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# Simple $H_2$-free hydrogenation of unsaturated monoterpenoids catalyzed by Raney nickel

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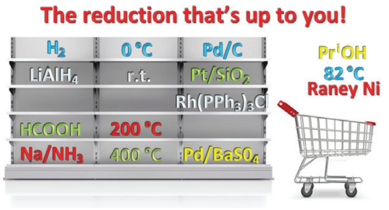
**A series of monoterpenoids (citral, carvone, menthone, camphor) as well as cyclohexanone and hex-5-en-2-one were subjected to transfer hydrogenation with Pr$^i$OH/Raney nickel system at 82 or 150 °C. Among monoterpenoids, citral and carvone underwent full conversion at 82 °C within 5 h.**

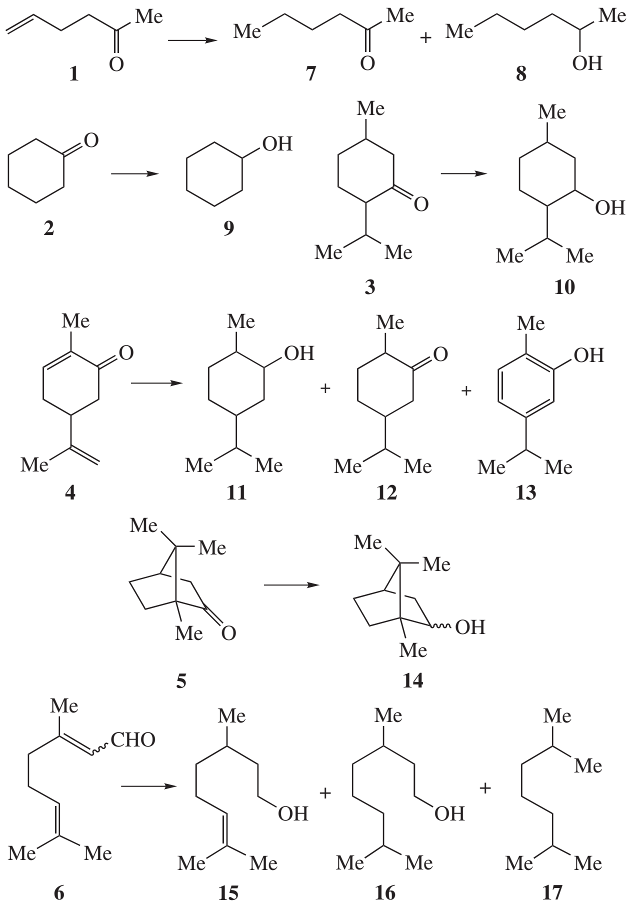


Nickel based heterogeneous catalysts including Raney nickel are widely used in many reductive transformations.[1,2] A wide range of the Raney nickel applications continues to grow in aspect of transfer hydrogenation (TH) reactions,[3–5] mostly reduction of carbonyl compounds to alcohols[6,7] and olefins to alkanes.[8,9] However, the heterogeneous TH of complex multifunctional molecules is still a challenge for chemists due to their special reactivity and stereo/chemo/regioselectivity problems. This study aimed to demonstrate our results of TH of some monoterpenoids (including low-reactive ones) catalyzed by Raney nickel in Pr$^i$OH medium. High H-donor activity of secondary Pr$^i$OH compared to primary alcohols was recently reported for reduction of menthone.[10]

Raney nickel was previously used in conventional hydrogenation of monoterpenoids.[1,11] The heterogeneous TH of monoterpenoids with alcohols was also described.[12–14] However, we failed to find the Raney nickel applications for TH of any monoterpenoids. The TH is usually processed at elevated temperature (95–120 °C) and long time is often needed for the full conversion. For example, the selectivity in TH of carbonyl group in citral and carvone catalyzed by zirconium-based metal-organic framework UiO-66 or its modified versions was studied.[13] Despite the well-known high reactivity of aldehydes and simple alkenes, the conversion of citral (2,6-dienal) was not complete, namely, only 80% within 24 h at 120 °C in Pr$^i$OH. Under the same conditions, the conversion of unsaturated carvone (2,7-dienone) was only 15%. Better results were achieved[12] when other Zr-MOF catalyst (Zr-MOF-808-P) was used. The C=O group of citral and carvone was converted in 100 and 50% extent, respectively, for 8 h at 120 °C in Pr$^i$OH. Similar results were reported for reduction of camphor,[14] namely, 75% yield of borneol was achieved for 5 h at 25 °C using nickel nanoparticles as a catalyst.

Conventional hydrogenation of aldehydes usually proceeds under milder conditions compared to TH. For example, citral can be totally transformed to 3,7-dimethyloctan-1-ol within 1 h with Raney nickel at 40 °C.[15] Nevertheless, it is difficult to perform conventional hydrogenation of sterically hindered carbonyl substrates such as menthone or camphor. The hydrogenation of menthone with molecular hydrogen catalyzed by Raney nickel is effective only at 180–200 °C,[11], while the conversion of camphor was 40% within 10 h at 80 °C in the case of Pt/SiO$_2$.[16] Thus, the simple synthetic procedure of reduction under hydrogen-free mild conditions is in high demand.

