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Hydrogenation of Biphenyl Using a Hydrogen Storage Alloy as a Hydrogenation Reagent

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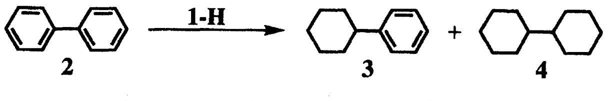
A detailed investigation of the hydrogenation reaction of biphenyl with $MmNi_{3.5}Co_{0.7}Al_{0.8}H_{4.2}$ [Mm: mixture of La, Ce, Pr, and Nd (30 : 52 : 5 : 13 wt ratio)] to give either cyclohexylbenzene or bicyclohexyl was performed. Time profiles of the amounts of hydrogen evolved from the alloy and that introduced into biphenyl during the reaction were measured; it was suggested that the hydrogen absorbed by the alloy could predominantly react with the substrate, and the hydrogen released into the gas phase played only a minor role in the reaction. The deuteration of biphenyl with the deuterated alloy, $MmNi_{3.5}Co_{0.7}Al_{0.8}D_{3.5}$, was also examined; a GC-MS analysis of the reaction mixture indicated that a H–D exchange between the hydrogen in the substrate and the deuterium in the alloy took place as a parallel reaction to hydrogenation of the aromatic rings, and, as a result, the product cyclohexylbenzene appeared to contain 3-9 deuterium atoms.

Some intermetallic compounds between rare-earth elements and transition metals such as $LaNi_5$, $PrCo_5$, and $SmCo_5$ are known as hydrogen-storage alloys.[1—5] These alloys are able to absorb hydrogen and to store it in an atomic state under high pressure, and readily release it at low pressure. On the basis of these properties, they are expected to act as hydrogenation catalysts or reagents. Soga et al.[6—10] investigated the hydrogenation of alkenes over $LaNi_5H_6$ as a hydrogenation reagent under ambient conditions. Imamoto et al.[11] carried out reductions of various organic functional groups employing $LaNi_5H_6$ and $LaNi_{4.5}Al_{0.5}H_5$ at 0—30 °C; the reactions of nitroarenes, aldehydes, and ketones were found to successfully proceed to give the corresponding aromatic amines and *primary*- and *secondary*-alcohols, respectively. The hydrogenation of aromatic nuclei, however, could not take place under the mild reaction conditions, probably because of their resonance stabilization.

In a previous preliminary study[12] we undertook the hydrogenation of aromatic hydrocarbons using a hydrogen storage alloy, $MmNi_{3.5}Co_{0.7}Al_{0.8}$ [Mm: mixture of La, Ce, Pr, and Nd (30 : 52 : 5 : 13 wt ratio)] (**1**), even at an elevated temperature, and found that biphenyl (**2**) could be efficiently reduced to give either cyclohexylbenzene (**3**) or bicyclohexyl (**4**) (Scheme 1). Subsequently, we carried out a detailed investigation of the hydrogenation reaction, including the behavior of hydrogen in **1**. The results are described herein.



Scheme 1. Hydrogenation of **2** using **1-H**.

Results and Discussion

Hydrogenation of Biphenyls (2 and 5a—c) Using a Hydrogenated Alloy, $MmNi_{3.5}Co_{0.7}Al_{0.8}H_{4.2}$ (1-H). The results from the reaction of **2** (10 mmol) with an activated and hydrogenated alloy (**1-H**) (prepared from 3.5 g of **1**) at 120—180 °C for 3 h (see Experimental) are summarized in Table 1. Under the specified conditions, cyclohexylbenzene (**3**) was the sole detectable product. At 120 °C, both the conversion of **2** and the yield of the hydrogenated product **3** were rather low. When the reaction temperature was raised, the conversion of **2** and the product yield simply increased up to 160 °C, reaching 42 and 41%, respectively. A further increase in the temperature to 180 °C resulted in only a slight increase in the yield of **3**.

