10.6 Hz, H-6 (*S*)), 5.89 (ddd, 0.5 H, *J* = 1.83, 2.19, and 10.6 Hz, H-6 (*R*)); $^{13}$C NMR $\delta$ 17.43 (q, C-3), 20.66 and 20.92 (q, MeCOO), 28.87 (q, C-1), 35.5 and 35.61 (t, C-4), 42.86 and 43.86 (d, C-3), 62.46 (t, C-10), 64.88 (d, H-8), 68.92 (d, C-9), 70.75 (d, C-5), 123.26 and 123.97 (d, C-7), 132.61 and 133.46 (d, C-6), 170.16 and 170.46 (s, MeCO), 207.98 (s, C-2). Anal. Calcd for $C_{15}H_{22}O_6$: C, 60.40; H, 7.38. Found: C, 60.10; H, 7.59.

**Acknowledgment.** We gratefully acknowledge the financial support of the "Association pour la Recherche sur le Cancer" (ARC), Villejuif, France.

**Registry No.** 1, 34819-86-8; 4, 513-42-8; 5, 53250-10-5; 6 (*R* diastereomer), 111160-63-5; 6 (*R* diastereomer, 2,4-dinitro-phenylhydrazone), 111160-84-0; 6 (*S* diastereomer), 111160-64-6; 6 (*S* diastereomer, 2,4-dinitrophenylhydrazone), 111160-85-1; 7 (*R* diastereomer), 111160-77-1; 7 (*S* diastereomer), 111160-78-2; 8 (*R* diastereomer), 111160-79-3; 8 (*S* diastereomer), 111160-80-6; 9, 111160-81-7; 10, 111160-82-8; 11, 25195-85-1; 12, 111160-83-9; 13, 111160-62-4; 14, 111160-65-7; 15 (*R* diastereomer), 111160-66-8; 15 (*S* diastereomer), 111160-67-9; 16, 3152-43-0; 17 (*R* diastereomer), 111160-68-0; 17 (*S* diastereomer), 111160-69-1; 18, 101052-70-4; 19 (*R* diastereomer), 111160-70-4; 19 (*R* diastereomer, 2,4-dinitrophenylhydrazone), 111160-86-2; 19 (*S* diastereomer), 111160-71-5; 19 (*S* diastereomer, 2,4-dinitrophenylhydrazone), 111160-87-3; 20, 111160-72-6; 21 (*R* diastereomer), 111160-73-7; 21 (*S* diastereomer), 111160-74-8; 22 (*R* diastereomer), 111160-75-9; 22 (*S* diastereomer), 111160-76-0.

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# Reduction of Organic Compounds with Rare-Earth Intermetallics Containing Absorbed Hydrogen

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*Received March 11, 1987*

The hydrogenation of organic compounds with rare-earth intermetallic hydrides has been investigated. Alkynes, alkenes, aldehydes, ketones, nitriles, imines, and nitro compounds are hydrogenated in excellent yields with $LaNi_5H_6$ or $LaNi_{4.5}Al_{0.5}H_5$ at 0–60 °C. The present hydrogenation method has the following characteristic features. (1) The intermetallic compounds (alloys) are not poisoned by compounds containing an amino group or a halogen atom. (2) The alloys can be used repeatedly without decrease in activity. (3) The reaction conditions are mild, and selective hydrogenations of some organic functional groups can be achieved. The reaction mechanism of this hydrogenation is briefly discussed in terms of stereochemistry and H/D exchange reactions.

Rare-earth intermetallics (alloy) such as $LaNi_5$, $PrCo_5$, and $SmCo_5$ absorb large quantities of hydrogen rapidly and reversibly under mild conditions, and hence they possess a high potential for uses as hydrogen storage substances. These classes of alloys are currently receiving considerable attention, particularly from the standpoint of energy storage, and their physicochemical characteristics have been extensively studied.[1]

On the other hand, relatively less attention has been paid to the utilization of these alloys in chemical reactions as reagents and catalysts. The works reported hitherto are mostly concerned with the kinetic investigation on the hydrogenation activity of the alloys from a physicochemical point of view.[2] The substrates used in the previous investigations are limited to several selected model compounds such as carbon monoxide, ethylene, butadiene, and acetonitrile.[3] Consequently, there have been little precedent investigations directed toward the practical utili-

zation of these alloys in organic synthesis.