Here, substrates **1**–**6** were tested under $H_2$-free TH in the presence of Raney nickel (Scheme 1). Among them there were terpenoids, menthone **3**, carvone **4**, camphor **5** and citral **6**, while trivial hex-5-en-2-one **1** and cyclohexanone **2** served as the



**Scheme 1** *Reagents and conditions*: Pr$^i$OH, Raney nickel, 82 or 150 °C, 5 h.

**Table 1** Transfer hydrogenation of carbonyl compounds in $Pr^iOH$ catalyzed by Raney nickel.[a]

| Entry | Substrate | $T$/°C | Conversion (%) | Product composition[b] (%) |
|---|---|---|---|---|
| 1 | **1** | 82 | > 98 | **7** (2) + **8** (98) |
| 2 | **1** | 150 | >98 | **7** (4) + **8** (96) |
| 3 | **2** | 82 | >98 | **9** (>98) |
| 4 | **2** | 150 | >98 | **9** (>98) |
| 5 | **3** | 82 | 65 | **10** (>98) |
| 6 | **3** | 150 | 98 | **10** (>98) |
| 7 | **4** | 82 | >98 | **11** (97) + **12** (3) |
| 8 | **4** | 150 | 98 | **11** (98) + **12** (1) + **13** (1) |
| 9 | **5** | 82 | 27 | **14** (>98) |
| 10 | **5** | 150 | 53 | **14** (>98) |
| 11 | **6** | 82 | >98 | **15** (25) + **16** (73) + **17** (2) |
| 12 | **6** | 150 | >98 | **15** (94) + **17** (6) |

[a] Conditions: substrate (0.3–0.5 g, 3.2 mmol), $Pr^iOH$ (120 ml, 1.5 mol), Raney nickel (0.25 g, ~3.8 mmol of nickel), 5 h at specified temperature.
[b] GC–MC data, the starting substrate is excluded.

reference substrates.† All reaction courses were monitored by GC–MS.

Under the reaction conditions, both C=C and C=O bonds underwent hydrogenation. Conversion of hex-5-en-2-one **1**, cyclohexanone **2**, carvone **4**, and citral **6** achieved *ca.* 100% at both temperatures 82 and 150 °C (Table 1, entries 1–4, 7, 8, 11, 12). Due to steric and electronic hindrances, the reduction of menthone **3** and camphor **5** occurred slower than that of cyclohexanone **2**.[16] Conversion of menthone **3** reached 67 and 98% for 5 h at 82 and 150 °C, respectively (entries 5, 6). Since reactivity of camphor **5** is lower, only 27 and 53% of it was converted under the same conditions (entries 9, 10). The process was chemoselective as diastereomeric menthols **10** or borneols **14** were the only products.

Unlike menthone **3**, the conversion of structurally similar carvone **4** was higher (~100%) at both reference temperatures (see Table 1, entries 7,8) to provide the same fully hydrogenated carvomenthol **11** (as a mixture of diastereomers) with selectivity of 97–98%. The possible reason could be difference in adsorption of menthone **3** and carvone **4** on the catalyst surface, the conjugated enone moiety of carvone **4** having facilitated its adsorption and subsequent reduction. A small amount of carvone **4** was also isomerized to carvacrol **13** at 150 °C. This reaction can be accelerated at high temperatures using many catalysts including Raney nickel.[17]

Citral **6** (as a mixture of neral and geranial) demonstrates high activity in TH at both reaction temperatures (see Table 1, entries 11, 12). At 82 °C for 5 h, the main product was citronellol **15** (73%), while the yield of fully hydrogenated dihydrocitronellol **16** was 25% only. Apparently, conjugated enal moiety of citral is reduced faster than remote C=C bond that makes contribution in selectivity of TH. Expectedly, dihydrocitronellol **16** becomes the main product (94%) at 150 °C when nothing of citronellol **15** is detected. Obviously, decrease in reaction time and/or reaction temperature can help to control the reaction selectivity from partial to full hydrogenation. Another feature of this reaction is a little decarbonylation of citral[3] followed by fast reduction of thus formed $C_9$-hydrocarbon to fully hydrogenated 2,6-dimethylheptane **17** (2% at 82 °C *vs.* 6% at 150 °C).

In conclusion, the TH reaction catalyzed by Raney nickel at boiling point of $Pr^iOH$ demonstrates the synthetic potential for reduction of unsaturated monoterpenoids or other olefins/aldehydes/ketones. The method is simple and does not require the use of flammable gaseous $H_2$ or corrosive strong bases. The reaction is carried out in standard laboratory glassware without special equipment. The procedure is applicable for reduction of sterically hindered or low-reactive substrates.

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*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.07.006.

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[†] The reactions were carried out at 82 °C (the boiling point of $Pr^iOH$) in standard laboratory glassware or at 150 °C in 300 ml autoclave with magnetic stirring for 5 h under argon atmosphere. The temperature of 150 °C was reasoned by low reactivity of monoterpenoids in the TH reaction.[13,16] Monoterpene compound (0.3–0.5 g, 3.2 mmol) dissolved in $Pr^iOH$ (120 ml, 1.5 mol) was mixed with Raney nickel catalyst (0.250 g, ~3.8 mmol of nickel) freshly prepared by well-known method based on leaching with aq. NaOH at 50 °C from Raney alloy (Al : Ni = 50 : 50).[18] Physicochemical properties of prepared Raney nickel were in good agreement with reported data.[18] BET surface area of the catalyst was 50–70 $m^2\,g^{-1}$ and did not change dramatically during the reactions. Thus, despite the high nickel-to-substrate molar ratio (1.2 : 1), only about 5% of all Ni atoms were located on the surface of the catalyst. According to XPS method, the residual aluminum content in the catalyst was 10.3%. X-ray powder diffraction demonstrated the phase of metallic nickel formed from $Al_3Ni$ and $Al_3Ni_2$ intermetallics of initial alloy.