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# Excellent and Convenient Procedures for Reduction of Benzene and Its Derivatives

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Reductions of benzene, toluene, ortho-xylene, cumene, anisole and benzoic acid to corresponding nonconjugated dienes were realized at room temperature by gas $NH_3$ and Li. The reduced products were easily isolated because THF and dioxane were dissolved in the water. The yields and conversions of the reactions were 70-89% and 80-100%, respectively.

**Key Words:** Arenes, lithium, reductions, alcohols, protonations, ethers.

## Introduction

Reduction reactions of aromatic compounds such as the Birch reduction and related reactions are important in synthetic organic chemistry and therefore these reactions have been investigated by many chemists[1−6]. The reduction products, especially 1,4-cyclohexadiene or intermediates formed in these reactions, serve as starting materials for many target molecules[7−13].

The reduction of aromatic rings by solutions of alkali metals in liquid ammonia was discovered by Wooster and Godfrey[14], who reacted toluene with sodium in ammonia followed by the addition of water. They reported a "highly unsaturated liquid product", which was not identified further. However, the real development of this reaction was to follow in the work by Birch[15]. This reaction is generally referred to as the Birch reduction, although in some cases it is simply called metal-ammonia reduction. Wild and Nelson[16] found adding alcohol last to be advantageous, as opposed to having it present when the metal is added, and it was subsequently discovered that it should be avoided altogether with polynuclear compounds.

Among all aromatic compounds, benzene is the first to come to mind. The reduction of benzene to 1,4-cyclohexadiene is important. The first observation of crucial importance in this field was Wooster's observation[5,17,18]. Wooster showed that the presence of alcohol in liquid ammonia permitted the reduction of benzene to 1,4-cyclohexadiene. Other reduction reactions of benzene by alkali metal in liquid ammonia

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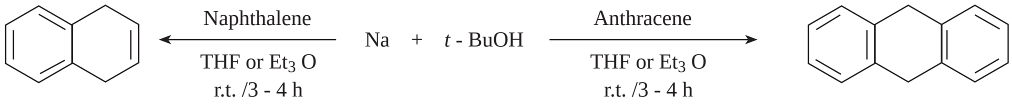
were realized in different conditions[3,6,19−22]. Dumanski and Swerew[23] reduced benzene with metallic calcium into 1,4-cyclohexadine at room temperature and gas ammonia. Preparation of 1,4-cyclohexadiene by this method does not seem suitable as a preparative method because its yield is very low[18]. Benzene and its derivatives were reduced in low molecular weight amines and ethylenediamine by Li[24−27].



**Scheme 1**

We realized the reduction of naphthalene and anthracene with sodium and tert-butyl alcohol (t-BuOH) to 1,4-dihydronaphthalene and 9,10-dihydroanthracene respectively in high yields at room temperature (r.t.) as the sole products (Scheme 1)[28]. We investigated in this study a convenient Birch reduction procedure with mild conditions and high yields for reductions of benzene and its derivatives because reduction products are important in organic synthesis[7−13].

# Experimental

**General Method:** All chemicals and solvents are commercially available and were used after distillation or treatment with drying agents. The $^1$H- and $^{13}$C- NMR spectra were recorded on a 200 (50)-MHz Varian spectrometer; $\delta$ in ppm, with $Me_4Si$ as the internal standard.

**Procedure 1: Reduction of benzene to 1,4-cyclohexadine**.

In a 500-mL, 2-necked, round-bottomed flask fitted with a reflux condenser and a stirring bar were placed tert-butanol (72 g, 0.963 mol, 2.85 equivalents), dry benzene (27.3 g, 0.35 mol, 1 equivalent) and dry THF (120 mL). The flask was attached to gas ammonia ($NH_3$) whose pressure was approximately 1 atmosphere (atm) and the resulting solution was stirred. The reaction mixture was cooled in an ice-water bath and then freshly cut lithium (7.35 g, 1.05 g-atom, 3 equivalents) was added over 3-5 min. The temperature of the bath was allowed to rise gradually to room temperature. After the addition of lithium was completed, the reaction mixture was stirred for 5 h. Two phases appeared in the reaction mixture. The top and bottom phases were brown and gray, respectively. The mixture was cooled in an ice-water bath again. Cold water was added slowly and carefully to the flask until all the lithium was consumed, as evidenced by the conversion of the colors to white. The reaction mixture was poured into a mixture (250 g) of water and ice and was acidified with the addition of 2 N cold hydrochloric acid. The organic layer was separated and washed with cold water (100 mL), a solution of $NaHCO_3$ (5%, 50 mL) and water (75 mL), in order that. The reduction product, 1,4-cyclohexadiene, was dried over $CaCl_2$ and filtered. The yield (23.5 g) and conversion of the reaction were 84% and 100%, respectively.