In our continuing study on the utilization of lanthanoid elements in organic synthesis,[4] we have been interested in the characteristic properties of the rare-earth intermetallics and intended to utilize them in the reduction of organic functional groups.[5]

## Results and Discussion

**Hydrogenation of Organic Functional Groups over $LaNi_5H_6$.** Our initial study was undertaken with the use of lanthanum–nickel alloys ($LaNi_5$) which is one of the representative rare-earth alloys. The hydrogen absorption/desorption pressure of this alloy is 1–2 atm at room temperature, and it is capable of absorbing hydrogen up to the composition represented by the formula $LaNi_5H_6$.[1] This intermetallic hydride is known to be pyrophoric and often burns on contact with air. Therefore, we devised an experimental procedure, by which experiments could be carried out safely (see Experimental Section). By employing this procedure, we tried the reduction of many organic functional groups. The results are summarized in Table I.

Mono- and disubstituted olefins were hydrogenated at around room temperature in essentially quantitative yields (entries 1–6). The more highly substituted olefins were virtually inert to these reducing conditions (entries 3 and 5).

Alkynes were also reduced to saturated compounds under the similar conditions (entries 7 and 8). Semi-hydrogenation of alkynes to (*Z*)-olefins was attempted at

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(2) Coon, V. T.; Takeshita, T.; Wallace, W. E.; Craig, R. S. *J. Phys. Chem.* **1976**, *80*, 1878. Takeshita, T.; Wallace, W. E.; Craig, R. S. *J. Catal.* **1976**, *44*, 236. Soga, K.; Imamura, H.; Ikeda, S. *Nippon Kagaku Kaishi* **1977**, 1304. Atkinson, G. B.; Nicks, L. J. *J. Catal.* **1977**, *46*, 417. Luengo, C. A.; Cabrera, A. L.; MacKay, H. B.; Maple, M. B. *J. Catal.* **1977**, *47*, 1. Barrault, J.; Duprez, D.; Percheron-Guégan, A.; Achard, J. C. *J. Less-Common Met.* **1983**, *89*, 537.

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(5) A preliminary account of this work has appeared: Imamoto, T.; Mita, T.; Yokoyama, M. *J. Chem. Soc., Chem. Commun.* **1984**, 163.

## Table I. Hydrogenation of Organic Functional Groups with LaNi₅H₆

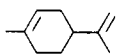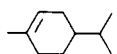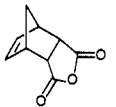Table I. Hydrogenation of Organic Functional Groups with $LaNi_5H_6$

