Journal of the Korean Chemical Society
1994, *Vol. 38, No. 5*
Printed in the Republic of Korea

히드라진과 질산니켈-아연과의 반응에서 얻은 활성화시킨 촉매를 이용한 방향족 니트로화합물의 환원

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(1994. 1. 27 접수)

Reduction of Nitroarenes with Hydrazine Monohydrate by Activated Nickel Nitrate-Zinc Catalyst

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(Received January 27, 1994)

요 약. 질산니켈과 아연을 에탄올 용매에서 환류반응시켜 얻은 활성화시킨 촉매는 히드라진 존재하에서 방향족 니트로화합물을 주로 아족시 화합물로 환원시켜 주었다. 그러나 질산니켈 대신 염화니켈을 사용하여 얻은 촉매는 같은 조건하에서 단지 방향족 아민만을 얻을 수 있었다. 활성화시키지 않고, 방향족 니트로화합물, 염화니켈이나 질산니켈, 아연 그리고 히드라진 혼합물을 환류반응 시킬 때는 낮은 수율의 아조, 아족시와 아민 화합물을 얻을 수 있었다.

ABSTRACT. An activated catalyst prepared from a mixture of nickel nitrate hexahydrate with zinc in dry ethanol under reflux showed exceptional catalytic activity for the reduction of nitroarenes to the corresponding azoxy compounds exclusively in the presence of hydrazine monohydrate. However, when nickel nitrate hexahydrate was replaced by nickel chloride dihydrate with zinc, only the aminoarenes were formed in high yields. With unactivated catalyst, the reduction reaction from a mixture of nitroarenes, nickel nitrate or chloride, excess zinc and hydrazine monohydrate gave the corresponding azo, azoxy and amino compounds in much lower yields.

INTRODUCTION

The application of activated metal powders, as developed by Rieke *et al.*[1] in organic synthesis has recently received more attention. However, only a few reports on activated nickel powder have appeared. These include activated nickel catalyzed hydrosilylation[2], Ulmann coupling reaction[3], oxidative coupling of benzylic halides in the synthesis of homocoupled products[4], 1,3-diarylpropan-2-ones[5], and hydrogenation[6]. These methods are merely the reduction of a metal halide with a group 1 element (Li, Na, K) in an ether or THF. But no example was reported on the preparation of activated metal powders from other metal salts instead of metal halides using group II elements in water or alcohol as a solvent. We recently reported that the treatment of nitroarenes with activated copper-zinc metal powders, prepared by the reaction of copper (II) sulfate with excess zinc and hydrazine monohydrate in dry ethanol under reflux, easily reduces nitroarenes to the corresponding amino compounds in high yields[7]. In continuation of our work, we decided to study the reactivity of Ni-Zn catalyst towards nitroarenes. It was observed that an activated catalyst (A) prepared from a mixture of nickel nitrate hexahydrate with 100% excess zinc in dry ethanol under reflux showed exceptional catalytic activity for the reduction of nitroarenes. We now wish to report the further results of this investigation followed by a short

communication[8].

RESULTS AND DISCUSSION

The preparation of the highly reactive catalyst was carried out by using a mixture of nickel nitrate hexahydrate with 100% excess zinc dust in dry ethanol under reflux for 16 h under nitrogen. When the green color had almost faded, the solvent was evaporated off under reduced pressure to afford a finely divided pale gray powder.

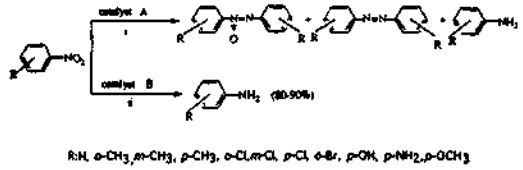
The results of the reduction of nitroarenes with this catalyst in the presence of hydrazine monohydrate are presented in *Table* 1.

