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Selective Reduction of Aromatic Nitro Compounds with Nickel Boride

Atsuko NOSE and Tadahiro KUDO*

Daiichi College of Pharmaceutical Sciences, 22-1 Tamagawa-cho, Minami-ku, Fukuoka 815, Japan.

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Nickel boride (Ni_2B) easily reduced aromatic nitro compounds at 40 °C in 3 N HCl or 15 N NH_4OH medium to afford the corresponding amines in good yields. However, olefin, aldehyde, ketone, nitrile, amide, carboxylic acid and ester functional groups were unaffected under these conditions.

Keywords selective reduction; nickel boride; nitro compound; primary amine; azoxybenzene; azobenzene; hydrazobenzene

Little work has been reported on reduction with nickel boride (Ni_2B) alone, except for the reduction of allylic silyl ether by Sarma and Sharma.[1] In the previous investigation,[2] we found that Ni_2B reduced nitrobenzene in methanol to afford a small amount of aniline. Based on this result, we believed that Ni_2B possessed an intrinsic reducing ability and might become a good reagent for reducing the nitro group if proper conditions could be established. We have found that Ni_2B can reduce aromatic nitro compounds in excellent yields when the reduction is carried out in strongly acidic or basic medium.

As shown in Table I, the reduction of nitrobenzene (**1**) with Ni_2B or cobalt boride (Co_2B) in a variety of media afforded aniline (**2**). In these experiments, the yields of **2** were excellent in 3 N hydrochloric acid and 15 N ammonium hydroxide, but low in absolute methanol, water or dilute sodium hydroxide. The yield of **2** also decreased with decreasing amount of transition metal boride. The reducing ability of Ni_2B was found to be superior to that of Co_2B.

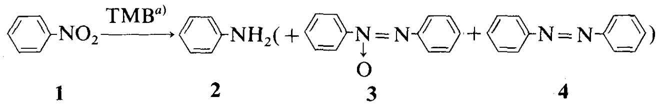
Similarly, as shown in Table II, various aromatic nitro compounds (**5**—**10**) were reduced with Ni_2B in 3 N hydrochloric acid or 15 N ammonium hydroxide to afford the corresponding amines (**11**—**16**) in good yields.

Furthermore, according to the method described above, the reductions of nitrosobenzene (**17**), azoxybenzene (**3**), azobenzene (**4**) and hydrazobenzene (**18**) were carried out to give **2** (Table III). In these experiments, reduction in 15 N ammonium hydroxide produced **2** in better yield compared to 3 N hydrochloric acid.

With regard to the reduction of other functional groups, such as olefin (1-dodecene), a heterocyclic compound (quinaldine), aldehyde (nonanal and benzaldehyde), ketone (2-octanone and acetophenone), nitrile (benzonitrile), carboxylic acid (benzoic acid), ester (benzyl benzoate) and amide (benzamide), not even a trace of the reduction product was detected in either 3 N hydrochloric acid or 15 N ammonium hydroxide, and the starting materials were recovered quantitatively. Therefore, as shown in Table IV, the expected selective reduction of the nitro group of **29**—**33** was attained under similar conditions and the corresponding amines (**34**—**38**) were obtained in good yields.

It was presumed that 1 mol of Ni_2B produced 7 electron equivalents in hydrochloric acid or ammonium hydroxide, as shown in Chart 1. Actually the reduction of the nitro

TABLE I.



1 **2** **3** **4**

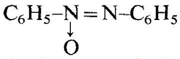
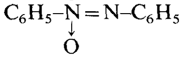
TMB^a)	eq	Medium	Temperature (°C)	Time (min)	Product yield (%)^b) 2	3	4	Recovery (%)
Ni_2B	2	Ab. MeOH	40	30	3.4			93.0
Ni_2B	1	H_2O	40	30	36.7			88.5
Ni_2B	1	H_2O	40	120	28.0	24.4		41.0
Ni_2B	1/2	3 N HCl	40	30	44.4			40.0
Ni_2B	1	3 N HCl	40	30	90.5			—
Co_2B	1	3 N HCl	40	30	46.6			45.0
Ni_2B	1	2 N NaOH	40	30	30.2			64.5
Ni_2B	1	10 N NaOH	40	30	14.9	32.9	5.1	38.5
Ni_2B	1/2	15 N NH_4OH	40	30	52.3			37.0
Ni_2B	1	15 N NH_4OH	40	30	91.0			—
Co_2B	1	15 N NH_4OH	40	30	72.1			13.5
Co_2B	2	15 N NH_4OH	40	30	96.3			—

a) TMB = transition metal boride. *b*) Yields of products were calculated by gas chromatography.