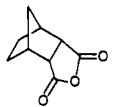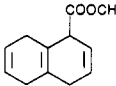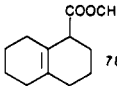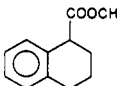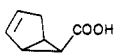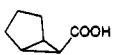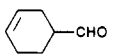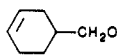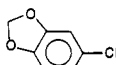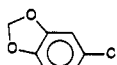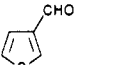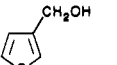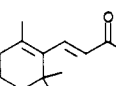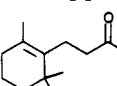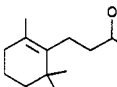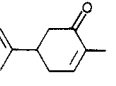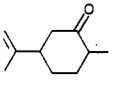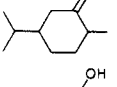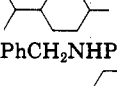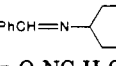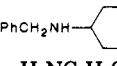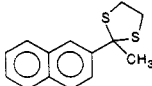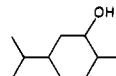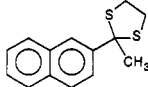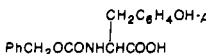| entry | compound | conditions[a] | product | yield,[b] % |
|---|---|---|---|---|
| 1 | $C_{10}H_{21}CH{=}CH_2$ | rt,[c] 15 h | $C_{12}H_{26}$ | 86 |
| 2 | $Ph_2P(O)CH_2CH{=}CH_2$ | rt, 11 h | $Ph_2P(O)C_3H_7$ | 90 |
| 3[d] |  | rt, 11 h |  | 88 |
| 4[d] |  | rt, 18 h |  | 93 |
| 5 |  | rt, 4 h |  | 78 |
|  |  |  |  | 19 |
| 6[d] |  | 0 °C, 3 h |  | 93 |
| 7[d] | $PhC{\equiv}CPh$ | rt, 9 h | $Ph(CH_2)_2Ph$ | 96 |
| 8 | $PhC{\equiv}CC{\equiv}CPh$ | rt, 11 h | $Ph(CH_2)_4Ph$ | 97 |
| 9[d] | $HOCH_2C{\equiv}CCH_2OH$ | 0 °C, 6 h | $(Z)\text{-}HOCH_2CH{=}CHCH_2OH$ | 67 |
|  |  |  | $HO(CH_2)_4OH$ | 10 |
| 10[d] | $C_{11}H_{23}CHO$ | rt, 14 h | $C_{12}H_{25}OH$ | 98 |
| 11[d] |  -CHO | rt, 8 h |  -CH₂OH | 91 |
| 12[d] |  -CHO | rt, 9 h |  -CH₂OH | 99 |
| 13[d] | $p\text{-}ClC_6H_4CHO$ | rt, 8 h | $p\text{-}ClC_6H_4CH_2OH$ | 95 |
| 14 |  CHO | rt, 14 h |  CH₂OH | 96 |
| 15[d] | $C_6H_{13}COCH_3$ | rt, 37 h | $C_6H_{13}CHOHCH_3$ | 91 |
| 16 | 2-adamantanone | rt, 16 h | 2-adamantanol | 92 |
| 17[d] | $p\text{-}CH_3OC_6H_4COCH_3$ | rt, 37 h | $p\text{-}CH_3OC_6H_4CHOHCH_3$ | 85 |
| 18[d] | $PhCOCOPh$ | rt, 11 h | $PhCOCHOHPh$ | 96 |
| 19 | $PhC{\equiv}CCOOH$ | rt, 15 h | $Ph(CH_2)_2COOH$ | 99 |
| 20 | $PhCH{=}CHCOOC_2H_5$ | rt, 15 h | $Ph(CH_2)_2COOC_2H_5$ | 93 |
| 21[d] | $PhCH_2OCOC(CH_3){=}CH_2$ | 0 °C, 4 h | $PhCH_2OCOCH(CH_3)_2$ | 91 |
| 22[d] | $PhCH{=}CHCOCH_3$ | rt, 17 h | $Ph(CH_2)_2CHOHCH_3$ | 95 |
| 23 | citral | 0 °C, 3 h | citronellal | 89 |
| 24 |  | rt, 12 h | citronellol | 95 |
| 25[d] | $PhCH{=}CHCOPh$ | 0 °C, 6 h | $Ph(CH_2)_2COPh$ | 89 |
| 26[d] |  | rt, 43 h | $Ph(CH_2)_2CHOHPh$ | 99 |
| 27[d] |  | 0 °C, 6 h |  | 89 |
| 28[d] |  | rt, 33 h |  | 95 |
| 29 |  | 0 °C, 3 h |  | 70 |
|  |  |  |  | 25 |
| 30[d] |  | rt, 3 h |  | 90 |
| 31 | $PhCH{=}NPh$ | rt, 11 h | $PhCH_2NHPh$ | 95 |
| 32[d] | PhCH=N—⟨⟩ | rt, 13 h | PhCH₂NH—⟨⟩ | 97 |
| 33 | $p\text{-}O_2NC_6H_4COOC_2H_5$ | rt, 13 h | $p\text{-}H_2NC_6H_4COOC_2H_5$ | 97 |
| 34 | $PhC({=}NOH)CH_2Ph$ | rt, 44 h | e |  |
| 35 | $PhC({=}NOAc)CH_2Ph$ | rt, 50 h | e |  |
| 36 | $PhSCH_2CH{=}CH_2$ | rt, 28 h | e |  |
| 37 | $PhCOCH_2S(O)CH_3$ | rt, 15 h | e |  |
| 38 | $PhCOCH_2SO_2CH_3$ | rt, 19 h | e |  |

**Table I** (Continued)

| entry | compound | conditions[a] | product | yield,[b] % |
|---|---|---|---|---|
| 39 | $PhSO_2CH=C(SCH_3)_2$ | rt, 34 h | e | |
| 40 |  | rt, 38 h | e | |
| 41 | $PhCH_2OCONHCH(CH_2C_6H_4OH-p)COOH$ | rt, 18 h | e | |
| 42 | $PhCH_2OCONHCH(CH_2CH_2SCH_3)CONHCH_2COOCH_3$ | rt, 36 h | e | |
| 43[f] | $p\text{-}CH_3OC_6H_4COCl$ | rt, 48 h | e | |
| 44 | $PhCH=CHCOSC(CH_3)_3$ | rt, 18 h | e | |

[a] All reactions were carried out in THF–MeOH(2:3) on a 1-mmol scale using 3 g of $LaNi_5H_6$. [b] Isolated yield. [c] Room temperature. [d] A recovered alloy was used. [e] No reaction took place. [f] The reaction was carried out in dry THF.

