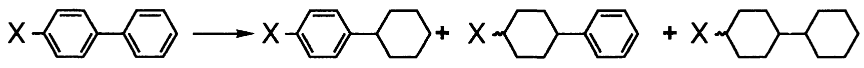
CHEMISTRY LETTERS, pp. 431-432, 1994.

Hydrogenation of Biphenyls over the Hydrogen Storage Alloy $MmNi_{3.5}Co_{0.7}Al_{0.8}H_4$

Shin-ichi NAKAGAWA, Satoru MURATA, Tetsuo SAKAI,† and Masakatsu NOMURA*
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565
†Government Industrial Research Institute, Osaka, Ikeda 1-8-31, Osaka 563

Hydrogenation of biphenyl with the activated hydrogen storage alloy, $MmNi_{3.5}Co_{0.7}Al_{0.8}H_4$ (Mm: La, 30; Ce, 52; Pr, 5; Nd, 13 wt%), as a stoichiometric reductant proceeded effectively at 160 °C for 3 h under nitrogen to give either phenylcyclohexane or bicyclohexyl selectively, according to the ratio of the alloy to biphenyl.

Some intermetallic compounds between rare-earth and transition metals such as $LaNi_5$, $PrCo_5$, and $SmCo_5$1) are known as hydrogen storage alloys. These alloys are expected to act as hydrogen storage media, electrodes for nickel-metal hydride battery, and hydrogenation catalysts or reagents,2-4) because these alloys can absorb hydrogen at high pressure and release it rapidly at low pressure. In fact, it was reported that LaM_5 (M= Ni, Co, or Al), a well-known hydrogen storage alloy, could hydrogenate alkenes2-4) and alkynes4) to alkanes at ambient temperature under nitrogen atmosphere. Hydrogenation of aromatic hydrocarbons, however, could not proceed under similar conditions, probably because of their electronic stability. We investigated the hydrogenation reaction of aromatic hydrocarbons and found that biphenyl (**2a**) was reduced efficiently by using $MmNi_{3.5}Co_{0.7}Al_{0.8}$ (Mm: La, 30; Ce, 52; Pr, 5; Nd, 13 wt%)5) (**1**) as a stoichiometric reductant at 160 °C under nitrogen for 3 h to afford either phenylcyclohexane (**3a**) or bicyclohexyl (**5a**) selectively according to the ratio of **1** to **2a**. This is the first example, to our knowledge, of application of such an alloy as a reductant for aromatic hydrocarbons.



(1)

2 **3** **4** **5**

a: X=H, **b**: X=MeO, **c**:X=Me, **d**: X=Br

Activation of the alloy **1** was carried out according to the following method: **1** (3.5 g) was put into a 50 cm^3 autoclave (Hastelloy-X) and hydrogen was introduced up to 50 $kg\cdot cm^{-2}$. The autoclave was put into an electric furnace preheated at 200 °C and held at this temperature for 1 h. After cooling to room temperature, hydrogen (50 $kg\cdot cm^{-2}$) was introduced again. This process was repeated for three times. During this activation process, about 18 mmol of hydrogen was introduced to 3.5 g of **1** to give $MmNi_{3.5}Co_{0.7}Al_{0.8}H_4$.

Using this activated alloy, we tried to hydrogenate biphenyl derivatives. **2a** (1.54 g, 10 mmol) was added to **1** (3.5 g) in the autoclave at -78 °C under a nitrogen stream and the apparatus was heated at 120-180 °C for 3 h with shaking. Products were extracted with benzene and analyzed with GC and GC-MS. At 120 °C, conversion of **2a** was still low, while the yield of **3a** reached a maximum value, 41-42%, at 160-180 °C. In the latter case, hydrogen introduced to **2a** reached to 12.3-12.6 mmol, corresponding to 68-70% of hydrogen contained in **1**.