TABLE II. Reduction of Nitro Compounds with Ni_2B in Acidic and Basic Solution

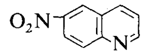
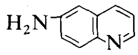
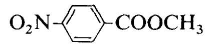
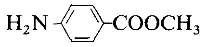
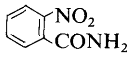
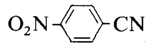
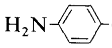
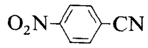
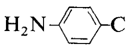
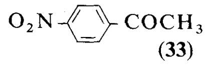
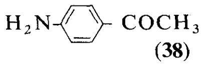
R–NO_2 R (No.)	Ni_2B (eq)	Medium	Temperature (°C)	Time (min)	Product (No.)	Yield (%)
p-$CH_3C_6H_4$ (**5**)	1	3 N HCl	40	30	*p*-$CH_3C_6H_4NH_2$ (**11**)	93.7
o-$CH_3C_6H_4$ (**6**)	1	3 N HCl	40	30	*o*-$CH_3C_6H_4NH_2$ (**12**)	83.5
p-ClC_6H_4 (**7**)	1	3 N HCl	40	30	*p*-$ClC_6H_4NH_2$ (**13**)	96.4
o-ClC_6H_4 (**8**)	1.1	3 N HCl	40	30	*o*-$ClC_6H_4NH_2$ (**14**)	80.1
p-$CH_3OC_6H_4$ (**9**)	1	3 N HCl	40	30	*p*-$CH_3OC_6H_4NH_2$ (**15**)	87.6
1-Naphthyl (**10**)	1	3 N HCl	40	30	1-Naphthylamine (**16**)	80.3
p-$CH_3C_6H_4$ (**5**)	1	15 N NH_4OH	40	30	**11**	96.3
o-$CH_3C_6H_4$ (**6**)	1	15 N NH_4OH	40	30	**12**	93.2
p-ClC_6H_4 (**7**)	1/2	15 N NH_4OH	40	30	**13**	87.0
o-ClC_6H_4 (**8**)	1.2	15 N NH_4OH	40	30	**14**	84.6
p-$CH_3OC_6H_4$ (**9**)	1.2	15 N NH_4OH	40	30	**15**	80.1
1-Naphthyl (**10**)	1	15 N NH_4OH	40	30	**16**	83.2

Table III. Reduction of Related Functional Groups with Ni_2B

Compound (No.)	Ni_2B (eq)	Medium	Temperature (°C)	Time (min)	Product yield (%)[a] Amine (2)	Hydrazo (18)	Azo (4)
$C_6H_5\text{-}N=O$ (17)	1	3 N HCl	40	30	70.9		
$C_6H_5\text{-}N=O$ (17)	1	15 N NH_4OH	40	30	94.4		
 $C_6H_5\text{-}\underset{\substack{\downarrow\\ O}}{N}=N\text{-}C_6H_5$ (3)	1	3 N HCl	40	30	58.3		
 $C_6H_5\text{-}\underset{\substack{\downarrow\\ O}}{N}=N\text{-}C_6H_5$ (3)	1	15 N NH_4OH	40	30	93.8		5.1
$C_6H_5\text{-}N=N\text{-}C_6H_5$ (4)	1	3 N HCl	40	30	14.1	68.8	
$C_6H_5\text{-}N=N\text{-}C_6H_5$ (4)	1	15 N NH_4OH	40	30	66.4		
$C_6H_5\text{-}NHNH\text{-}C_6H_5$ (18)	1	3 N HCl	40	30	14.2		
$C_6H_5\text{-}NHNH\text{-}C_6H_5$ (18)	1	15 N NH_4OH	40	30	82.7		

a) Yields of products were calculated by gas chromatography.

Table IV. Selective Reduction of Nitro Group with Ni_2B

Compound (No.)	Ni_2B (eq)	Medium[a]	Product (No.)	Yield (%)
 (29)	1	15 N NH_4OH	 (34)	86.5
 (30)	2	3 N HCl	 (35)	96.9
 (31)	2	15 N NH_4OH	 (36)	70.0
 (32)	2	3 N HCl	 (37)	60.2
 (32)	2	15 N NH_4OH	 (37)	80.8
 (33)	2	3 N HCl	 (38)	89.0

a) Reaction conditions: at 40 °C for 30 min.

$$Ni_2B \xrightarrow{HCl,\ H_2O} 2NiCl_2 + B(OH)_3 + 7H^+ + 7e$$

$$Ni_2B \xrightarrow{NH_4OH} 2[Ni(NH_3)_6](OH)_2 + B(OH)_3 + 7H^+ + 7e$$

Chart 1

group using 0.5 mol of Ni_2B resulted in half the yield of amine, as shown in Table I, since 6 electron equivalents are necessary for the reduction of a nitro group. For comparison, the reducing acivity of Ni powder at 40 °C for 4 h in 3 N hydrochloric acid or 15 N ammonium hydroxide was examined, but no reduction of **1** was detected.

It is noteworthy that nitro compounds were selectively reduced with Ni_2B in dilute hydrochloric acid or concentrated ammonium hydroxide to the corresponding amines under mild conditions in good yields.