**Table II. Hydrogenation of Organic Functional Groups with $LaNi_{4.5}Al_{0.5}H_5$**

| entry[a] | compound | time, h | product | yield,[b] % |
|---|---|---|---|---|
| 1 | $PhC\equiv CPh$ | 2 | $PhCH_2CH_2Ph$ | 96 |
| 2 | | 32 | | 91 |
| 3[c] | $PhCH=CHCOOC_2H_5$ | 3 | $PhCH_2CH_2COOC_2H_5$ | 97 |
| 4[c] | $p\text{-}O_2NC_6H_4COOC_2H_5$ | 2 | $p\text{-}H_2NC_6H_4COOC_2H_5$ | 95 |
| 5[c] | $PhCH=NPh$ | 2 | $PhCH_2NHPh$ | 95 |
| 6[d] | $PhCN$ | 15 | $PhCH_2NHCOCH_3$ | 92 |
| 7 | $PhCH=CHCOS(CH_3)_3$ | 20 | e | |
| 8 |  | 20 | e | |
| 9 | $PhCH_2OCONH\overset{CH_2C_6H_4OH-p}{\underset{}{C}HCOOH}$ | 20 | e | |

[a] All reactions were carried out at 60 °C in THF–MeOH (2:3) on a 1-mmol scale using 3 g of $LaNi_{4.5}H_5$. [b] Isolated yield. [c] A recovered alloy was used. [d] This reaction was carried out in the presence of acetic anhydride. [e] No reaction took place.

0 °C by the use of 2-butyne-1,4-diol as a model compound. Unfortunately, however, the result indicates that this method is not superior over the previously established methods such as the hydrogenation using the Lindlar catalyst.[6]

Aldehydes were subjected to hydrogenation at room temperature to give primary alcohols. The reaction of 3-thiophenecarboxaldehyde is worthy to mention. The reaction proceeded smoothly without decrease of the activity of the alloy. This result is in contrast to the conventional hydrogenations using heterogeneous catalysts,[7] which are often poisoned by thiophenes. On the other hand, the hydrogenation of ketones required prolonged reaction time generally more than 15 h. This was particularly notable in the reduction of aromatic ketones having an electron-releasing group.

The hydrogenation of $\alpha,\beta$-unsaturated carboxylic acids or esters proceeded smoothly at room temperature to yield the corresponding saturated carboxylic acids or esters (entries 19–21).[8] For $\alpha,\beta$-unsaturated carbonyl compounds, the conjugated double bond was most easily hydrogenated, but the subsequent reduction of the carbonyl

group proceeded slowly. Thus, selective reduction was easily achieved by control of the reaction temperature and time, as exemplified by the reduction of citral, 1,3-diphenylprop-2-en-1-one, and $\beta$-ionone (entries 23, 25, and 27). This method for the selective reduction is favorably compared with previously existing methods.[9]

The present method was effective also for the reduction of nitro compounds and imines, especially as the $LaNi_5$ alloy was not poisoned by the liberated amines (entries 31–33).

The hydrogenation of other functional groups was also attempted. However, no fruitful results were obtained for the reduction or reductive desulfurization of oximes, sulfoxides, sulfones, and dithioketals; no reaction took place even at elevated temperature (ca. 60 °C). The reductive cleavage of benzyloxycarbonyl group attached to amino acids or peptides was unsuccessful, too.

(6) For a review, see: Marvell, E. N.; Li, T. *Synthesis* **1973**, 457.

(7) For selected reviews on catalytic hydrogenations, see: Friefelder, M. *Catalytic Hydrogenation in Organic Synthesis*; Wiley: New York, 1978. Rylander, P. N. *Catalytic Hydrogenation in Organic Synthesis*; Academic: New York, 1979. Johnstone, R. A. W.; Wilby, A. H.; Entwistle, I. D. *Chem. Rev.* **1985**, *85*, 129. Hudlicky, M. *Reductions in Organic Chemistry*; Ellis Horwood: West Sussex, 1984.

(8) For examples of the hydrogenation of $\alpha,\beta$-unsaturated carboxylic acids or esters into saturated carboxylic acids or esters, see: Castro, C. E.; Stephens, R. D.; Moje, S. *J. Am. Chem. Soc.* **1966**, *88*, 4964. Harmon, R. E.; Parsons, J. L.; Cooke, D. W.; Gupta, S. K.; Schoolenberg, J. *J. Org. Chem.* **1969**, *34*, 3684. Shaw, J. E.; Knutson, K. K. *J. Org. Chem.* **1971**, *36*, 1151. Satoh, T.; Nanba, K.; Suzuki, S. *Chem. Pharm. Bull.* **1971**, *19*, 817.