Interestingly, nitroarenes were reduced mainly to azoxyarenes in fair yield along with amino compounds (*Table* 1). However, when nitrobenzene was treated with a mixture of commercially available nickel, zinc and zinc nitrate in dry ethanol and refluxed under nitrogen for 24 h, 30% of azoxybenzene, 10% of azobenzene and 5% of aniline were

Table 1. Reduction of nitroarenes using an activated catalyst prepared by the reaction of nickel nitrate with excess zinc in the presence of hydrazine monohydrate[a]

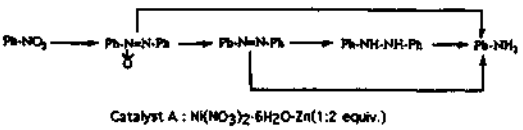
Entry	Nitro-Compound	Solvent	Time	Product (yield, %)[b]		
				Amine	Azo	Azoxy
1	Nitrobenzene	*t*-BuOH	40 min	8	2	90 (89)[c]
		EtOH	3 h	18	28 (20)	54 (45)
		EtOH	24 h	5	10	30[d]
2	*p*-Nitrotoluene	*t*-BuOH	30 min	23		77 (69)
		EtOH	3 h	25	12 (10)	63 (50)
3	*m*-Nitrotoluene	*t*-BuOH	40 min	27 (18)	13	60 (54)
		EtOH	5 h	30	22 (10)	48 (40)
4	*o*-Nitrotoluene	*t*-BuOH	40 min	8	2	90 (89)
		EtOH	5 h	35 (28)	13 (6)	52 (40)
5	*p*-Nitroanisole	*t*-BuOH	30 min	14	4	82 (69)
		EtOH	3 h	4	38 (25)	58 (42)
6	*p*-Chloronitrobenzene	*t*-BuOH	20 min	10 (7)	3	87 (84)
		EtOH	3 h	15	17 (12)	68 (54)
7	*m*-Chloronitrobenzene	*t*-BuOH	20 min	12 (5)	6	82 (78)
		EtOH	3 h	15	31 (12)	54 (43)
8	*o*-Chloronitrobenzene	*t*-BuOH	30 min	35 (32)	8	57 (45)
		EtOH	3 h	32 (20)	20 (12)	48 (43)
9	*p*-Nitroaniline	*t*-NuOH	50 min	42 (40)	2	56 (54)
		EtOH	5 h	52 (51)	24 (21)	24 (23)
10	*p*-Bromonitrobenzene	*t*-BuOH	20 min	10 (8)	6	84 (82)
		EtOH	3 h	6 (5)	14 (13)	80 (79)
11	1-Nitronaphthalene	*t*-BuOH	50 min	32 (30)	2	66 (56)
		EtOH	3 h	25 (21)	12	63 (54)
12	*p*-Nitrophenol	*t*-BuOH	50 min	26	8	66 (50)
		EtOH	4 h	26 (18)	17	57 (40)

[a]Activated catalyst, 0.4 g; $NH_2NH_2 \cdot H_2O$, 6 ml; solvent, 10 ml; reflux. [b]Yields in entries 1~8 were determined by GLC and yields in entries 9~12 were determined by HPLC based on relative area percent from crude product comparison with those of authentic samples. [c]Parentheses are isolated yields. [d]Nitrobenzene was treated with a mixture of commercially available nickel, zinc and zinc nitrate in dry ethanol and refluxed for 24 h to give the products along with 55% of unreacted nitrobenzene.



R:H, *o*-CH_3,*m*-CH_3, *p*-CH_3, *o*-Cl,*m*-Cl, *p*-Cl, *o*-Br, *p*-OH, *p*-NH_2,*p*-OCH_3

Scheme 1. Reagent and conditions; Catalyst A: Ni $(NO_3)_2$-Zn(1 : 2 eq.); Catalyst B: $NiCl_2$-Zn(1 : 2 eq.), for more details, see experimental section. i: NH_2-$NH_2 \cdot H_2O$, EtOH, reflux, 3 hr; ii: $NH_2NH_2 \cdot H_2O$, EtOH, reflux, 20~60 min (80~90%, isolated yield).



Catalyst A : $Ni(NO_3)_2 \cdot 6H_2O$-Zn(1:2 equiv.)

