

# Reduction of resin immobilized aryldiazonium ions in solid phase by aqueous sodium borohydride – A simple synthesis of arylhydrazines

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**Abstract:** A series of arylhydrazines were successfully synthesized by reducing resin immobilized aryldiazonium ions with aqueous NaBH<sub>4</sub> solution under biphasic condition at room temperature. The reduction is clean with simple work-up procedure. The products were identified by comparing their melting points with authentic samples. The characterization of compounds was also done by conversion to their hydrazone derivatives with benzophenone as standard carbonyl compound followed by representative spectral data analysis.

**Keywords:** Aryldiazonium ions; Resin immobilization; Solid phase reduction; Arylhydrazine.

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## I. INTRODUCTION

Diazonium salts were first discovered by Peter Griess [1, 2, 3]. He prepared a diazonium salt by the action of nitrous gas on picramide. The azo functional group is one of the most important functional groups in organic chemistry primarily because of its presence in azo dyes and in many free radical initiators. Development of azo chemistry and its application in the dye stuff industry was influenced significantly by the investigations of Schraube and Schmidt [4]. The azo dyes constitute the largest single class of dyes making up over half of the total number of synthetic colours of commercial importance. As far as synthetic utilities of aryl diazonium ions are concerned, one of the most important utility is their conversion into corresponding arylhydrazines, because the organic derivative of hydrazine is phenylhydrazine, the simplest of the arylhydrazines. It was first prepared [5] in 1875 by Fischer and later proved to be one of the most valuable reagents in organic chemistry. The most striking illustration of its importance is that before phenylhydrazine was known, the chemistry of the sugar group was to a large extent an unsolved problem because of the difficulty of preparing crystalline derivatives, but with the aid of phenylhydrazine, Fischer was able to obtain such derivatives and arrive at the characteristics of sugars. The preparation of phenylhydrazine was a consequence of Griess's work on diazo compounds in 1869. It has been found that from benzenediazonium chloride and sodium or potassium sulphite, a compound could be obtained which is now known to be the alkali diazosulphonate, PhN=NSO<sub>3</sub>K/Na and this was reduced by more sulphite. Fischer showed that the resulting compound was the salt of phenylhydrazinesulphonic acid, PhNHNHSO<sub>3</sub>Na and on boiling with hydrochloric acid, it was hydrolyzed to phenylhydrazine and sulphuric acid. Thus all the more important methods of preparing the monoarylhydrazines consist in the reduction of a diazo compound, and since any primary aromatic amine can be diazotized, hydrazines containing various substituted aryl groups can be readily obtained. The reduction can be carried out in several ways. Certain diazo compounds, such as that derived from p-nitroaniline, give a hydrazine disulphonate, and not a monosulphonate, but these are hydrolyzed to the hydrazine so that the method of

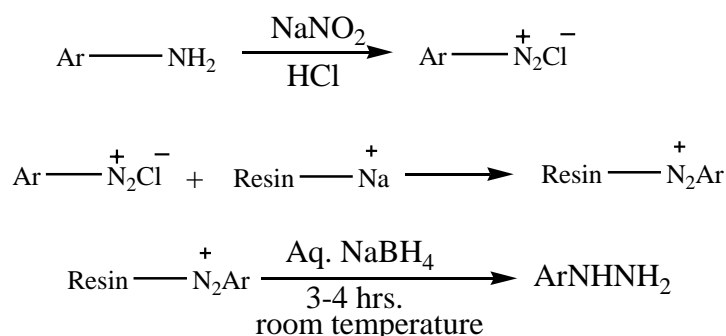
preparation is unaffected [6]. In some cases, it is better to reduce the diazosulphonate with Zn-dust and CH<sub>3</sub>COOH or with sodium hydrosulphite [7]. Alternatively, the diazonium salt can be reduced directly to the hydrazine with stannous chloride in acid solution. This method, which was discovered by Meyers, is often very convenient, because the hydrazines hydrochloride are sparingly soluble in HCl and crystallize out from the reaction mixture ; the method is, of course unsuitable if easily reduced groups such as the nitro group are present. Sulphur dioxide or triphenylphosphine may also be used as the reducing agent [8, 9].