(9) For conjugate reduction of $\alpha,\beta$-unsaturated carbonyl compounds, see the following: Ojima, I.; Kogure, T.; Nagai, Y. *Tetrahedron Lett.* **1972**, 5035. Wolf, H. R.; Zink, M. P. *Helv. Chim. Acta* **1973**, *56*, 1062. Kursanov, D. N.; Loim, N. M.; Baranova, V. A.; Moiseeva, L. V.; Zalakaev, L. K.; Parnes, Z. N. *Synthesis* **1973**, 420. Semmelhack, M. F.; Stauffer, R. D.; Yamashita, A. *J. Org. Chem.* **1977**, *42*, 3180. Cortese, N. A.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 3985. Collman, J. P.; Finke, R. G.; Matlock, P. L.; Wahren, R.; Komoto, R. G.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 1119. Mueller, R. H.; Gillick, J. G. *J. Org. Chem.* **1978**, *43*, 4647. Reger, D. L.; Habib, M. M.; Fauth, D. J. *Tetrahedron Lett.* **1979**, 115. Mordenti, L.; Brunet, J. J.; Caubere, P. *J. Org. Chem.* **1979**, *44*, 2203. Contento, M.; Savoia, D.; Trombini, C.; Umani-Ronchi, A. *Synthesis*, **1979**, 30. Yamashita, M.; Kato, Y.; Suemitsu, R. *Chem. Lett.* **1980**, 847. Tsuda, T.; Fujii, T.; Kawasaki, K.; Saegusa, T. *J. Chem. Soc., Chem. Commun.* **1980**, 1013. Gammill, R. B.; Sobieray, D. M.; Gold, P. M. *J. Org. Chem.* **1981**, *46*, 3555. Ojima, I.; Kogure, T. *Organometallics* **1982**, *1*, 1390. Keinan, E.; Gleize, P. A. *Tetrahedron Lett.* **1982**, *23*, 477. Caporusso, A. M.; Giacomelli, G.; Lardicci, L. *J. Org. Chem.* **1982**, *47*, 4640. Ohta, H.; Konishi, J.; Tsuchihashi, G. *Chem. Lett.* **1983**, 1895. Nakamura, K.; Fujii, M.; Ohno, A.; Oka, S. *Tetrahedron Lett.* **1984**, *25*, 3983. Chikashita, H.; Itoh, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1747.

**Table III. Reduction of Organic Compounds with LaNi₅H₆ in the Presence of D₂O**

| entry | compound | conditions[a] | product[b,c] |
|---|---|---|---|
| 1 | PhCH=CHCOCH₃ | LaNi₅H₆, D₂O/THF, 0 °C, 3 h | PhCH₂CH₂COCH₃[d] |
| 2 | | LaNi₅H₆, D₂O/THF, rt, 14 h | 70% / OD–25% / Ph / CH₃ / 10% |
| 3 | PhCH₂CH₂COCH₃ | LaNi₅H₆, D₂O/THF, rt, 24 h | 60% / OD–25% / Ph / CH₃ / 5% |
| 4 | PhCH=CHCOCH₃ | LaNi₅HₘDₙ,[e] D₂O/THF, 0 °C, 3 h | 35% / O / Ph / CH₃ / 35% |
| 5 | PhCH₂CH₂CHOHCH₃ | LaNi₅H₆, D₂O/THF, rt, 24 h | 85% / OD–0% / Ph / CH₃ / 5% |
| 6 | PhCH₂CH₂COCH₃ | LaNi₅,[f] D₂O/THF, rt, 15 h | PhCH₂CH₂COCH₃[d] |

[a] All reactions were carried out in D₂O–THF (1:5) (6 mL) on a 1-mmol scale using 3 g of LaNi₅H₆. [b] Yields of the products were almost quantitative except entries 1, 5, and 6. [c] Figures indicate contents of deuterium which were determined by ¹H NMR integration. [d] Deuterium was not incorporated. [e] This intermetallic hydride was prepared by treatment of LaNi₅H₆ with D₂O at room temperature for 22 h. [f] Adsorbed hydrogen of LaNi₅H₆ was removed in vacuo before use.

The results described above indicate that the intermetallic hydride (LaNi₅H₆) exhibits different reactivities in comparison with conventional catalytic hydrogenation agents, e.g., Raney nickel, Pd/charcoal, and PtO₂.[7,10–14] The alloy is generally less reactive than the catalysts employed frequently, but this nature of reactivity allows the selective hydrogenation of some organic functional groups (entries 4, 6, 21, 23, and 27).