Scheme 2. Reagents and conditions; Catalyst A: NH_2-$NH_2 \cdot H_2O$, EtOH, reflux, 3 h.

observed by GLC along with 55% of unreacted nitrobenzene (entry 1). Also, in the absence of activated catalyst, a mixture of nitrobenzene, zinc dust, nickel nitrate and hydrazine monohydrate in dry ethanol was refluxed fro 24 h and it was found that only 8% of aniline and 7% (by GLC) of azoxybenzene were formed and most of the nitrobenzene was recovered. Most reactions were faster and yields were higher using *t*-butyl alcohol, regardless of the substituent on the benzene ring. Amino compound was always obtained as a minor product, the amount increasing when ethanol was used as a solvent. No difficulty was experienced in reducing nitroaryl halides, *p*-nitroaniline, *p*-nitrophenol or 1-nitronaphthalene.

Surprisingly, it appears that a single change in the nature of the metal salts dramatically changes the reactivity and selectivity of the reduction of nitroarenes. For example, the reduction of nitrobenzene was performed with activated catalyst (B) prepared by nickel chloride hexahydrate with excess zinc and hydrazine monohydrate in dry ethanol under reflux for 20 min gave only aniline in 90% isolated yield (*Scheme* 1). However, when nitrobenzene was treated with other activated catalysts prepared from metal nitrates (such as Al, Cu, Fe, Hg, Pb, Co) with excess zinc and hydrazine

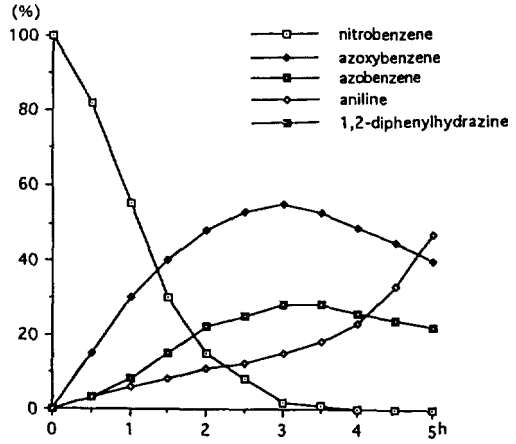


Fig. 1. Reduction of nitrobenzene with activated catalyst prepared from nickel nitrate with zinc refluxed in ethanol.

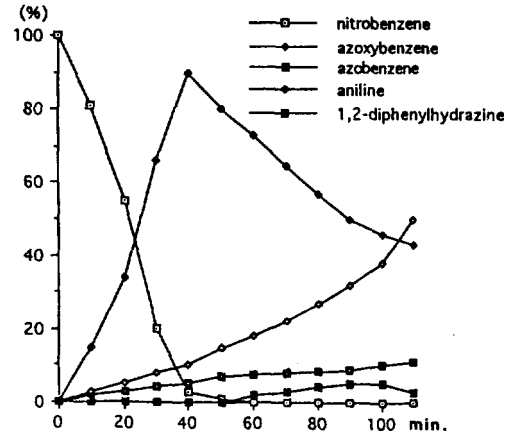
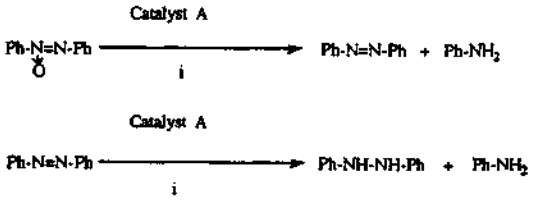


Fig. 2. Reduction of nitrobenzene with activated catalyst prepared from nickel nitrate with zinc refluxed in *t*-butylalcohol.

monohydrate, aniline was formed in only 12~40% yield (GLC) along with starting material and no other product was detected.

In order to determine the timing by which the various observed products are formed and thus to aid in obtaining more information on the active species in our system, the reduction of nitrobenzene in dry ethanol was monitored using gas chromatography to measure the disappearance of nitrobenzene and the appearance of azoxybenzene, azobenzene, aniline and 1,2-diphenylhydrazine.