The effect of the ratio of **2** to **1-H** by varying the amount of the substrate (1.0—10 mmol) on the product distribution in

Table 1. Hydrogenation of **2** with **1-H**[a]

Substrate	Temp	Conversion	Yield / %[b]	
mmol	°C	of **2** / %[b]	**3**	**4**
10	120	5	4	—
10	140	27	26	—
10	160	42	41	—
10	180	49	48	—
1.0	160	98	—	95
2.0	160	99	7	89
5.0	160	95	83	11
5.5	160	95	90	4

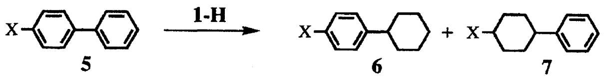
a) The reaction of **2** with **1-H** (prepared from 3.5 g of **1**) was performed in a 50 cm^3 autoclave for 3 h under N_2 (0.5 MPa).
b) Determined by GC analysis.

a reaction at 160 °C is also shown in Table 1. In the case of using 1.0 mmol of **2**, **4** was obtained as the only product, the yield being 95%. Upon increasing the ratio of **2** to **1-H**, the yield of **3** increased, while the yield of **4** decreased. Thus, **3** was predominantly produced with more than 5.5 mmol of the substrate. These results indicate that both **3** and **4** can be selectively prepared.

4-Substituted biphenyls (**5a**—**c**) were also treated with the hydrogenated alloy **1-H** (Scheme 2). In the case of 4-methoxybiphenyl (**5a**), the reaction did not take place under the conditions employed. The reaction of 4-methylbiphenyl (**5b**) gave a mixture of 4-cyclohexyltoluene (**6b**) (21%) and (4-methylcyclohexyl)benzene (**7b**) (15%), the conversion of **5b** being 37%. The fact that the reactivity order (judged from the conversion of **2**, **5a**, and **5b**) follows the sequence **2**>**5b**≫**5a** may indicate that electron-donating groups retard the reaction; that is, the hydrogen absorbed in **1** attacks the biphenyls nucleophilically, provided that the hydrogen is directly transferred to the substrates (vide infra). The precedent formation of **6b** relative to **7b** in the reaction of **5b** may be attributed to this property of the alloy. On the other hand, **5b** was also reacted over Ni powder at 160 °C for 3 h under 1.0 MPa H_2 pressure. The conversion of **5b** was 36%, and both **6b** and **7b** were obtained in 17 and 18% yield, respectively. In the case of Ni powder, hydrogen attacks aromatic rings of **5b** without discriminating each other. The reaction of 4-bromobiphenyl (**5c**), which might be expected to have the highest reactivity among the substrates examined, gave only **2** in 95% yield, and further hydrogenation did not occur. This was probably due to the fact that hydrodebromination of **5c** is the preferable reaction compared with hydrogenation of the aromatic rings, and the resulting hydrobromic acid causes a deterioration of the alloy.

Role of Hydrogen in the Alloy for Hydrogenation. There may be two major roles of the alloy: One is that it functions as a hydrogenation reagent (transferring the hydrogen in the alloy to the substrate); the other is that it acts as a hydrogenation catalyst (releasing dihydrogen into the gas phase and then reacting with the substrate over the surface of the alloy).

Johnson et al.[13,14] have investigated the hydrogenation of 1-alkenes using $LaNi_5H_x$ ($x=0.3$, 1.0, 4.5, and 5.5) as a hydrogenation reagent at a relatively low temperature, typically at 30 °C; they have proposed that the reaction proceeds via hydrogen abstraction from the hydride phase (β-phase, $x=$ 4.5 and 5.5) of the alloy by 1-alkenes, and, consequently, that the phase is altered to a hydrogen solid-solution phase (α-phase, $x=0.3$ and 1.0). They have also suggested that the α-phase has a smaller hydrogen-donating activity than does the β-phase. On the other hand, Takeshita et al.[15] examined a series of $LnNi_5$-type intermetallic compounds (Ln= lanthanide elements) in order to evaluate their efficiency as catalysts for the hydrogenation of nitrogen at relatively high temperatures (> 300 °C). However, the reaction at medium temperatures (100—200 °C) has not yet been investigated.



a: X=MeO, b: X=Me, c: X=Br

Scheme 2. Hydrogenation of **5a**—**c** using **1-H**.