Another characteristic of this method is that the alloy can be used repeatedly. Thus, the recovered alloy readily absorbs hydrogen by activation, and the reproduced intermetallic hydride is capable of reducing functional groups without any decrease of the activity.

**Hydrogenation over LaNi₄.₅Al₀.₅H₅.** Another representative rare-earth intermetallic compound is LaNi₄.₅Al₀.₅. This alloy is known to absorb hydrogen to form a hydride represented by the formula LaNi₄.₅Al₀.₅H₅.[15] The hydrogen absorption/desorption pressure is approximately 1 atm at about 60 °C. Thus, the hydrogenation with this intermetallic hydride would be performed at that temperature.

We examined the hydrogenation activity of this hydride toward several organic functional groups. As is shown in Table II, alkynes, alkenes, carbonyl compounds, imines, nitriles, and nitro compounds were readily reduced at 60 °C. However, the reduction of compounds containing sulfur functionality was extremely sluggish. The reductive cleavage of benzyl esters was unsuccessful, too. These results indicate that LaNi₄.₅Al₀.₅H₅ displays similar reactivities as LaNi₅H₆, although the reactions are conducted at higher temperature.

**Stereochemistry of the Hydrogenation.** The stereochemistry of the hydrogenation with rare earth alloys was studied by the use of (*E*)- and (*Z*)-dimethylstilbenes as the model compounds. (*E*)-Dimethylstilbene was converted into *rac*- and *meso*-2,3-diphenylbutanes in a ratio of 62:1 (eq 1). The Z isomer afforded almost exclusively *meso*-

(10) Mosettig, E.; Mozingo, R. *Org. React.* (*N. Y.*) **1948**, *4*, 362.
(11) Hartung, W. H.; Simonoff, R. *Org. React.* (*N. Y.*) **1953**, *7*, 263.
(12) Pettit, G. R.; Van Tamelen, E. E. *Org. React.* (*N. Y.*) **1962**, *12*, 356.
(13) Hauptmann, H.; Walter, W. F. *Chem. Rev.* **1962**, *62*, 347.
(14) Pizey, J. S. *Synthetic Reagents*; Ellis Horwood: Chichester, 1974; Vol. 2, p 175.
(15) Mendelsohn, M. H.; Gruen, D. M.; Dwright, A. E. *Nature* (*London*) **1977**, *269*, 45.

2,3-diphenylbutane (eq 2). These results indicate that the addition of hydrogen to double bond proceeded through cis addition which is well observed in the conventional catalytic hydrogenations.[7]
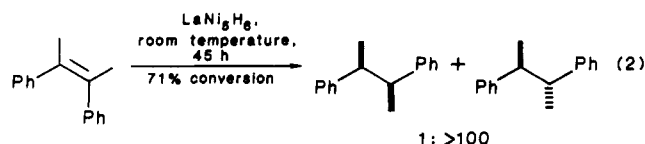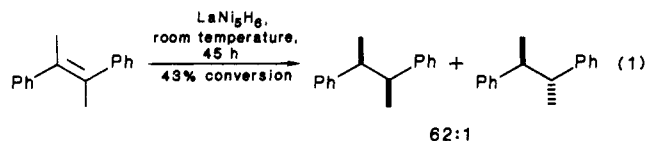




**Hydrogenation in the Presence of D₂O.** Numerous mechanistic studies on catalytic hydrogenation of olefins[7] suggest that the reaction with LaNi₅H₆ also involves the initial hydrometallation followed by reductive cleavage of the carbon–metal bond. However, there remains a possibility that the reaction might involve a stable metal hydride species which does not undergo reductive elimination but is subjected to protonation with protic solvent. Because of this, the present method requires large excess of LaNi₅H₆ to complete the reactions[16] (eq 3).
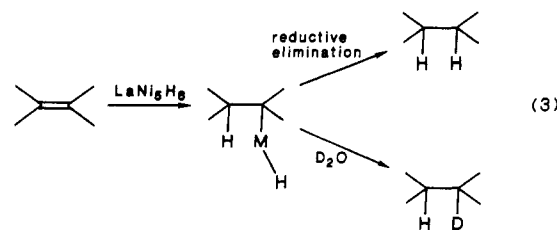


In order to obtain the mechanistic aspects, particularly to ascertain that the latter process is not involved in the reaction sequence, we tried the hydrogenation of a few model compounds with LaNi₅H₆ in the presence of D₂O.