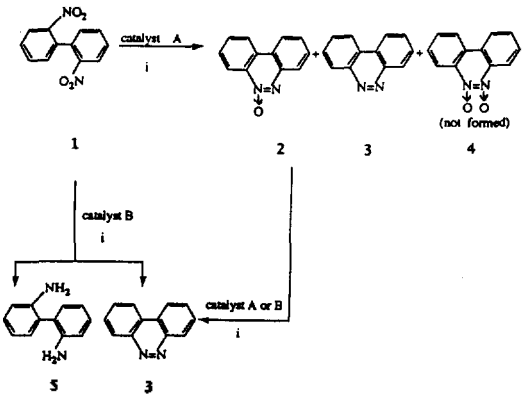


Scheme 3. Reagent and conditions; Catalyst A: Ni $(NO_3)_2$-Zn(1 : 2 eq.); i: $NH_2NH_2 \cdot H_2O$, EtOH, reflux, 3 h.

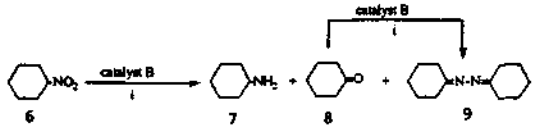
Small aliquots of the reaction mixture were removed at appropriate time intervals, quenched in water, and extracted with methylene chloride and the organic solution was analyzed. The results of such studies shows that the classical reduction of aromatic nitro compounds occurs in four sequential steps (*Scheme* 2). These are plotted in *Fig.* 1 and 2.

Further evidence for this reduction pathway is provided by the activated catalytic reduction of azoxybenzene to azobenzene and aniline. The rate of formation of azoxy compounds is much faster than their subsequent reduction in *t*-butyl alcohol at reflux temperature and the concentration of nitrobenzene is dropped to zero after 40 min when the concentration of azoxybenzene reaches its maxinum of 92% (*Fig.* 2). The concentration of aniline increases gradually from the initial period as the azoxy concentration increases. However, the concentration of azoxy compound decreases again when the azo compound begins to appear after 40 min. In particular, aniline appears in small quantities along with azobenzene, which suggests that aniline may arise from the known reduction of azobenzene[5]. When the reduction of azobenzene was carried out using nickel-zinc, 38% of aniline and 33% (by GLC) of 1,2-diphenylhydrazine were formed. However, in the case of azoxybenzene under the same conditions, 10% of aniline and 40% of azobenzene were detected along with starting material (*Scheme* 3).

In an extension of this work, we have studied the reduction of 2,2-dinitrobiphenyl (1). Using our reagents in ethanol under reflux for 3 h, benzo[c] cinnoline *N*-oxide (2) and benzo[c]cinnoline (3) were isolated in 76% and 18% yields, respectively.



Scheme 4. Reagents and conditions; Catalyst A: Ni $(NO_3)_2$-Zn(1 : 2 eq.); Catalyst B: $NiCl_2$-Zn(1 : 2 eq.); i: $NH_2NH_2 \cdot H_2O$, EtOH, reflux, 3 h.



Scheme 5. Reagents and conditions; Catalyst B: $NiCl_2$-Zn(1 : 2 eq.); i: $NH_2NH_2 \cdot H_2O$, EtOH, reflux, 3 h; GLC yields: 7.89%, 8.6%, 9.5%.

Interestingly, no further reduction products were detected in this reaction. Benzo[c]cinnoline *N,N'*-dioxide(4) was not formed amongst the products, incontrast to a report by Uemura[8] who used a sodium arene tellurolate catalyst system.

Benzo[c]cinnoline *N*-oxide (2) was readily and quantitatively reduced to benxo[c]cinnoline (3) using either catalyst A or B with hydrazine monohydrate in dry ethanol under reflux for 3 h. However, no reduction of (3) to 2,2-diaminobiphenyl (5) occurred. The formation of (3) from 2,2-dinitrobiphenyl (1) with catalyst A and hydrazine monohydrate indicates that benzo[c]cinnoline *N*-oxide (2) is reduced (*Scheme* 4).