In order to obtain information concerning the function of the alloy in the present hydrogenation reaction, the following examination was performed. After charging **1-H**, prepared from 3.5 g of **1**, and **2** (10 mmol) into an autoclave equipped with a pressure gauge under a nitrogen atmosphere, the reactor was placed in an electric furnace preheated at 160 °C, where the temperature of the reactor reached 160 °C within 10 min. The amount of dihydrogen released into the gas phase from **1-H** was then estimated based on the change in the pressure. To calculate the amount of the hydrogen introduced into **2** during the different reaction times, the reaction was carried out for various times (20, 40, 60, 120, and 180 min) and the yield of **3** was quantified by a GC analysis. The amount of hydrogen remaining in the alloy was calculated by subtracting the sum of the above two amounts from 18 mmol, which corresponded to the amount of hydrogen absorbed in 3.5 g of **1**. The results are summarized in Fig. 1. It can be seen that ca. 8 mmol of hydrogen was released to the gas phase as hydrogen molecules within 15 min, and that the amount was almost constant after this period. On the other hand, the amount of hydrogen introduced into **2** was increased by increasing the reaction time. Consequently, ca. 10 mmol of hydrogen in **1** was found to be transferred into **2** after 3 h.

There may be two possible explanations for these results with respect to the origin of the hydrogen introduced into **2**, as considered above: (a) the gaseous hydrogen evolved was activated on the surface of the alloy to hydrogenate **2**, and the hydrogen in **1** was simultaneously released to keep the pressure in an almost steady state; (b) only the hydrogen remaining in **1** can hydrogenate **2**, and that released in the gas phase did not contribute to the reaction. To examine these two possibilities, the following experiment was carried out. At first, **1** was hydrogenated by the usual method using an autoclave; **2** was then added into the reactor at −78 °C under nitrogen. The atmosphere was then replaced by deuterium (0.5 MPa), and the reactor was heated at 160 °C for

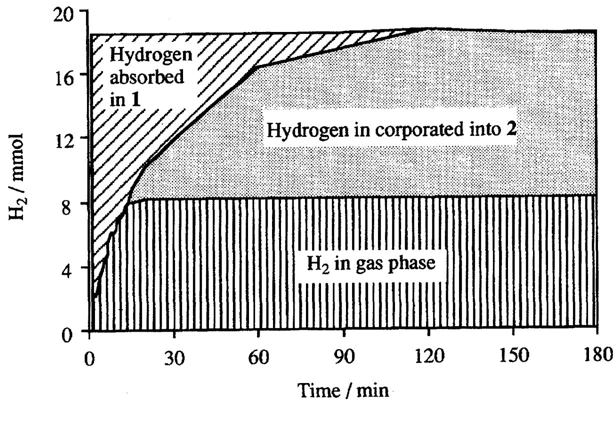


Fig. 1. Time profile of the amounts of hydrogen in gas phase, absorbed in **1**, and incoporated into **2**.

3 h. A GC-MS analysis of the **3** produced from the reaction indicated that it contained ca. 0.7 deuterium atom per one molecule (average molecular formula: $C_{12}H_{15.3}D_{0.7}$). This may suggest that the hydrogen introduced into **2** was predominantly derived from that which remained in the alloy, and that only a small amount of the hydrogen in the gas phase participated in the hydrogenation.

Reaction Scheme. To obtain further insight into the mechanism of the reaction, **2** was treated with the deuterated alloy. The deuteration of the alloy **1** was performed by the same method as that for hydrogenation of **1**, with the exception of using deuterium (3 MPa) instead of hydrogen (5 MPa). By this process, ca. 15 mmol of deuterium was introduced to 3.5 g of **1** to give an alloy having a formal formula of $MmNi_{3.5}Co_{0.7}Al_{0.8}D_{3.5}$ (**1-D**). The reaction of **2** with **1-D** was conducted at 160 °C for 0.5—3 h (Table 2). The distribution of the number of deuterium atoms incorporated into the starting material **2** and product **3** were estimated by a GC-MS analysis (Fig. 2). It can be seen from Fig. 2a that 1—3 deuterium atoms were incorporated per one molecule of **2**, and the total amount increased with elongation of the reaction time. This suggests that the H–D exchange reaction proceeds in **2** during the reaction. The ^{2}H NMR spectrum of recovered **2** was also measured in order to estimate the relative average deuterium amount at each position of the aromatic ring (Fig. 3). The relative contents of deuterium at the *o*-, *m*-, and *p*-positions in **2** were calculated to be 21, 48, and 31%, respectively, the deuterium concentration in the *o*-position being smaller than those at the other two positions. This may have been due to the fact that the *o*-positions are relatively more sterically hindered, although it is not definitive at the present stage whether the H–D exchange reaction takes place by the dehydrogenation of partially hydrogenated **2** or by direct activation of the C–H bonds in **2**. Figure 2b indicates that 3—9 deuterium atoms were incorporated into **3**, and that hexa-deuterated **3** was formed as the major product. As the reaction time was increased, the distribution of the number of deuterium atoms in **3** was flattened, while the concentration of **3-d_6** was the highest, irrespective of the reaction time. These results could be interpreted as follows: During the early stage of the reaction, it may be expected that the H–D exchange reaction in **2** proceeded to a small extent. Therefore, **2** contained a small amount of deuterium, and there existed a small amount of hydrogen on the surface of the alloy. Thus, deuteration of **2** may have been the major reaction to give **3-d_6** as the predominant product. On the other hand, upon prolonging the reaction time, both the amount of

