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# SYNTHESIS OF DIPHENYLAMINE DERIVATIVES ON Pd/C CATALYST

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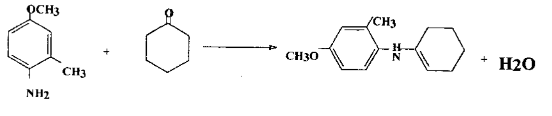
**Abstract** – 2-Methyl-3'-hydroxydiphenylamine was synthesized from the mixture of 3-aminophenol, 3-nitrophenol, and 2-methylcyclohexanone in the presence of Pd/C catalyst. The optimum composition of the reaction mixture was determined for maximum yield of the diphenylamine derivative: with the molar ratio of 3-aminophenol : 3-nitrophenol fixed at 1 mmol : 2 mmol, the relative molar amounts of 2-methylcyclohexanone were varied between 3 and 96. At the optimum composition the amounts of Pd/C catalyst were varied threefold in order to investigate the effect of Pd on the product yield. The results obtained from the reaction mixture containing 1 mmol of 3-aminophenol were satisfactorily reproduced for the reaction mixture containing more than 10 mmol of 3-aminophenol. The formation of this diphenylamine derivative could be interpreted using the mechanism for the catalytic synthesis of 2-methyl-4-methoxydiphenylamine which we had optimized previously.

Key words : 2-Methyl-3'-Hydroxydiphenylamine, Optimum Composition of Reaction Mixture, Maximum Yield of Diphenylamine Derivative, Effect of Pd, Mechanism for Catalytic Synthesis

## INTRODUCTION

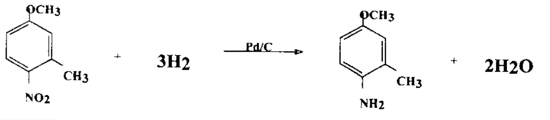
Diphenylamine and its derivatives are known as useful organic intermediates for manufacturing dyes, agrichemicals, medicines, and compounding agents for rubber [Nagata et al., 1996]. For example, 2-methyl-4-alkoxydiphenylamines, which can be obtained from nucleus-substituted aniline derivatives, are valuable raw-materials for fluoran dyes used in heat- or pressure-sensitive recording paper [Akamatsu, 1993]. Also, 2-methyl-3'-hydroxy-diphenylamine is the useful intermediate for acid-black 94 dye, which has been imported to meet the demand of approximately 120 tons per year in Korea [IRI report, 1990].

Recently we reported the catalytic synthesis of 2-methyl-4-methoxydiphenylamine from a reaction mixture of 2-methyl-4-methoxyaniline, 3-methyl-4-nitroanisole, and excess cyclohexanone in the presence of hydrogen transfer catalyst [Kim et al., 1995; Cho et al., 1995]. The excess cyclohexanone played a role in promoting the condensation of 2-methyl-4-methoxyaniline and cyclohexanone,



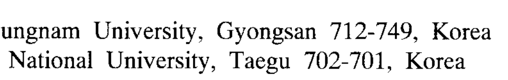
(i)

and 3-methyl-4-nitroanisole furnished the ultimate source of the aromatic amine through its reduction.



(ii)

The hydrogen transfer catalyst, Pd/C, was used to dehydrogenate the intermediate species formed by condensation [reaction (i)],



(iii)

and to hydrogenate the methylnitroanisole via reaction (ii) to the methylmethoxyaniline. The rate-determining step of the overall reaction was hydrogen-abstraction of the intermediate species via reaction (iii), and the molar ratio of cyclohexanone to 2-methyl-4-methoxyaniline exhibited an optimum range for maximum yield of 2-methyl-4-methoxydiphenylamine.

In this study, we investigate catalytic synthesis of 2-methyl-3'-hydroxydiphenylamine in the presence of Pd/C to ascertain the applicability of the above procedure for formation of another diphenylamine derivative and to determine the optimum composition of the relevant reaction mixture for maximum yield of the product. In addition the effect of catalyst amount upon product yield is studied for the reaction mixtures variant in molar quantity.