Varying the amount of **2a** gave a change in product distribution. With 1 mmol of **2a**, only **5a** was obtained, while **3a** was obtained selectively with 5.5 or 10 mmol of **2a**. Using 2-5 mmol of **2a**, a mixture of **3a** and **5a** was obtained. This suggests that either **3a** or **5a** can be synthesized selectively by changing the ratio of **2a** to hydrogenated **1**.$^{6)}$

Hydrogenation of 4-substituted biphenyls (**2b-d**) was also investigated. In the case of 4-methoxybiphenyl (**2b**), reaction did not take place. With 4-methylbiphenyl (**2c**), conversion was lower than that of **2a** and the yield of **3c** was slightly higher than that of **4c**. These results indicate that electron donating groups retard the reaction, that is, hydrogen in **1** attacks the substrates nucleophilically. The reaction of 4-bromobiphenyl (**2d**) gave **2a** in 95% and further hydrogenation did not take place. This is probably due to deterioration of **1** by hydrobromic acid that evolves from **2d** as the reaction proceeds.

1,2-Diphenylethane and diphenylmethane (1 mmol) also could be hydrogenated to give dodeca-hydrogenated derivatives in 88 and 67% yield, respectively, along with the hexahydrogenated ones (11 and 8 %).

Further investigation concerning scope and limitation of the reaction and its mechanism is now in progress.

Table 1. Hydrogenation of biphenyl derivatives with the hydrogen storage alloy$^{a)}$

Substrate	Temp	Conv. of	Yield / %$^{b)}$			H_2 introduced
	°C	(**2**) / %$^{b)}$	(**3**)	(**4**)	(**5**)	mmol$^{c)}$
2a (10 mmol)	120	5	4		-$^{d)}$	1.2
2a (10 mmol)	140	27	26		-	7.8
2a (10 mmol)	160	42	41		-	12.3
2a (10 mmol)	180	56	42		-	12.6
2a (1 mmol)	160	98	-		95	5.6
2a (2 mmol)	160	99	7		89	11.0
2a (3 mmol)	160	98	48		41	11.4
2a (5 mmol)	160	95	83		11	14.9
2a (5.5 mmol)	160	95	90		4	16.2
2b (5 mmol)	160	0	-	-	-	-
2c (5 mmol)	160	37	21	15$^{e)}$	-	3.3
2d (5 mmol)$^{f)}$	160	99	-	-	-	-

a) Reaction was carried out for 3 h under nitrogen with the room-temperature pressure of 5 kg·cm^{-2}.
b) Determined by GLC analysis. c) Calculated from the yield of products. d) Not detected. e) **4c** was obtained as a mixture of *trans*- and *cis*-isomers. f) **2a** was obtained in 95% yield.

References

1) For reviews, see: W. E. Wallace, "Rare Earth Intermetallics," Academic, New York (1973); J. J. Reilly and G. D. Sandrock, *Sci. Am.*, **242**, 118 (1982); E. Snape and F. E. Lynch, *Chemtech.*, **10**, 578 (1980); G. D. Sandrock and E. L. Huston, *ibid.*, **11**, 754 (1981); H. Wenzl, *Int. Met. Rev.*, **27**, 140 (1982).
2) K. Soga, H. Imamura, and S. Ikeda, *Chem. Lett.*, **1976**, 1387; *Nippon Kagaku Kaishi*, **1977**, 1299; **1978**, 923; *J. Phys. Chem.*, **81**, 1762 (1977); K. Soga, Y. Sano, H. Imamura, M. Sato, and S. Ikeda, *Nippon Kagaku Kaishi*, **1978**, 930.
3) J. R. Johnson, Z. Gavra, P. Chyou, and J. J. Reilly, *J. Catal.*, **137**, 102 (1992).
4) T. Imamoto, T. Mita, and M. Yokoyama, *J. Org. Chem.*, **52**, 5695 (1987).
5) T. Sakai, T. Hazama, H. Miyamura, N. Kuriyama, A. Kato, and H. Ishikawa, *J. Less-Common Met.*, **172/174**, 1175 (1991).
6) Hydrogenation of biphenyl to cyclohexylbenzene using catalysts such as Pd, Pt, and Ni was also reported. However, when these catalysts were used, the selectivity for the formation of cyclohexylbenzene was generally not so high at higher conversion of biphenyl: for example, see H. A. Smith, D. M. Alderman, Jr., C. D. Shacklett, and C. M. Welch., *J. Am. Chem. Soc.*, **71**, 3772 (1949).

(Received November 8, 1993)