Aliphatic nitro compounds, such as nitrocyclohexane (6), were also readily reduced by catayst B to the corresponding cyclohexylamine (7) along with a small amount of cyclohexanone (8) and cyclohexanoneazine (9), while catalyst A was inactive for this reduction (*Scheme* 5).

In conclusion, we have shown that the activated nickel-zinc powder provides a reduction of nitroa-

renes, thus extending the field of application of easily activated and handled reagents. Further extensions of this methods to other functional group transformations are under current investigation and will be reported in due course.

EXPERIMENTAL

Commercial nitro compounds (Aldrich, Junsei, Yakuri) and solvents were purified and dried prior to use when deemed necessary. Ethyl alcohol was distilled over sodium ethoxide and *t*-butyl alcohol was distilled with sodium.

Metal salts were dried in vacuum at room temperature for 15 h. Melting points were determined with an Electrothermal apparatus (ENG, LTD.S NO F-01265) and are uncorrected. ^{1}H-NMR spectra were recorded on a Bruker AC 80 spectrometer. Chemical shifts and coupling constants were obtained from first-order analysis of the spectra. Analytical TLC was performed on precoated aluminum plates with Merck silica gel 60 F-254 as the adsorbent (layer thickness 0.2 mm). The developed plates were air dried and irradiated with UV light. All column chromatography was carried out on Merck silica gel 60 (70-230 mesh).

Mass spectra (70 eV electron impact) were taken on a Finnigan 4510 instrument equipped with a Finnigan-incos data system. GLC-Mass analyses were performed on a Hewlett-Packard MSD 5890 series equipped with a capillary column (HP1, 25 m). GLC was done on a Varian 3300 instrument equipped with a FID detector and a stainless steel column packed with 10% OV-101, Chromosob W HP 80/100 (2 m×1/8 in). HPLC were performed on a μ-Bondapak $^{TM}NH_2$ stainless steel column (3.9 ×300 mm) in a Waters Associates instrument fitted with a 254 nm wavelength UV detector, with a flow rate of 0.2 m*l* min^{-1} and as the mobile phase the following solvent systems: normal phase: CH_2Cl_2; n-C_6H_{14} (50 : 50 v/v), reverse phase; C_2H_5OH : H_2) (50 : 50, v/v).

Preparation of activated catalyst [A and B]

Activated catalyst A from nickel nitrate and zinc: Typical procedure. Into a 250 m*l* single-necked round bottom flask equipped with nitrogen inlet were placed nickel nitrate hexahydrate (29 g, 0.1 mol), zinc (13 g, 0.2 mol) and dry ethanol (50 m*l*). The reaction mixture was refluxed for 16 h until the green color had almost faded. Flash evaporation of the solvent under reduced pressure gave a pale gray dust which was stored at room temperature under nitrogen.

Activated catalyst B from nickel chloride and zinc. Nickel chloride (23 g, 0.1 mol) was used instead of nickel nitrate while other procedures were same as described for catalyst A. The initial green color faded over 16 h under feflux. Flash evaporation of the solvent under reduced pressure gave a black dust which was stored at room temperature under nitrogen. Catalyst A and B were used directly for this investigation without any further treatment. The activities of these catalysts did not decrease during storage for a month.

Reduction of nitro compounds to azoxy and azo compounds. General Procedure

A mixture of the aromatic nitro compound (0.01 mol), catalyst A (0.4 g) and hydrazine monohydrate (80%, 6 m*l*, 0.09 mol) in 10 m*l* of dry ethanol was stirred and refluxed under nitrogen. After the time indicated in *Table* 1, the reaction mixture was filtered to remove the catayst and the filtrate was concentrated by evaporation under reducd pressure and poured into 30 m*l* of H_2O and then extracted with three 25 m*l* portion of methylene chloride or diethyl ether. The organic layer was again treated with 1 *M* HCl (30 m*l*) to form the corresponding amine salt and was then separated. Amino compounds were isolated by treatment of the aqueous solution with base and extracted with methylene chloride and diethyl ether (3×30 m*l*). The organic layer was then dried over $MgSO_4$, the solvent was evaporated and the residue (yellow oil or solid) was subjected to column chromatography to give the pure azoxy and azo compounds. In most cases (see *Table*), the azo/azoxy compounds were isolated by column chromatography with the solvent indicated below as an eluent.