## EXPERIMENTAL

### 1. Optimum Composition of the Reaction Mixture Containing 1 mmol of 3-Aminophenol

Mixed in an autoclave-type high pressure reactor (Parr 4564 M) with various amounts of 2-methylcyclohexanone (99 %, Aldrich) were 1.0 mmol of 3-aminophenol (98 %, Fluka), 2.0 mmol of 3-nitrophenol (99 %, Wako Pure Chem.) and 0.1 g of 5 % Pd/C catalyst (Aldrich). The reactor was purged, pressurized with 4 bar of nitrogen, and heated to 203 °C. After 1 to 14 hrs the reactor was depressurized to one atmosphere

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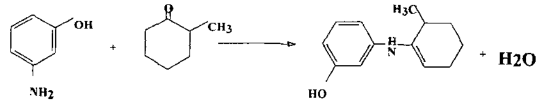
and the reaction mixtures were cooled to room temperature and filtered. The filtrates were analyzed by gas chromatography (Donam, DS6200), mass spectrometry (Micromass Co., VG Autospec), and $^1$HNMR (BRUKER, ARX300). Data for product yield as well as mole% of reactants and intermediate species were collected at various reaction times. An authentic sample of 2-methyl-3'-hydroxydiphenylamine was obtained from reacting o-toluidine (99 %, Aldrich) with resorcinol (98 %, Janssen) in the presence of sulfuric acid [Elmar and Somerville, 1969; Friedrich and Heinz, 1981]. Used 2-methylcyclohexanone was purified by vacuum distillation for reuse. Used catalyst was cleaned by soaking in acetone followed by rinsing and drying for reuse.

### 2. Variation of Catalyst Amounts for the Reaction Mixtures of the Optimum Composition

Once the optimum composition was determined for the reaction mixture containing 1 mmol of 3-aminophenol using 0.1 g of 5 % Pd/C catalyst, the catalyst amounts were varied between 0.05 and 0.15 g and product yield data were collected for each input of the catalyst. Similar experiments were also conducted for the reaction mixture of the optimum composition containing 13 mmol of 3-aminophenol by collecting the product yield data for the catalyst amounts of 1.3 and 1.625 g.

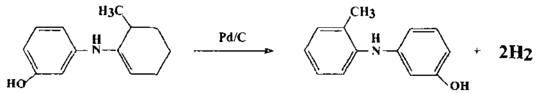
## RESULTS AND DISCUSSION

Several preliminary experiments tested various combinations of possible reactants for the catalytic synthesis of 2-methyl-3'-hydroxydiphenylamine. We found that a mixture of o-toluidine and dihydroresorcinol appeared to form an intermediate species [Otto et al., 1994] in the presence of Pd/C; however, the desired diphenylamine derivative was not produced because dihydroresorcinol decomposes at relatively low temperature [Friedrich and Heinz, 1981]. Likewise, a mixture of 3-aminophenol and o-cresol (likely to produce the diphenylamine derivative in the presence of acid catalysts such as sulfuric acid, p-toluene sulfonic acid, and ferric chloride) did not react to form the desired condensation product. However, the relevant reaction mixture was found to contain 3-aminophenol, 3-nitrophenol, and 2-methylcyclohexanone, when we discovered that both the intermediate species and the diphenylamine derivative are formed in the vapor phase from this reaction mixture in the presence of Pd/C catalyst. As characterized in Fig. 1, the intermediate species was identified as N-cyclohexylideneaniline species formed by condensation of 3-aminophenol and 2-methylcyclohexanone,



(iv)

This intermediate species, undergoing dehydrogenation catalyzed by palladium, would give birth to the desired diphenylamine derivative (characterized in Fig. 2),



(v)

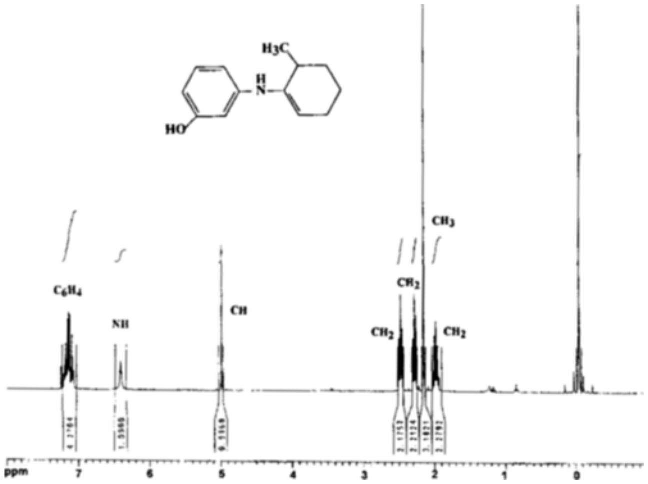
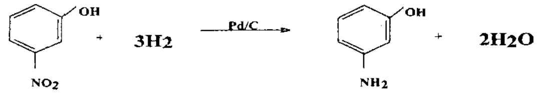