Table 2. Hydrogenation of **2** with **1-D**[a)]

Time	Conversion	Yield	Deuterium incorporated[c)]	
h	of **2** / %[b)]	of **3** / %[b)]	**2**	**3**
0.5	16	15	0.1	5.9
1	21	19	0.2	5.7
3	32	30	0.7	5.8

a) The reaction of **2** (10 mmol) with **1-D** (prepared from 3.5 g of **1**) was performed in a 50 cm^3 autoclave at 160 °C under N_2 (0.5 MPa). b) Determine by GC analysis. c) Calculated according to the following equation; $\sum_{n=0}^{4}$[%Yield (in mmol) of $C_{12}H_{10-n}D_n$]$\times\frac{n}{2}$ for **2**. $\sum_{n=3}^{9}$[%Yield (in mmol) of $C_{12}H_{16-n}D_n$]$\times\frac{n}{2}$ for **3**.

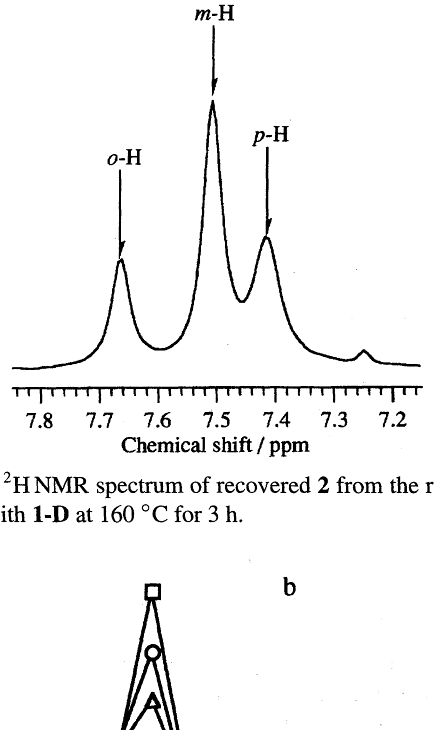


Fig. 3. ^{2}H NMR spectrum of recovered **2** from the reaction of it with **1-D** at 160 °C for 3 h.

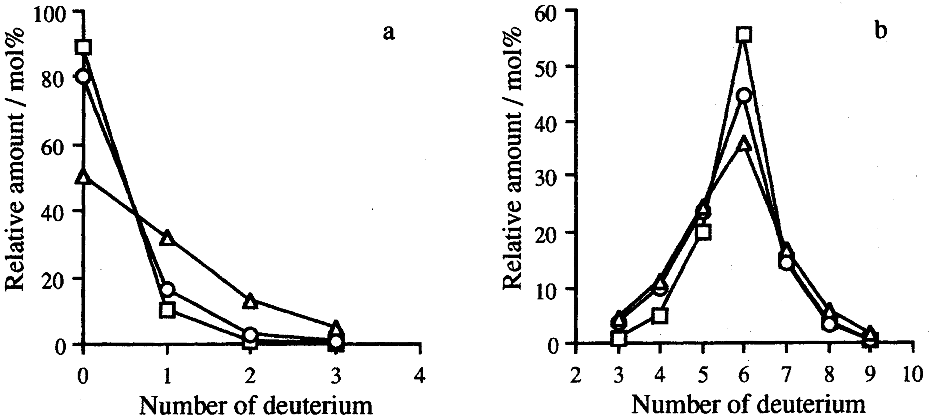


Fig. 2. Distributions of deuterium in recovered **2** (a) and **3** (b) in the reaction of **2** with **1-D** at 160 °C for 0.5 h (□), 1 h (○), and 3 h (△).

