, CH_2CN, $J = 8.6$ Hz).

Tricyclo[5.2.1.0^{2,6}]decane (31) was obtained from 26.4 g (0.2 mol) of dicyclopentadiene (**30**); 6 h, 40°C. Yield 24.9 g (95%), bp 192–193°C [19]. ^{1}H NMR spectrum, δ, ppm: 1.20 t (2H, CH_2, $J = 8.4$ Hz), 1.25–1.58 m (10H, CH_2), 2.02 s (2H, CH), 2.27 s (2H, CH).

Bicyclo[2.2.1]heptane-2-carbonitrile (33) was obtained from 15.75 g (0.15 mol) of nitrile **32**; 6 h, 50°C. Yield 11.2 g (70%), bp 191–193°C, mp 47–50°C [23]. ^{1}H NMR spectrum, δ, ppm: 0.93–1.04 m (2H, CH_2), 1.17–1.53 m (6H, CH_2), 2.24–2.37 m (2H, CH), 2.52–2.68 m (1H, CHCN).

Hydrogenation of α-pinene. The reaction mixture obtained from 0.36 g (10 mmol) of $NaBH_4$, 20 mL of propan-2-ol, 0.65 g (5 mmol) of $NiCl_2$, and 34.4 g (0.25 mol) of α-pinene (**34**) after bubbling hydrogen for 5 h at 50°C contained 45% of 2,6,6-trimethylbicyclo[3.1.1]heptane (**36**). Mass spectrum, m/z (I_{rel}, %): 138 (3) $[M]^+$, 95 (91), 81 (93), 67 (100), 55 (58), 41 (34).

Hydrogenation of β-pinene. The reaction mixture obtained from 0.5 g (14 mmol) of $NaBH_4$, 20 mL of propan-2-ol, 1 g (8 mmol) of $NiCl_2$, and 27.2 g (0.2 mol) of β-pinene (**35**) after bubbling hydrogen for 5 h at 50°C contained 47% of **36**. Mass spectrum, m/z (I_{rel}, %): 138 (8) $[M]^+$, 95 (88), 81 (100), 67 (47), 41 (34).

2,2,3-Trimethylbicyclo[2.2.1]heptane (38). The reaction mixture obtained from 0.5 g (14 mmol) of $NaBH_4$, 20 mL of propan-2-ol, 0.9 g (7 mmol) of $NiCl_2$, and 25 g (0.184 mol) of camphene (**37**) after bubbling hydrogen for 6 h at 50°C contained 56% of **38**. Mass spectrum, m/z (I_{rel}, %): 138 (18) $[M]^+$, 109 (67), 95 (100), 82 (30), 67 (47), 41 (53).

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