**Fig. 1. $^1$HNMR spectrum of N-cyclohexylideneaniline species formed by condensation of 3-aminophenol and 2-methylcyclohexanone.**

(Note that this type of reaction has been described above as the rate-determining step in catalytic synthesis of diphenylamine derivatives.). Hydrogen species liberated via reaction (v) could be readily consumed, in the presence of palladium catalyst, for reducing 3-nitrophenol to 3-aminophenol,



(vi)

3-aminophenol produced via reaction (vi) would follow reaction (iv) as the route of its disappearance by reaction with 2-methylcyclohexanone, feeding the N-cyclohexylidene-aniline species necessary for formation of the desired diphenylamine derivative. These propositions are essentially consistent with the mechanism for the catalytic synthesis of 2-methyl-4-methoxydiphenylamine (described in the introduction section of this paper), thus, would lead one to verify the role of excess 2-methylcyclohexanone in catalytic synthesis of 2-methyl-3'-hydroxydiphenylamine.

Therefore, at first, we fixed the molar ratio of 3-aminophenol : 3-nitrophenol at 1 mmol : 2 mmol (according to the stoichiometry of overall reaction) and investigated the synthesis of 2-methyl-3'-hydroxydiphenylamine in the presence of 0.1 g of 5 % Pd/C by varying the relative molar amounts of 2-methylcyclohexanone between 3 and 96. As shown in Table 1, the molar ratio of 3-aminophenol : 3-nitrophenol : 2-methylcyclohexanone of 1 : 2 : 48 produced the highest yield of 2-methyl-3'-hydroxydiphenylamine, 91.2 % at 6hrs, whereas at the stoichiometric molar ratio of 1 : 2 : 3 no desired diphenylamine was produced even after 10 hrs. These data evidently denote that ① excess amount of 2-methylcyclohexanone is required in the reaction mixture in order to obtain substantial product yield as well as complete conversion of 3-nitrophenol to 3-aminophenol, and ② an optimum range of the molar ratio of 2-methylcyclohexanone to 3-aminophenol is exhibited around 1 : 2 : 48 for maximum yield of the product. As shown in Fig. 3, at the smaller than optimum ratio of 2-methylcyclohexanone, e.g., at molar ratio of 1 : 2 : 30, a relatively low-

