



Hydrogenation of Olefins with Hydrated Nickel Chloride, Lithium and a Catalytic Amount of Naphthalene†

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Abstract: The reaction of different olefins or dienes with a mixture of nickel (II) chloride dihydrate, an excess of lithium powder and a catalytic amount of naphthalene (17 mol%) in THF at room temperature, leads to the formation of the corresponding alkanes. The incorporation of deuterium oxide to the nickel salt complex yields deuterated hydrocarbons. Finally, in the case of dienes as starting materials the method can serve for mono or dihydrogenation depending on the amount of nickel salt used.
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In almost all catalytic hydrogenations of olefins molecular hydrogen has been used as the hydrogen source.¹ Since hydrogen is a dangerous, difficult to handle, and rather expensive reagent it would be very interesting to find other hydrogen sources in order to perform the transformation of olefins into the corresponding paraffins, the most attractive molecule for this purpose being possibly water.² This idea has been developed successfully, for instance, by Luche *et al.*³ using aqueous zinc-nickel chloride under ultrasonic conditions in the reduction of α,β -unsaturated carbonyl compounds. In this paper we report about the combination of hydrated nickel (II) chloride and lithium powder, in the presence of a catalytic amount of naphthalene as electron carrier, for the conversion of alkenes and dienes into alkanes.

The reaction of nickel (II) chloride dihydrate (1.5 mmol),⁴ an excess of lithium powder (1:12 molar ratio, referred to the olefin) and a catalytic amount of naphthalene (0.25 mmol, 17 mol%)⁵ with 1-octene (1 mmol) in THF at room temperature gave, after stirring overnight, octane in almost quantitative yield (GLC; Table 1, entry 1). The reaction is applicable not only to monoolefins (*trans*-stilbene or cyclododecene; Table 1, entries 5 and 7) but also to functionalised alkenes such as *o*-allylphenol (Table 1, entry 10). When the process is applied to dienes, it is possible to control the mono or dihydrogenation just by using 1.5 or 2.5 equivalents of the nickel salt, respectively; thus, for instance 1,5-cyclooctadiene can be transformed into cyclooctene (Table 1, entry 3)

† This paper is dedicated to Prof. G. Wilke on occasion of his 70th birthday for his fundamental contribution to organonickel chemistry.

or cyclooctane (Table 1, entry 4) using the mentioned procedure. When both double bonds in the starting diene are different the process works regioselectively: the monoreduction of cyclopentadiene dimer led to the hydrogenation of the six-membered ring double bond (Table 1, entry 8); as in the case of 1,5-cyclooctadiene, the double hydrogenation of cyclopentadiene dimer (Table 1, entry 9), as well as of (*E,E*)-1,4-diphenyl-1,3-butadiene (Table 1, entry 6), occurred with complete saturation of both double bonds.

The water content in the nickel salt is essential in order to achieve the mentioned hydrogenation: when the corresponding commercially available nickel (II) chloride hexahydrate was used instead of the dihydrate, the reaction failed.

An interesting extension of the hydrogenation reaction reported here is the use of a deuterium oxide containing nickel (II) salt. Thus, using nickel (II) chloride complexed with two equivalents of deuterium oxide⁶ is possible to obtain dideuterioalkanes from olefins. An example proving this possibility is the transformation of 1-octene into 1,2-dideuteriooctane showed in Table 1, entry 2.

Concerning to a possible reaction mechanism, we think that the most convincing pathway would involve two processes: (a) reduction of nickel (II) to Ni (0) (a black suspension is formed during the reaction)⁷ and (b) molecular hydrogen is formed by reaction of lithium with the water contained in the nickel salt. Although no gas evolution was observed, the hydrogen could be adsorbed by the metal and over its surface a catalytic hydrogenation type process could take place, probably involving nickel hydride species which by hydride olefin insertion and final alkyl-hydride reductive elimination would yield the corresponding alkanes.⁸

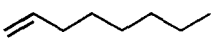
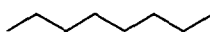
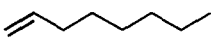
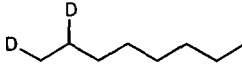
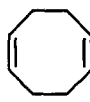
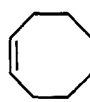
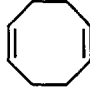
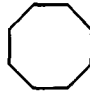
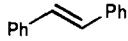
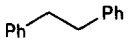
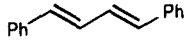
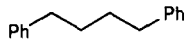
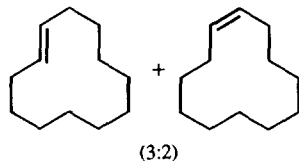
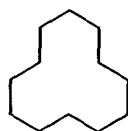
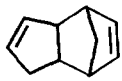
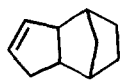
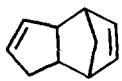
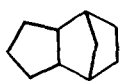
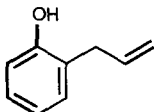
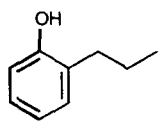
As a conclusion, we report here a new and simple method to hydrogenate (or deuterate) alkenes or dienes using the water (or deuterium oxide) of a nickel salt as the hydrogen source, avoiding so the use of molecular hydrogen. The procedure can be applied to the monohydrogenation of dienes just by adjusting the stoichiometry of the nickel salt used. Work is under way in order to study the scope of this reaction using different types of functionalised olefins and alkynes.