(16) In order to test the catalytic activity of LaNi₅, ethyl cinnamate (2.03 g, 11.5 mmol) was stirred in ethanol with LaNi₅ (135 mg, 0.31 mmol) under 15 atm of hydrogen at room temperature. The reaction was sluggish and required 4 days to furnish ethyl 3-phenylpropionate (2.04 g, 99%). Under similar conditions, piperonal and ethyl p-nitrobenzoate were hydrogenated only in 19% and 15% yields, respectively.

These experiments were carried out on the assumption that if the reaction would proceed through the latter pathway, deuterium should be incorporated in the product.

At first, 4-phenyl-3-buten-2-one was treated with LaNi$_5$H$_6$ in D$_2$O/THF at 0 °C for 3 h. The $^1$H NMR analysis of the product (4-phenyl-2-butanone) indicated that no detectable amount of deuterium was incorporated in the product (entry 1 in Table III). This result clearly demonstrates that the hydrogenation does not proceed through the latter pathway.

On the other hand, when 4-phenyl-3-buten-2-one and 4-phenyl-2-butanone were treated at room temperature for long time, considerable amounts of deuterium were incorporated in the product (4-phenyl-2-butanol), as indicated in entries 2 and 3. Incorporation of deuterium was also observed even at 0 °C by the use of the intermetallic hydride which was previously stirred in D$_2$O at room temperature for 22 h (entry 4). Another finding is that the hydrogens at the benzylic position of 4-phenyl-2-butanol were preferentially exchanged with deuterium on treatment with LaNi$_5$H$_6$ in D$_2$O/THF for 24 h at room temperature. Contrary to these results, not only reduction but also H/D exchange were not induced by alloy containing no absorbed hydrogen (entry 6).

These reactions are considered to proceed through the following pathways. LaNi$_5$H$_6$ is initially subjected to H/D exchange with D$_2$O to form intermetallic hydride (LaNi$_5$H$_m$D$_n$) containing deuterium (see eq 4-6). This H/D exchange reaction is sluggish at 0 °C but proceeds at room temperature.[17] The reduction of 4-phenyl-3-buten-2-one and 4-phenyl-2-butanone with the hydride provides 4-phenyl-2-butanol containing deuterium. These reductions proceed through hydrometalation and subsequent reductive elimination. The hydrometalation is reversible, and hence hydrogens at benzylic position are preferentially exchanged with deuterium under the conditions.

$$\text{LaNi}_5\text{H}_6 \xrightarrow{\text{D}_2\text{O}} \text{LaNi}_5\text{H}_m\text{D}_n \qquad (4)$$

$$\text{PhCH=CHCOCH}_3 \xrightarrow[0\,°C]{\text{LaNi}_5\text{H}_m\text{D}_n}$$
$$\text{PhCH(D)CH(D)COCH}_3 \xrightarrow[\text{room temperature}]{\text{LaNi}_5\text{H}_m\text{D}_n}$$
$$\text{PhCH(D)CH(D)C(D)(OD)CH}_3 \xrightarrow[\text{room temperature}]{\text{LaNi}_5\text{H}_m\text{D}_n}$$
$$\text{PhC(D)}_2\text{CH(D)C(D)(OD)CH}_3 \qquad (5)$$

$$\text{PhCH}_2\text{CH}_2\text{CHOHCH}_3 \xrightarrow[\text{room temperature}]{\text{LaNi}_5\text{H}_m\text{D}_n}$$
$$\text{PhC(D)}_2\text{CH}_2\text{CH(OD)CH}_3 \qquad (6)$$
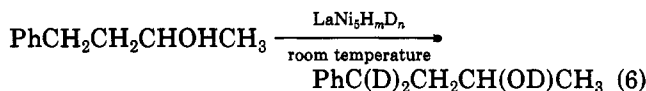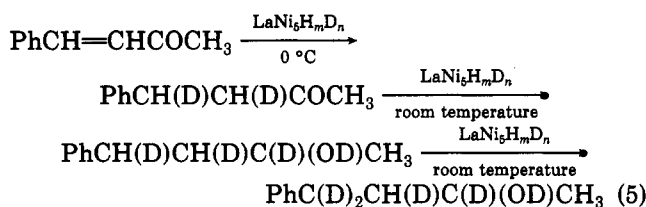
## Experimental Section