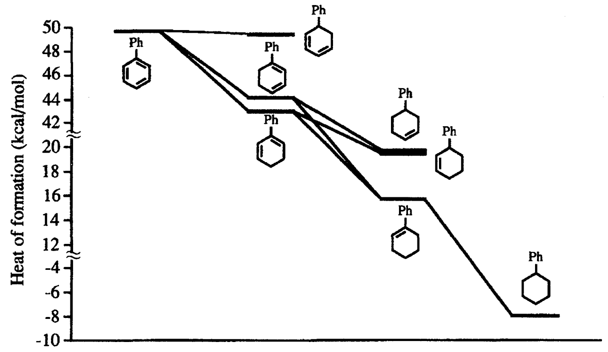


Fig. 4. Standard heats of formation of biphenyl and its hydrogenated products calculated by MOPAC-AM1 method.

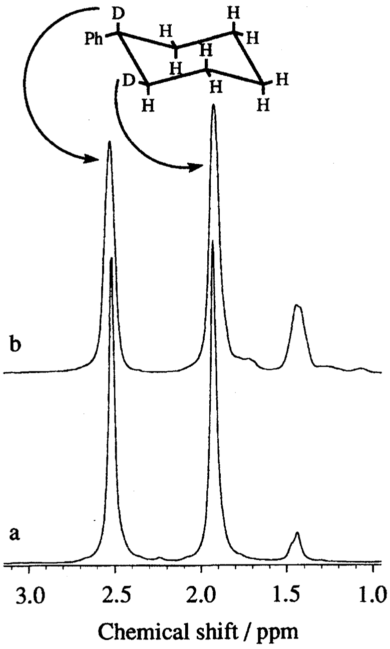


Fig. 5. Aliphatic region of the ^{2}H NMR spectrum of **3** obtained from the reaction of **8** a) with **1-D** at 160 °C for 5 min and b) with Ni powder-D$_2$ (0.5 MPa) system at 160 °C for 5 min.

2 having deuterium atoms and the hydrogen content in the alloy increased because of the progressing H–D exchange reaction. Consequently, the relative amounts of **3** containing both more than and less than six deuterium atoms increased.

In order to examine the hydrogenation sequence of **2**, standard heats of formation of the plausible intermediates, i.e. partially hydrogenated biphenyl derivatives, as well as **2** and **3** were calculated by a semiempirical molecular-orbital calculation program, MOPAC-AM1 (see Experimental). The obtained values are given in Fig. 4. Among the three possible dihydrogenated biphenyls, the heat of formation of the 1,2-dihydro isomer appears to be considerably high, suggesting that the formation of 2,3- and 3,4-dihydro isomers is preferable to that of the 1,2-dihydro compound. Similarly, it seems that the formation of 2,3,4,5-tetrahydrobiphenyl, i.e. (1-cyclohexenyl)benzene (**8**), is preferable to that of 1,2,3,4- and 1,2,3,6-tetrahydro isomers, and, therefore, that **8** may be the most plausible intermediate in the final step of the reaction.

