

NICKELOCENE/LITHIUM ALUMINIUM HYDRIDE--A "HOMOGENEOUS RANEY NICKEL"  
FOR CATALYTIC HYDROGENATION<sup>1</sup>

Kin Man Ho, Man-Chor Chan and Tien-Yau Luh\*

Department of Chemistry, The Chinese University of Hong Kong  
Shatin, N.T., Hong Kong

Abstract. Nickelocene/lithium aluminum hydride in THF has been found to be an active homogeneous catalyst for catalytic hydrogenation. The reaction behaviour is very similar to Raney nickel.

Raney nickel is a useful catalyst and reducing agent for various purposes.<sup>2</sup> The actual modes of these reactions are not well-understood. We recently uncovered a new organonickel agent which can reduce various kinds of carbon-sulfur bond and behaves very similar to Raney nickel.<sup>3</sup> This newly developed homogeneous reagent may contain some kind of metal hydride moiety (moieties) which may play a significant role in the reduction of the carbon-sulfur bond.<sup>3</sup> It is noted a number of transition metal hydrides are active homogeneous catalysts for hydrogenation.<sup>4</sup> Since Raney nickel is also a useful catalyst for hydrogenation reaction,<sup>2</sup> it would be interesting to find out if our nickel reagent may also serve as a catalyst for the hydrogenation reaction. We have tested this viewpoint and now wish to report our results.

The catalyst was prepared under nitrogen atmosphere by mixing an equal molar of nickelocene and  $\text{LiAlH}_4$  in THF as described previously.<sup>3</sup> In a typical run, a THF solution of the substrate containing 1-5 mol percent of the catalyst was subjected to hydrogenation at ambient temperature and atmospheric pressure for several hours. The results are summarized in the Table 1. It is noted that disubstituted olefins, conjugated polyenes were readily reduced in good to excellent yields.

Selectivity has been observed in the hydrogenation of 2,3-disubstituted norbornadiene derivative where more sterically hindered olefin remained intact (run 5). Trisubstituted double bond has been found to be inactive under these conditions. Thus, cholesteryl acetate was unreactive toward hydrogenation with our catalyst. Functional groups such as ester and carbonyl groups are stable under the reaction conditions. Nitro group is poisonous to the catalyst. Consequently, when the catalyst was mixed with nitrotoluene and acenaphthylene in THF under our normal conditions, only starting materials were recovered. Indeed, nitro group can be reduced when stoichiometrical amount of the catalyst is employed.<sup>3</sup>

Alkynes can also smoothly be reduced under these conditions. Both diphenylacetylene (run 13) and dimethyl acetylenedicarboxylate (run 14) afforded bibenzyl and dimethyl succinate, respectively, in excellent yields.

The stereochemistry of the hydrogen addition under these conditions is an intriguing problem. Thus, dimethyl acetylenedicarboxylate was allowed to be partially hydrogenated under our normal conditions to give, in addition to dimethyl succinate, a small amount of dimethyl fumarate and dimethyl maleate in a ratio of 4:1. Control experiments showed that neither maleate nor fumarate underwent cis-trans isomerization under the reaction conditions.

Table 1 Nickelocene/LiAlH<sub>4</sub> catalyzed hydrogenation of alkenes and alkynes

Run	Substrate <sup>a</sup>	Product (%Yield <sup>b</sup> )
1	1,5-Cyclooctadiene	Cyclooctane (85) <sup>c</sup>
2	1,3,5-Cycloheptatriene	Cycloheptane (95) <sup>c</sup>
3	2,5-Norbornadiene	Norbornane (99) <sup>c</sup>
4	1,4-Diphenyl-1,3-butadiene	1,4-Diphenylbutane (95)
5	Dimethyl 2,5-norbornadiene-2,3-dicarboxylate	Dimethyl 2-norbornene-2,3-dicarboxylate (72)
6	Methyl cinnamate	Methyl 3-phenylpropionate (86)
7	Acenaphthylene	Acenaphthene (93)
8	Camphene	2,3,3-Trimethylbicyclo-[2.2.1]heptane (82)
9	Indene	Indan (99)
10	trans-4-Phenyl-3-buten-2-one	4-Phenylbuta-2-one (98)
11	Diethyl fumarate	Diethyl succinate (95)
12	Diethyl maleate	Diethyl succinate (97)
13	Diphenyl acetylene	Bibenzyl (96)
14	Dimethyl acetylene-dicarboxylate	Dimethyl succinate (98)

a. Typical procedure: 5 mmol of substrate in THF (ca. 20 mL) was mixed under nitrogen atmosphere with 0.5 to 2 mL of THF solution of the catalyst (ca. 0.1 M) and the mixture was subjected to atmospheric hydrogenation. The solution was filtered through filter aid and the solvent was evaporated and the residue was recrystallized or distilled or subjected to GC analysis.

b. Isolated yield unless otherwise specified.

c. GC yield.

Consequently, both *cis* and *trans* addition may occur in the hydrogenation of triple bond under these conditions.

In summary, we have depicted a homogeneous organonickel catalyst for hydrogenation. This study further establishes that our reagent may serve as a homogeneous model for the study of the mechanism of the reaction promoted by Raney nickel.

**Acknowledgment.** This research was made possible by the generous financial support of the Croucher Foundation. Thanks are also due to Chung Chi and United Colleges of the Chinese University of Hong Kong for partial support.

#### References:

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(Received in Japan 24 June 1986)