**Materials.** Rare-earth intermetallics LaNi$_5$ and LaNi$_{4.5}$Al$_{0.5}$ were supplied by Santoku Metal Industry Co. Ltd. Allyldiphenylphosphine oxide[18] was prepared by the reaction of diphenylphosphine oxide with allyl bromide in the presence of KOH in methanol. Methyl 1,4,5,8-tetrahydro-1-naphthalenecarboxylate[19] was synthesized from 1-naphthalenecarboxylic acid by the Birch reduction with Li/NH$_3$ followed by the methylation with diazomethane. Bicyclo[3.1.0]hex-2-ene-6-*endo*-carboxylic acid,[20] (*S*)-*tert*-butyl 3-phenylpropenethioate,[21] and 1,1-bis-(methylthio)-2-(phenylsulfonyl)ethene[22] were obtained by the literature procedures. Other simple chemicals were purchased and purified before use.

**Hydrogenation with LaNi$_5$H$_6$ (General Procedure).** A 20-mL long-necked flask containing LaNi$_5$ ingot[23] (3 g) was placed in an autoclave. The system was evacuated (ca. 0.1 mmHg), and the autoclave was heated to 200 °C. After the temperature was kept at 200 °C for 10 min, hydrogen was introduced up to 30 atm. The temperature was kept for 10 min, the autoclave was cooled to room temperature. This operation was repeated five times.[24,25] Then, the autoclave was immersed in an ice bath and finally in a dry ice-acetone bath. Excess hydrogen was released, and the flask was taken out in a stream of nitrogen and was set on a magnetic stirrer.

A solution of organic compound (1 mmol) in THF–MeOH (2:3)[26] (5 mL) was added by the use of a syringe at −78 °C. Then, the dry ice bath was removed, and the mixture was stirred under nitrogen at 0 °C through to room temperature. After completion of the reduction, the mixture was filtered by suction to recover the alloy.[27] The filtrate was concentrated, and the residue was purified by preparative thin-layer chromatography (TLC) on silica gel.

**Hydrogenation with LaNi$_{4.5}$Al$_{0.5}$H$_5$ (General Procedure).** The alloy LaNi$_{4.5}$Al$_{0.5}$ (3 g) was activated according to the method mentioned above. To the obtained intermetallic hydride, a solution of organic compound (1 mmol) in THF–MeOH (2:3) (5 mL) was added at −78 °C under nitrogen. The mixture was gradually warmed with stirring to 60 °C. The stirring was continued until the reaction was complete. The reaction mixture was worked up in a similar procedure described above and the product was isolated by preparative TLC.

**Hydrogenation in the Presence of D$_2$O.** A typical experimental procedure is described for entry 2 in Table III. To the intermetallic hydride (LaNi$_5$H$_6$) prepared from LaNi$_5$ (3 g) was added a solution of 4-phenyl-3-buten-2-one (157 mg, 1.07 mmol) in dry THF (5 mL) at −78 °C under nitrogen. The cooling bath was replaced by an ice bath, and D$_2$O (1 mL) was added. The mixture was stirred for 14 h at room temperature. The reaction mixture was filtered by suction, and the filtrate was concentrated. The residual oil was subjected to preparative TLC on silica gel to afford 4-phenyl-2-butanol (162 mg, 100%). The content of deuterium in the product was determined by $^1$H NMR integration.

(17) Hydrogen occluded in Raney nickel is known to exchange with deuterium in D$_2$O. Khan, N. A. *J. Am. Chem. Soc.* **1952**, *74*, 3018.
(18) Downie, I. M.; Morris, G. *J. Chem. Soc.* **1965**, 5771.

(19) Sims, J. J.; Honwad, V. K.; Selman, L. H. *Tetrahedron Lett.* **1969**, 87.
(20) Meinwald, J.; Labana, S. S.; Chadha, M. S. *J. Am. Chem. Soc.* **1963**, *85*, 582.
(21) Imamoto, T.; Kodera, M.; Yokoyama, M. *Synthesis* **1982**, 134.
(22) Yokoyama, M.; Tsuji, K.; Imamoto, T. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2954.
(23) LaNi$_5$ and related alloys are supplied from Aldrich Chemical Co.
(24) Activated alloy absorbing hydrogen is black powder. The composition of the hydrogenated alloy is estimated to be LaNi$_5$H$_6$; 3 g of the alloy contains ca. 20 mmol of hydrogen.
(25) When recovered alloy is used, the repetition of this operation is not necessary.
(26) THF was added to make a complete solution of organic substrate.
(27) Care must be taken in handling the recovered alloy, although we have not seen the alloy to ignite in air through this work. For the disposal of the used alloy, it is recommended to dissolve it in hydrochloric acid.