In a *typical reaction*, to a mixture of nickel (II) chloride dihydrate (250 mg, 1.5 mmol), lithium powder (85 mg, 12 mmol), and naphthalene (31 mg, 0.24 mmol), a solution of the corresponding olefin (1 mmol) in dry THF (10 ml) was added at room temperature under argon. The reaction mixture, which was initially green, changed to black after stirring overnight at the same temperature. The resulting suspension was then diluted with ether (20 ml) and filtered off through a pad containing silica gel and celite (*ca.* 3:1). After drying the filtrate with anhydrous sodium sulfate it was evaporated (15 Torr) and the resulting residue purified by column chromatography (silica gel, hexane) to give the pure reduced compounds.

ACKNOWLEDGEMENTS

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Table 1. Hydrogenation of Olefins and Dienes

| Entry | Starting material | NiCl ₂ ·2H ₂ O eq. | Product ^a | Yield (%) ^b |
|-------|---|--|---|------------------------|
| 1 |  | 1.5 |  | 99 ^c |
| 2 |  | 1.5 ^d |  | 99 ^c |
| 3 |  | 1.5 |  | 90 ^c |
| 4 |  | 2.5 |  | 96 ^c |
| 5 |  | 1.5 |  | 94 |
| 6 |  | 2.5 |  | 72 |
| 7 |  | 1.5 |  | 93 |
| 8 |  | 1.0 |  | 87 |
| 9 |  | 2.5 |  | 90 |
| 10 |  | 1.5 |  | 97 |

^a All isolated compounds (entries 5-10) were fully characterised by spectroscopic means (IR, ¹H and ¹³C NMR and MS); in the case of volatile compounds (entries 1-4), the characterisation was carried out by tandem GLC-MS by comparison with authentic samples.^b Isolated yield after column chromatography unless otherwise stated (footnote c).^c GLC yield.^d NiCl₂·2D₂O was used instead of the corresponding dihydrate.

REFERENCES AND NOTES

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2. The use of other hydrogen sources such as trialkylammonium formates,^{2a} boron hydrides,^{2b} or transition metal-containing reagents has been reported: (a) See, for instance: Cortese, N. A.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 3985-3987. (b) See, for instance: D'Incan, E.; Loupy, A. *Tetrahedron* **1981**, *37*, 1171-1179. (c) See, for instance: Fort, Y.; Vanderesse, R.; Caubere, P. *Tetrahedron Lett.* **1986**, *27*, 5487-5490.
3. Petrier, C.; Luche, J. L. *Tetrahedron Lett.* **1987**, *28*, 2347-2350, 2351-2352, and references cited therein.
4. This compound was prepared from commercially available nickel (II) chloride hexahydrate by heating *in vacuo* (ca. 0.5 torr) at 100°C in Kugelrohr during 2h: Nichols, D. In *Comprehensive Inorganic Chemistry*; Bailar, J. C.; Emeléus, H. J.; Nyholm, R.; Trotman-Dickenson, A. F., Eds.; Pergamon Press: Oxford, 1973; Vol. 3, p. 1126. After this treatment we found a loss of weight corresponding to ca. 4 H₂O per mol; anyhow, the thermogravimetric analysis (TG) indicated that a sample of the partially dehydrated nickel (II) chloride lost around 3.6 molecules of water in the range between 125 and 225°C.
5. For the use of a catalytic amount of an arene, as electron carrier in lithiation reactions, see: (a) Yus, M.; Ramón, D.J. *J. Chem. Soc., Chem Commun.* **1991**, 398-400. For a review, see: (b) Yus, M. *Chem. Soc. Rev.*, in the press. For the last paper from our laboratory on the subject, see: (c) Almena, J.; Foubelo, F.; Yus, M. *J. Org. Chem.* **1996**, *61*, 1859-1862.
6. This deuterated salt was prepared by treating commercially available anhydrous nickel (II) chloride with an excess of deuterium oxide and then the corresponding hexacoordinated complex was transformed into the dicoordinated one by the same procedure as for the hydrated salt (ref. 4).
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