The reaction progress diagrams given in *Fig.* 1 were obtained by following the disappearance

of nitrobenzene and the apperarance of products by gas chromatography. At appropriate time intervals, 1 ml of aliquots were removed, quenched with 3 ml of water, extracted with 1 ml of methylene chloride and analyzed. In this manner, the concentration of nitrobenzene, azoxybenzene, azobenzene, 1,2-diphenylhydrazine and aniline could be determined simultaneously using a predetermined standard for each compound.

Reduction of nitro compounds to amino compounds

A mixture of the aromatic nitro compound (0.01 mol), catalyst B (0.2 g), hydrazine monohydrate (80%, 3 ml, 0.045 mol) and 10 ml of dry ethanol was refluxed for 30 min under nitrogen. The solution was cooled to room temperature and filtered to remove the catalyst. The filtrate was diluted with water and extracted with ether or methylene chloride, and the extract was dried with $MgSO_4$ and evaporated to give the corresponding amino compounds. Each product was characterized by comparison of its IR, NMR and mp. with those of an authentic sample. Hydrazine monohydrate (80%, 6 ml, 0.09 mol) was employed in the case of 2,2-dinitrobiphenyl under otherwise similar reaction conditions as above.

Reduction of azoxybenzene to azobenzene and aniline

To a stirred solution of azoxybenzene (1.98 g, 0.01 mol) and catalyst A (0.4 g) in dry ethanol (10 ml) was added the hydrazine monohydrate (80%, 6 ml, 0.09 mol) in one portion under nitrogen. After refluxing for 3 h, the reaction mixture was allowed to attain room temperature and filtered to remove the catalyst. The reside, analyzed by GLC contained azoxybenzene, azobenzene and aniline in 50%, 40% and 10% yields, respectively.

The filtrate was concentrated by evaporation under reduced pressure and extracted with diethyl ether or methlyene chloride, dried ($MgSO_4$) and evaporated. The residue was subjected to column chromatography (chloroform : hexane; 2 : 1) to give the azobenzene (0.54, 30%) and the aniline (0.05 g, 6%).

Reduction of azobenzene to 1,2-diphenylhydrazine and aniline

To a stirred solution of azobenzene (1.82 g, 0.01 mol) and catalyst A (0.4 g) in dry ethanol (10 ml) was added the hydrazine monohydrate (80%, 6 ml, 0.09 mol) in one portion under nitrogen. After refluxing for 3 h, the reaction mixture was allowed to attain room temperature and filtered to remove the catalyst. The residue, analyzed by GLC contained azobenzene, 1,2-diphenylhydrazine and aniline in 29%, 33%, 38% yields, respectively. The filtrate was concentrated by evaporation under reduced pressure and extracted with ether or methylene chloride, dried ($MgSO_4$) and evaporated. The residue was subjected to column chromatography (chloroform : hexane; 3 : 1) to give the 1,2-diphenyl hydrazine (0.40 g, 22%) and aniline (0.18 g, 20 %). 1,2-Diphenylhydrazine: mp. 124~126℃ (lit.[10], mp. 123~126℃): ^{1}H-NMR ($CDCl_3$) δ: 6.80~7.58 (m, 10 H), 5.30~5.70 (br, 2H); MS(m/z) : 184 (M^+).

Reduction of 2,2'dinitrobiphenyl to benzo[c]cinnoline *N*-oxide and benzo[c]cinnoline.

To 2,2-dinitrobiphenyl (2.44 g, 0.01 mol) and catalyst A (0.4 g) in dry ethanol (10 ml) was added the hydrazine monohydrate (80%, 6 ml, 0.09 mol) in one portion under nitrogen. The reaction mixture was refluxed for 3 h. The solution was diluted at room temperature with methlyene dichloride and filtered. The organic solvents were evaporated off and the residue was chromatographed on silica gel. Elution with ethylacetate-hexane (1 : 1) provided the benzo[c]cinnoline *N*-oxide (1.48 g, 76%) as a solid and benzo[c]cinnoline (0.32 g, 18%) as reddish yellow crystalline solid.