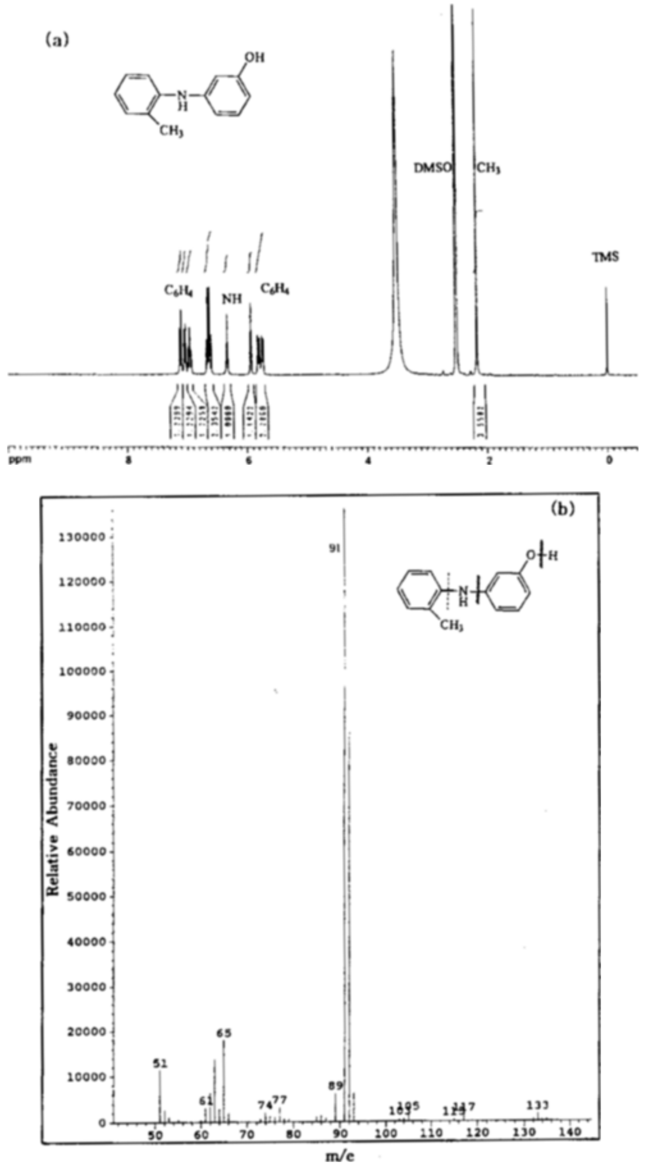


**Fig. 2. Characterization of 2-methyl-3'-hydroxydiphenylamine.** (a) $^1$HNMR spectrum, (b) GC-MS spectrum

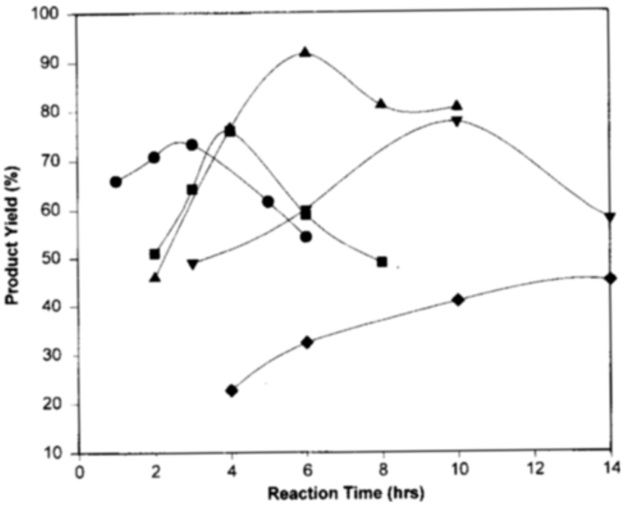


**Fig. 3. Product yield vs. reaction time at various molar ratios of 3-aminophenol : 3-nitrophenol : 2-methylcyclohexanone.** (0.1 g of 5 % Pd/C was used for the reaction mixture containing 1 mmol of 3-aminophenol)
● 1:2:30, ■ 1:2:40, ▲ 1:2:48, ▼ 1:2:72, ◆ 1:2:96

er maximum (73 %) of the product yield was observed at the reaction time (3 hrs) earlier than that (6 hrs) for the optimum 1:2:48 ratio. On the other hand, at the larger than optimum ratio, e.g., at molar ratio of 1:2:72, a relatively lower maximum (78 %) of the product yield was observed at the reaction time (10 hrs) later than that for the optimum molar ratio. For most of the molar ratios of excess 2-methylcyclohexanone, as the reaction time exceeded that of the maximum product yield, rehydrogenation of the diphenylamine derivative started being dominant, causing the diminution of product yield. For example, at the optimum molar ratio of 1:2:48, the product yield decreased from 91.2 % at 6hrs to 79.6 % at 10 hrs. Meanwhile, at the larger than optimum ratio of 2-methylcyclohexanone, e.g., at molar ratio of 1:2:72 or 1:2:96, both the condensation of 3-aminophenol and 2-methylcyclohexanone and the dehydrogenation of the condensation product were retarded as evidenced by the increase in fraction of unreacted 3-aminophenol and the decrease in yield of 2-methyl-3'-hydroxydiphenylamine.

Next, for the reaction mixture containing the reactants at the optimum molar ratio, i.e., 1:2:48 based on 1 mmol of 3-aminophenol, the amounts of 5 % Pd/C catalyst were varied between 0.05 and 0.15 g to examine the effect of Pd amount upon the product yield. As shown in Fig. 4, the product yield obtained at 6 hrs exhibited a maximum at the catalyst amount of 0.10 g of 5 % Pd/C, which was followed by slightly decreased yields at the larger amounts of catalyst. The loss of the product yield caused by the over-dosage of

**Table 1. Synthesis of 2-methyl-3'-hydroxydiphenylamine on 0.1 g of 5 % Pd/C**

| Mole ratio[a] of reaction mixture | Conversion of 3-nitrophenol to 3-aminophenol (%) | Fraction of unreacted 3-aminophenol (%) | 2-Methyl-3'-hydroxydiphenylamine yield[b] (%) |
|---|---|---|---|
| 1:2:3 | 0 | 100 | 0 (after 10 hrs) |
| 1:2:15 | 100 | 20.1 | 55.6 (at 3 hrs) |
| 1:2:48 | 100 | 1.1 | 91.2 (at 6 hrs) |
| 1:2:48 | 100 | 0.7 | 79.6 (at 10 hrs) |
| 1:2:96 | 100 | 41.7 | 40.8 (at 10 hrs) |