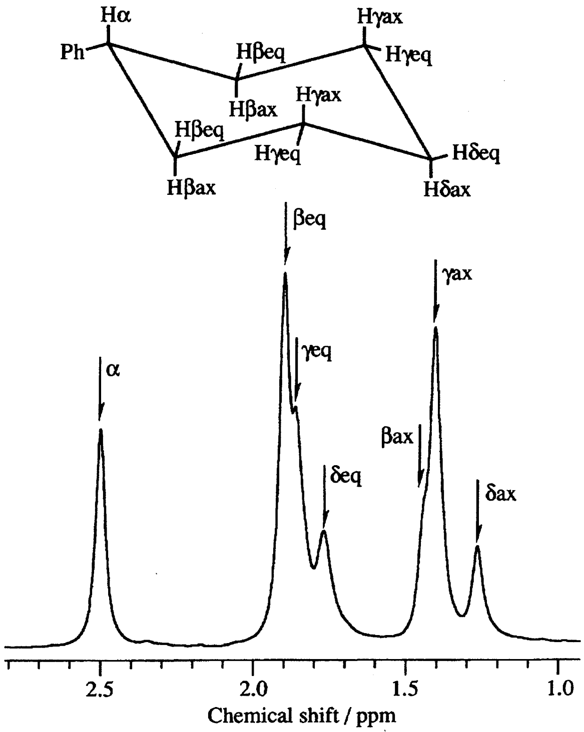


Fig. 6. Aliphatic region of the ^{2}H NMR spectrum of **3** obtained from the reaction of **2** with **1-D** at 160 °C for 3 h.

Consequently, the deuteration of **8** (10 mmol) was conducted at 160 °C for 5 min using **1-D** prepared from 3.5 g of **1** to provide information about the stereochemistry of the reaction. The ^{2}H NMR spectrum of product **3** (48% yield) showed two main peaks at 2.49 (46%) and 1.81 ppm (50%) along with minor peaks at 1.49—1.38 ppm (4%) (Fig. 5a). The ^{2}H NMR spectrum of **3**, obtained from the reaction of **2** with **1-D** along with the assignment of each peak, is also shown in Fig. 6. By comparing the spectrum in Fig. 5a with that in Fig. 6, the main peaks in Fig. 5a may be assigned as α-axial and β-equatorial deuteriums and the minor peaks as the β- and γ-axial ones. These results suggest that hydrogenation with **1-H** may proceed mainly via *syn*-1,2-addition, at least, in the reaction of **8**. In the reaction of **8** with Ni powder-D$_2$ system, **3** was obtained in 77% yield. The ^{2}H NMR spectrum of the resulting **3** is displayed in Fig. 5b. The relative peak area of the three peaks at 2.49, 1.81, and 1.49—1.38 ppm were found to be 35, 45, and 20%, respectively. These results indicate that Ni powder exhibits less selectivity that the alloy in 1,2-*syn* addition.

Experimental

^{1}H- and ^{2}H NMR spectra were recorded on a JEOL JNM-GSX-400 spectrometer for CDCl$_3$ (for ^{1}H NMR) or CHCl$_3$ (for ^{2}H NMR) solutions. GC-MS spectra were obtained with a JEOL JMS-DX-303 spectrometer. The hydrogen storage alloy (**1**)[16] and 4-methoxybiphenyl (**2b**)[17] were prepared by previously reported methods. Other reagents were commercially available and purified by recrystallization or distillation before use.

Activation and Hydrogenation of the Alloy. The alloy, $MmNi_{3.5}Co_{0.7}Al_{0.8}$ (**1**) (3.5 g), was put into a 50 cm^3 autoclave (Hastelloy-X) equipped with a pressure gauge, and then hydrogen (4.9 MPa) charged. The apparatus was placed in an electric furnace preheated at 200 °C and kept there for 1 h. After cooling to room temperature, hydrogen was charged up to 4.9 MPa and heated. This process was repeated three times. By this procedure, 18 mmol of hydrogen (determined by the change in the pressure) was introduced to 3.5 g of **1** to give $MmNi_{3.5}Co_{0.7}Al_{0.8}H_{4.2}$ (**1-H**).

General Procedure for the Hydrogenation of Biphenyl with the Alloy. After activating and hydrogenating the alloy, the atmosphere of the autoclave was replaced by nitrogen, and biphenyl (1—10 mmol) was added at −78 °C under a nitrogen stream. The apparatus was then heated at 120—180 °C under nitrogen pressure (0.5 MPa) for 3 h with shaking. After cooling, the reaction mixture was collected using acetone and analyzed by GC and GC-MS after the addition of an appropriate internal standard.

Semiempirical MO Calculations. All MO calculations were carried out on a Titan 750V workstation (Kubota Pacific Computer Co.) using a semiempirical molecular-orbital calculation program, MOPAC (version 5.0). For each calculation, the AM1 method was used. The Titan version of this program was purchased from Simulation Technology Inc.

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