**Procedure 2: Reduction of benzene to 1,4-cyclohexadine.** (This experimental procedure may also be used if gas $NH_3$ is not continuously present in any laboratory.)

In a 500-mL, 2-necked, round-bottomed flask fitted with a reflux condenser, a stirrer bar and dropping funnel was placed dry dioxane (100 mL). The flask was attached to a balloon, of gas ammonia ($NH_3$), at 1 atmosphere (atm) and then washed with $NH_3$while the dioxane was stirred. After stirring in an atmosphere of $NH_3$ for 15-20 min, freshly cut lithium (8.0 g, 1.152 g-atom, 3 equivalents) was added in quantities for

5 min, followed by stirring for 15-20 min. Dry benzene (30 g, 385 mmol, 1 equivalent) was added and the mixture was stirred for 30 min. The reaction mixture was cooled in an ice-water bath and then a solution of t-BuOH (85 g, 1.152 g-atom, 3 equivalents) in dioxane (10 mL) was added slowly by dropping funnel. To drop the t-BuOH well, the stopcock of $NH_3$ may be switched on and off. The heat of the reaction mixture has to be checked. $NH_3$was put in the balloon again and attached to the flask. When the addition of t-BuOH was complete, the reaction mixture was stirred for 2 h, and then the cold bath was removed. This mixture was stirred for an additional 20 h and then cooled by an ice-water bath. A mixture of water and ice was then added slowly until all the lithium was consumed, as evidenced by the conversion of the brown color to white-gray. A saturated solution (100 mL) of $NH_4Cl$ was added, and the organic phase was separated and then washed with a saturated solution (2 x 30 mL) of $NH_4Cl$ and water (2 x 30 mL), in order that. The reduction product, 1,4-cyclohexadiene, was dried over $CaCl_2$ and filtered. The yields and conversions of the reactions were 80-90% and 100%, respectively.

**Reduction of toluene to 1-methyl-cyclohexa-1,4-diene**: (Entry 2),

The reaction was realized according to procedure 1. Toluene (27.3 g, 0.3 mol), $HOBu^t$ (63 g, 0.85 mol), THF (100 mL) and Li (6.3 g, 0.9 mol) were used in the reaction. The reaction lasted 7 h. Pure 1-methyl-cyclohexa-1,4-diene (24.2 g, 87%) was obtained.

**Reduction of cumene to 1-isopropyl-cyclohexa-1,4-diene**: (Entry 3),

The reaction was realized according to procedure 1. Cumene (16.4 g, 0.24 mol), $HOBu^t$ (60 g, 0.81 mol), THF (100 mL) and Li (6.3 g, 0.9 mol) were used in the reaction. The reaction lasted 20 h. 1-Isopropyl-cyclohexa-1,4-diene and cumene were obtained in a mixture (25.3 g). Percentages of 1-isopropyl-cyclohexa-1,4-diene and cumene in the mixture were 80 and 20, respectively.

**Reduction of ortho-xylene to 1,2-dimethyl-cyclohexa-1,4-diene**: (Entry 4),

The reaction was realized according to procedure 1. Ortho-xylene (21.2 g, 0.2 mol), $HOBu^t$ (45 g, 0.6 mol), THF (80 mL) and Li (5.6 g, 0.8 mol) were used in the reaction. The reaction lasted 24 h. Pure 1,2-dimethyl-cyclohexa-1,4-diene (17.06 g, 79%) was obtained.

**Reduction of anisole to 1-methoxy-cyclohexa-1,4-diene**: (Entry 5),

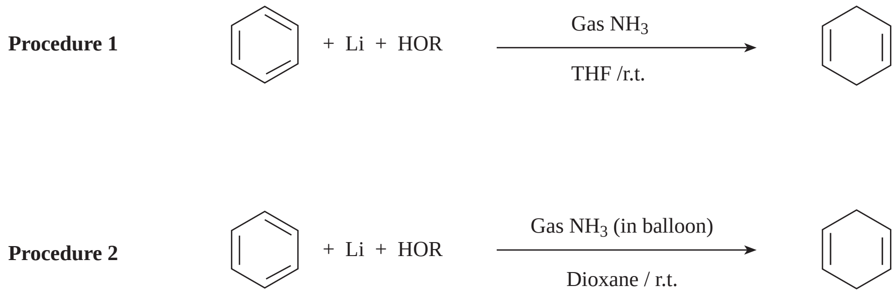
The reaction was realized according to procedure 1. Anisole (16.2 g, 0.15 mol), $HOBu^t$ (33.3 g, 0.45 mol), THF (60 mL) and Li (3.5 g, 0.5 mol) were used in the reaction. The reaction lasted 24 h. The solution of cold hydrochloride acid was not added to the reaction mixture. The mixture was extracted with ether (3 x 75 mL). The combined organic layer was dried over $Na_2SO_4$ and the solvent was evaporated. Pure 1-methoxy-cyclohexa-1,4-diene (14 g, 85%) was obtained.