[a] 3-aminophenol : 3-nitrophenol : 2-methylcyclohexanone (in millimoles)
[b] based on the moles of 3-aminophenol plus 3-nitrophenol put into the reaction mixture

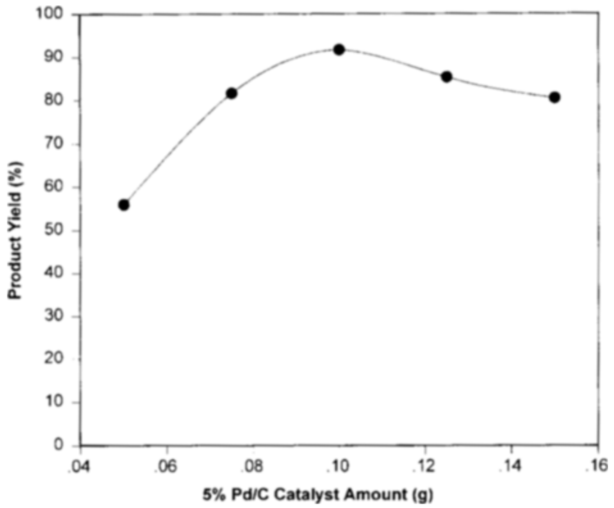


**Fig. 4. Product yield (at 6 hrs) vs. catalyst amount from the reaction mixture of the optimum 1 : 2 : 48 ratio containing 1 mmol of 3-aminophenol.**

Pd catalyst was attributed to the side reactions including rehydrogenation of the diphenylamine product. This trend could be satisfactorily reproduced for the reaction mixtures of the optimum composition, but, containing larger amounts of 3-aminophenol. For example, as shown in Fig. 5, product yield maxima of nearly 90 % were obtained around the reaction time of 8 hrs for the catalyst amounts of 1.3 and 1.625 g, respectively, from the reaction mixture containing the reactants at the optimum 1 : 2 : 48 ratio based on 13 mmol of 3-aminophenol. However, compared to the catalyst input of 1.3 g, the product yield for the catalyst input of 1.625 g reached its maximum earlier due to the excess amount of Pd catalyst, and subsequently dropped more steeply due to the more-facilitated rehydrogenation of the diphenylamine product.

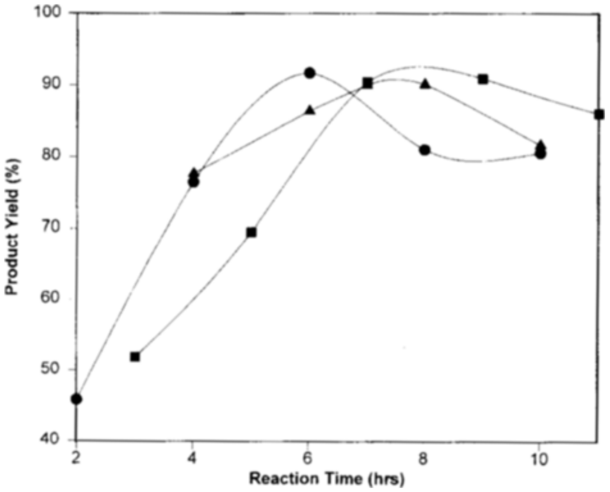


**Fig. 5. Product yield vs. reaction time from various reaction mixtures of the optimum 1 : 2 : 48 ratio.**

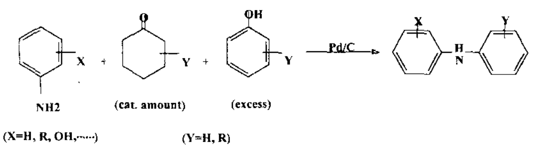
● the reaction mixture containing 1 mmol of 3-aminophenol and 0.1 g of 5 % Pd/C catalyst

■ the reaction mixture containing 13 mmol of 3-aminophenol and 1.3 g of 5 % Pd/C catalyst

▲ the reaction mixture containing 13 mmol of 3-aminophenol and 1.625 g of 5 % Pd/C catalyst

The results of this study may be distinguished from those of other investigators in the following manner.

(a) Nagata et al. reported an efficient process for preparing diphenylamine derivatives from the reaction mixture of aromatic amine, catalytic amount of cyclohexanone, and excess phenol in the presence of Pd catalyst.