Experimental

Commercially available $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$ and $NaBH_4$ were used throughout this work. Melting points were determined on a Yanagimoto micro-melting point apparatus, model MP-S3, and are uncorrected. Infrared (IR) spectra were measured in Nujol mulls or as liquid films with a JASCO A-100 (Nihon Bunko) infrared spectrometer, and ultraviolet (UV) spectra were recorded on a JASCO Uvidec-505 ultraviolet spectrometer. Gas chromatography was done on a JEOL JGC-20K gas chromatograph. Yields of amines were calculated by gas chromatography on a glass column, packed with SE-30, at 140—160 °C (column temperature) under 0.8 kg/cm^2 of nitrogen pressure, by comparison with standard amounts of authentic samples. The procedure for the reduction of **1** with Ni_2B will be described in detail as a typical example.

Ni_2B and Co_2B Ni_2B and Co_2B were prepared from $NaBH_4$ and $NiCl_2 \cdot 6H_2O$ or $CoCl_2 \cdot 6H_2O$ according to a published procedure.[3]

Reduction of 1 A) Compound **1** (1.00 g, 8.1 mmol) was suspended in 3 N HCl (20 ml) and freshly prepared Ni_2B (1.04 g, 8.1 mmol) was added to the suspension in portions with stirring at 40 °C. Stirring was continued for 30 min. The reaction mixture was basified by the addition of concentrated ammonium hydroxide, and extracted with ether, and the ethereal layer was dried over anhydrous magnesium sulfate. After the ether was evaporated off, the residue was distilled to give 683 mg (90.5%) of **2**, bp 184—184.3 °C. This product was identical with an authentic sample on the basis of comparisons of their IR and UV spectra.

B) Compound **1** (1.00 g, 8.1 mmol) was suspended in 15 N NH_4OH (20 ml) and freshly prepared Ni_2B (1.04 g, 8.1 mmol) was added to the suspension in portions with stirring at 40 °C. Stirring was continued for 30 min. The reaction mixture was extracted with ether and the ethereal layer was dried over anhydrous magnesium sulfate. After removal of the ether, the residue was distilled to give 686 mg (91.0%) of **2**.

C) Freshly prepared Ni_2B (1.04 g, 8.1 mmol) was added to a suspension of compound **1** (1.00 g, 8.1 mmol) in 10 N NaOH (20 ml) in the same manner as described above. After similar treatment of the reaction mixture, the residue was directly chromatographed over alumina (column) using petroleum ether as an eluent. The eluate was concentrated and the residue was recrystallized from 90% ethanol to give 38 mg (5.1%) of **4**, mp 66.5—67 °C (lit.[4] mp 66—67.5 °C). The eluate with petroleum ether–benzene (1 : 1) was concentrated, and the residue was recrystallized from 95% ethanol to give 264 mg (32.0%) of **3**, mp 35—36.5 °C (lit.[5] mp 35.5—36.5 °C). Further, the chloroform eluate was concentrated, and the residue was distilled to give 112 mg (14.9%) of **2**. Products **3** and **4** were identical with authentic samples on the basis of mixed melting point determination and comparisons of their IR and UV spectra.

Nitro compounds (**5**—**10**) were reduced similarly to give the corresponding amines (**11**—**16**); the reaction conditions and yields are listed in Table II. Products **11**—**16** were identical with authentic samples on the basis of comparisons of their IR and UV spectra.

Compounds **29**—**33** were reduced similarly to give the corresponding amines (**34**—**38**); the reaction conditions and yields are listed in Table IV. These products (**34**—**38**) were identical with authentic samples on the basis of mixed melting point determination and comparisons of their IR and UV spectra.

Reduction of 3 in NH_4OH Compound **3** (0.99 g, 5 mmol) and Ni_2B (0.64 g, 5 mmol) were reacted according to procedure B, and the reaction mixture was extracted with ether. The ethereal layer was extracted with 5% hydrochloric acid, and the ethereal layer was dried over anhydrous magnesium sulfate. After removal of the ether, the residue was recrystallized from 90% ethanol to give 46 mg (5.1%) of **4**, mp 66.5—67 °C. The acidic solution was basified with 10% sodium hydroxide and extracted with ether. The ethereal solution was dried over anhydrous magnesium sulfate. After removal of the ether, the residue was distilled to give 873 mg (93.8%) of **2**.

Reduction of 4 in HCl Compound **4** (0.91 g, 5 mmol) and Ni_2B (0.64 g, 5 mmol) were reacted according to procedure A. The reaction mixture was basified by the addition of concentrated ammonium hydroxide, and extracted with ether, and the ethereal layer was dried over anhydrous magnesium sulfate. After removal of the ether, the residue was directly chromatographed over alumina (column) using benzene as an eluent. The eluate was concentrated and the resulting residue was recrystallized from ethanol–ether to give 634 mg (68.8%) of **18**, mp 129—

131 °C (lit.[6] mp 128—132 °C). Product **18** was identical with an authentic sample on the basis of mixed melting point determination and comparisons of their IR and UV spectra. The chloroform eluate was treated similarly to give 131 mg (14.1%) of **2**.

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