**Reduction of benzoic acid to cyclohexa-2,5-dienecarboxylic acid:** (Entry 6),

The reaction was realized according to procedure 1. Benzoic acid (4.0 g, 32.78 mmol), THF (50 mL) and Li (1.15 g, 164.29 mmol) were used in the reaction. As mentioned in the literature[29], alcohol was not used for this procedure as a proton source. The reaction lasted 8 h. The mixture was extracted with $CHCl_3$ (3 x 25 mL). The combined organic layer was dried over $Na_2SO_4$ and the solvent was evaporated. Benzoic acid and cyclohexa-2,5-dienecarboxylic acid were obtained in a mixture (3.75 g). Percentages of benzoic acid and cyclohexa-2,5-dienecarboxylic acid in the mixture were 17 and 83, respectively.

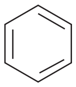
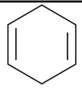
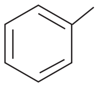
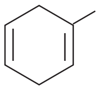
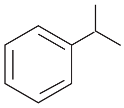
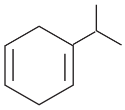
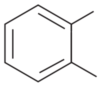
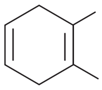
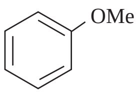
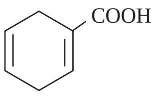
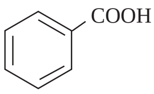
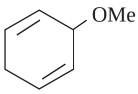
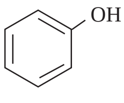
## Results and Discussion

We continued our investigation of the reduction of aromatic compounds in different conditions and reduced benzene and its derivatives with lithium (Li) and alcohol (ROH) in tetrahydrofuran (THF) or dioxane at room temperature and under ammonia atmosphere (Scheme 2 and Table). The pressure of gas ammonia is approximately atmospheric pressure. In these procedures, aromatic compounds in solvent are reacted with Li in the presence of gas ammonia, and then the reaction mixture is quenched by HOEt, water or a saturated solution of $NH_4Cl$. The reaction mixtures may be cooled to 0 °C. Both procedures were used for the reduction of benzene. Only procedure 1 was used for the reduction of benzene derivatives. As shown, procedure 1 is better than procedure 2.



**Scheme 2**

**Table.** Reactants, products, yields and conversions in the reductions (procedure 1).

| Entry | Reactant | Product | Yield (%) | Conversion (%) |
|---|---|---|---|---|
| 1 |  |  | 84 | 100 |
| 2 |  |  | 87 | 100 |
| 3 |  |  | 70 | 80 |
| 4 |  |  | 79 | 100 |
| 5 |  |  | 85 | 100 |
| 6 |  |  | 76 | 83 |
| 7 |  | - | 0 | 0 |

Phenol (Table) was not reduced by procedure 1, while the others were easily reduced. Relative rates of reduction of aromatic rings depend on the electron density of rings. Electron donating groups on the aromatic rings decrease the rate of the reaction. The electron density of ring in phenol is much greater than the others because phenol converts into phenoxide anion in the reaction mixture. However, regiochemistry in reduction reactions is affected by the type of groups present on the ring because they tend to stabilize or destabilize the radical anion[2]. Known regiochemistry was observed in these reactions (Table).

Compared to the other reduction procedures of converting benzene and its derivatives to corresponding nonconjugated dienes, the new reduction procedures have certain advantages. These include the following: 1) These reduction reactions are carried out at room temperature, avoiding the low temperatures, under -33°C, needed to obtain liquid $NH_3$. 2) The procedures are environmentally friendly[30−34]. Much more $NH_3$ is needed when liquid $NH_3$ is used as solvent. Evaporation of liquid $NH_3$ may damage the environment. 3) Control of moisture is easier in our method, and the reaction may go on for longer periods. When the reaction is conducted with liquid ammonia, it may be quenched by the developing moisture. 4) Evaporation of liquid $NH_3$ may take a long time and some side reactions such as isomerization and reoxidation may be observed. 5) It is unnecessary for the researcher to observe the reaction carefully and continuously in the present method because temperature control is not necessary, whereas the temperature must be checked in the reaction with liquid $NH_3$.

## Conclusion

We have found new, excellent and convenient procedures for the reduction of benzene and its derivatives to corresponding nonconjugated dienes. The structure and purities of the reduced products were determined by NMR spectroscopy. The procedure is environmentally friendly. The reduced products were easily isolated because dioxane and THF were dissolved in the water. The yields and conversions of the reactions were 70-89% and 80-100%, respectively. Further reactions of aromatic compounds with metals (Na, Li etc.) are under investigation.

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