 (vii)

The overall reaction was initiated by condensation of aromatic amine and cyclohexanone in the catalytic amount, and excess phenol was reduced by the hydrogen species available from dehydrogenation of the condensation product, furnishing the source of cyclohexanone. Although they could obtain high product yield by feeding a small amount of aromatic amine continuously to the reactor, the amount of diphenylamine produced was limited to the amount of aromatic amine fed.

(b) Akamatsu reported a process for preparing 2-methyl-4-alkoxydiphenylamines which quite closely resembles our reaction scheme; however, his reaction data were restricted to the mixtures of aniline, nitrobenzene, and cyclohexanone at the stoichiometric molar ratio of 1 : 2 : 3. Moreover, no details were available regarding the characterization of the intermediate species and the rate-determining step of the overall reaction.

In our study, by using the relevant combination of reactants consisting of aminophenol, nitrophenol, and excess cyclohexanone derivative, we could show that the limitation to the diphenylamine yield can be virtually removed since, under the optimum excess of cyclohexanone derivative, nitrophenol is easily converted to aminophenol (the key reactant of our diphenylamine synthesis); thus, the product yield would be dependent only on the amount of nitrophenol included in the reaction mixture (Currently the product yield data are confined to the reaction mixtures of the molar ratio of 3-aminophenol : 3-nitrophenol of 1 : 2; however, they will be extended to the reaction mixtures containing relatively more 3-nitrophenol.). Furthermore, by investigating the effects of reaction time and catalyst amount on the product yield, we could understand the various reaction pathways involved in the synthesis of diphenylamines on palladium catalyst, which are directly beneficial to optimization of our reaction scheme.

## CONCLUSIONS

The above results for catalytic synthesis of 2-methyl-3'-hydroxydiphenylamine are mechanistically identical to those for our catalytic synthesis of 2-methyl-4-methoxydiphenyl-amine in that: ① excess cyclohexanone derivative in an optimum amount promoted the condensation of aromatic amine and cyclohexanone derivative, and ② hydrogen-abstraction of the condensation product, N-cyclohexylideneaniline species, is the rate-determining step, while reduction of the nitro compound to its corresponding aromatic amine is easily accomplished. For the relevant reaction mixture of 3-aminophenol, 3-nitrophenol, and 2-methylcyclohexanone, the optimum composition for maximum yield of the desired diphenylamine was the molar ratio of aminophenol : nitrophenol : methylcyclohexanone of 1 : 2 : 48. At this optimum composition, a product yield as high as 90% was obtained at the reaction time of ① 6 hrs from the reaction mixture containing 1 mmol of 3-aminophenol and 0.1 g of 5% Pd/C catalyst, and ② 8 hrs from the reaction mixture containing 13 mmol of 3-aminophenol and 1.3 g of 5% Pd/C catalyst. Excess amount of palladium appeared to lower the product yield by catalyzing the rehydrogenation of the diphenylamine product.

## ACKNOWLEDGEMENT

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## REFERENCES

Akamatsu, N., "Improved Preparation of Diphenylamine Derivatives Comprising Reaction of Nitrobenzenes with Anilines and Cyclohexanone in Presence of Palladium Catalyst", Japanese Patent 05-117214 (1993).

Cho, J. W., Kim, K. S., Lee, T. J., Kim, J. C. and Kim, D. H., "Optimization of Catalytic Synthesis of Diphenylamine Derivative", *Theories and Applications of Chem. Eng.*, **1**, 89 (1995).

Elmar, R. S. and Somerville, N. J., "Preparation of Hydroxy Substituted Diarylamines", U.S. Patent 3,450,764 (1969).

Friedrich, W. C. and Heinz, U. B., "Process for the Preparation of Hydroxydiphenylamines", U.S. Patent 4,265,833 (1981).

Industry Research Institute Report, Korea (1990).

Kim, K. S., Lee, T. J., Kim, J. C. and Kim, D. H., "Optimization of Catalytic Synthesis of Diphenylamine Derivative", Proceedings of 7th Japan-China-USA Symp. on Catalysis, Tokyo, Japan, 41 (1995).

Nagata, T., Kusuda, C. and Wada, M., "Process for the Preparation of Diphenylamine of Nucleus-substituted Derivative Thereof", U.S. Patent 5,545,752 (1996).

Otto, I. K., Gerhard, D. and Hans, J. B., "Process for Preparation of Diphenylamine", U.S. Patent 5,338,885 (1994); "Process for Preparing Diphenylamine", U.S. Patent 5,344,987 (1994).