Benzo[c]cinnoline *N*-oxide: mp. 138~139℃ (lit.[9], mp. 139~140℃): ^{1}H-NMR ($CDCl_3$) δ : 7.58~7.98 (m, 5 H), 8.21~8.47 (m, 2 H), (8.68~8.81 (m, 1 H); MS (m/z) : 196 (M^+).

Benzo[c]cinnoline: mp. 155~156℃ (lit.[10], mp. 157~158℃): ^{1}H-NMR ($CDCl_3$) δ: 7.78~7.90 (m, 4 H), 8.43~8.76 (m, 4 H); MS (m/z) : 180 (M^+).

Reduction of benzo[c]cinnoline *N*-oxide to benzo[c]cinnoline with catalyst A and B

To benzo[c]cinnoline *N*-oxide (1.96 g, 0.01 mol) and catalyst A (0.4 g) or catalyst B (0.2 g) in dry ethanol (10 ml) was added the hydrazine monohy-

drate (80%, 6 ml, 0.09 mol) in one portion under nitrogen and the mixture was refluxed for 3 h. The solution was cooled to room temperature and filtered to remove the catalyst. The extract was poured into water (30 ml) and extracted with methlyene chloride (2×30 ml). The extract was dried over $MgSO_4$, evaporated under reduced pressure and the residue was recrystalized from hexane to give benzo[co]cinnoline (1.71 g, 94%) as reddish yellow crystalline solid.

Benzo[c]cinnoline: mp. 155~156℃ (lit.[10], mp. 157~158℃): ^{1}H-NMR ($CDCl_3$) δ: 7.78~7.90 (m, 4 H), 8.43~8.76 (m, 4 H); MS (m/z) : 180 (M^+).

Reduction of nitrocyclohexane to cyclohexylamine, cyclohexanone and cyclohexanone azine

To nitrocyclohexane (1.29 g, 0.01 mol) and activated catalyst B (0.2 g) in dry ethanol (10 ml) was added the hydrazine monohydrate (80%, 3 ml, 0.045 mol) in one portion under nitrogen and the mixture was refluxed at for 3 h. The solution was cooled to room temperature and filtered to remove the catalyst.

The filtrate was analyzed by GLC-mass spectrometry which showed cyclohexylamine, cyclohexanone and cyclohexanone and cyclohexanone azine in 89%, 65 and 5% yield respectively with comparison to those of an authentic sample. Further isolation of each product was as follows. The filtrate was diluted with 1 M HCl (30 ml) and extracted with diethyl ether or methylene chloride (2×30 ml). The extract was dried over $MgSO_4$ and evaporated and the residue was characterized by GLC in comparison with cyclohexanone and cyclohexanone azine.

The aqueous layer was neutralized with 1 *M* HCl and extracted with ether or methylene dichloride (3×30 ml). The extract was dried ($MgSO_4$), flash evaporated and the cyclohexylamine was isolated by simple distillation under vacuum to give cyclohexylamine (0.4 g, 41%).

Synthesis of cyclohexanone azine from cyclohexanone with activated catalyst B

To cyclohexanone (0.98 g, 0.01 mol) and activated catalyst B (0.2 g) in dry ethanol (10 ml) was added the hydrazine monohydrate (80%, 3 ml, 0.045 mol) in one portion under nirogen and the mixture was refluxed for 3 h. The solution was cooled to room temperature and filtered to remove the catalyst. The filtrate was poured into water (30 *l*) and extracted with ether or methylene chloride (3×30 ml). The extract was dried ($MgSO_4$), flash, evaporated and the residue was isolated by simple distillation under vacuum to give cyclohexanone azine in 72% (1.38 g) yields as a pale yellow liquid.

Some physical properties of the products are recorded below.

These were isolated by flash column chromatography (methylene dichloridehexane, 1 : 2) as crystalline solid.

Azobenzene: mp. 68~69℃ (lit.[11], 68~69℃); MS (m/z) : 182 (M^+).

Azoxybenzene: mp. 35.5~36℃ (lit.[11], 35~36℃); MS (m/z) : 196 (M^+).

2,2'-Dimethylazonenzene: mp. 53~54℃ (lit.[12], 53~54℃); MS (m/z) : 210 (M^+).

2,2'-Dimethylazoxybenzene: mp. 57~58℃ (lit.[13], 60℃); MS (m/z) : 226 (M^+).

These were isolated by flash column chromatography (methylene dichloride-hexane, 2 : 3) as yellow crystalline solid.

4,4'-Dimethylazobenzene: mp. 141~142℃ (lit.[14], 144~145℃); MS (m/z) : 210 (M^+).

4,4'-Dimethylazobenzene: mp. 67~68℃ (lit.[11], 68~69℃); MS (m/z) : 226 (M^+).

These were isolated by flash column chromatography (chloroform-hexane, 1 : 2) as yellow crystaline solid.

3,3'-Dimethylazobenzene: mp. 52~54℃ (lit.[15], 54~55℃); MS (m/z) : 210 (M^+).

3,3'-Dimethylazoxybenzene: mp. 33~35℃ (lit.[13], 38~39℃); MS (m/z) : 226 (M^+).

These were isolated by flash column cromotography (chloroform-hexane, 1 : 1) as yellow crystalline solid.

4,4'-Dichloroazoxybenzene: mp. 155℃ (lit.[11], 156~157℃); MS (m/z) : 267 (M^+).

4,4'-Dichloroazobenzene: mp. 182~184℃ (lit.[12], 184~185℃); MS (m/z) : 251 (M^+).

These were isolated by flash column chromatog-

raphy (methylene dichloride-hexane, 2 : 1) as yellow crystalline solid.

3,3'-Dichlorozaxybenezene: mp. 96~97℃ (lit.[16], 95.5~97℃); MS (m/z) : 267 (M^+).

3,3'-Dichlorozobenzene: mp. 100~101℃ (lit.[12], 101℃); MS (m/z) : 251 (M^+).

These were isolated by flash column chromatography (methylene dichloride-hexane, 1 : 1) as yellow crystalline solid.

2,2'-Dichloroazoxybenzene: mp. 53~54℃ (lit.[13], 55~56℃); MS (m/z) : 267 (M^+).

2,2'-Dichlorozaobenzene: mp. 135~136.5℃ (lit.[12], 136℃); MS (m/z) : 251 (M^+).

4,4'-Dibromoazoxybenzene: mp. 171~172.5℃ (lit.[17], 172℃); MS (m/z) : 356 (M^+).

4,4'-Dibromoazobenzene: mp. 202~204℃ (lit.[18], 204℃); MS (m/z) : 340 (M^+).

4,4'-Dimethoxyazoxbenzene: mp. 116~119℃ (lit.[19], 119~120℃); MS (m/z) : 258 (M^+).

4,4'-Dimethoxyazobenzene: mp. 158~160℃ (lit.[1c], 160℃); MS (m/z) : 242 (M^+).

4,4'-Diaminoazoxybenzene: mp. 249~250℃ (lit.[20], 250~251℃); MS (m/z) : 228 (M^+).

4,4'-Diaminoazobenzene: mp. 274~275.5℃ (lit.[21], 275℃); MS (m/z) : 228 (M^+).

These were isolated by flash column chromatography (chloroform-hexane, 1 : 3) as yellow crystalline solid.

1,1'-Diazoxynaphthalene: mp. 122~127℃); MS (m/z) : 298 (M^+).

Recrystallization from ethanol

2,2'-Dihydroxyazoxybenzene: mp. 150.5~155℃ (lit.[22], 153~154℃); MS (m/z) : 230 (M^+).

ACKNOWLEDGMENT

We wish to thank the Basic Science Research Institute Program, Ministry of Education (1993) of the Republic fo Korea for partial support of this study.

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