Other methods are known for obtaining monoarylhydrazines which do not involve the diazo compounds and these are useful in special cases. Naphthylhydrazines can be prepared by heating the naphthols with hydrazine, but with phenols in place of naphthol, the yield is poor, The chlorine atom in a compound such as chlorobenzene is too inert to react with hydrazine, but the valuable 2,4-dinitrophenylhydrazine is best made by the action of 1-chloro-2,4-dinitrobenzene with hydrazine by a nucleophilic substitution reaction. Arylhydrazines are also obtained by quantitative reduction [10] of corresponding aryl diazonium salts with CrCl<sub>2</sub>. Addition of excess CrCl<sub>2</sub> solution to a weakly acidic or neutral solution of the diazonium ions gives the hydrazines. By far the most important use of phenylhydrazine is its reaction with carbonyl compounds to give the well defined, crystalline hydrazones. However, the substitution products are often better, e.g. 2,4-dinitrophenylhydrazine (2,4-DNP) popularly known as Brady's reagent has been used most often. Others which have been used are 2-naphthylhydrazine, p-bromophenylhydrazine etc. The hydrazones derived from these compounds melt at higher temperature than the phenylhydrazones themselves and are less soluble; they are therefore used in case of simple ketones.

Immobilization of diazonium ions onto ion-exchange resin and their synthetic utility has been reported by *Das, P. J. et. al.* Solid phase diazocoupling reaction on ion-exchange resin support was carried out in organic solvent and under neutral condition [11], by reacting resin immobilized diazonium ions with suitable substrate to give azo compounds as the only product. The resin immobilized diazonium ions have also been used to synthesize the physiologically important 3-arylazoindoles [12] in good yield. Synthesis of 1-Aryl-3,3-disubstituted Triazines [13] on ion-exchange resin support was also effected by the reaction of resin immobilized diazonium ions with 2<sup>0</sup> amines. Further, solid phase synthesis of N-arylazoindoles [14] was also reported by the reaction of immobilized diazonium ions with sodioindole in dry tetrahydrofuran.

## II. REDUCTION OF RESIN IMMOBILIZED ARYL DIAZONIUM IONS IN SOLID PHASE BY AQUEOUS SODIUM BOROHYDRIDE

In the course of our study involving the application of ion-exchange resin supported reagents [15, 16, 17, 18] in organic synthesis, we, here, immobilized substrates onto ion-exchange resin instead of reagents. In this study, aryl diazonium ions, prepared by diazotization of the corresponding amines, were immobilized on a cation-exchange resin by elution technique and the loaded resins were subsequently reacted with aqueous NaBH<sub>4</sub> solution with stirring at room temperature under biphasic condition to give the corresponding arylhydrazines in good yield. The reduction is clean and the work-up procedure is simple. Although we tried the reduction with Ni<sub>2</sub>B-BER system [15], the method did not give the desired result. But the reduction was successful when diazonium ions were immobilized and stabilized on a resin and the reducing agent was taken in solution. The successful transformation is shown in scheme-I :



**Scheme-I**

The reaction was monitored by the colour change of the resin beads. The products were obtained by the extraction of the dried beads with 95% (v/v) ethanol. Removal of the solvent under reduced pressure or by passing HCl-gas through the ethanolic solution (done in some cases) gave the desired hydrazines or its hydrochloride salts. The products were identified by comparing their m.p.s with the authentic samples. Identification of products was also done by conversion to their hydrazones with a suitable carbonyl compound and percentage yield ascertained by this procedure.

### III. EXPERIMENTAL

Amberlite IRA-120 macroporous type according to Rohm & Haas specifications with type analysis  $\text{SO}_3^-$ , 20-50 mesh,  $\text{Na}^+$  form, styrene DVB (8%) was chosen as the cation exchanger. The resin beads were washed several times with deionised water before use. Melting points were determined in open capillaries and uncorrected. The aromatic amines, from which the diazonium ions were prepared, were procured from Loba-cheme (India) Ltd. and were used as obtained.

#### III.A. Preparation of Resin Immobilized Diazonium ion

15 g of the cation exchange resin was washed several times with deionized water, dried and taken in column. 0.05 mole of the aromatic amine was diazotized using  $\text{NaNO}_2/\text{conc. HCl}$  at  $0-5^\circ\text{C}$ . On passing the solution of diazonium ions through the column of the resin, the diazonium ions were grafted onto the cation exchanger by displacement of the  $\text{Na}^+$  ions. The loaded resin was washed several times with deionized water till the washing was free of diazonium ions (alkaline 2-naphthol test). The resin was then recovered and dried over  $\text{P}_2\text{O}_5$  at  $50^\circ\text{C}$  under reduced pressure (50 mm Hg).

#### III.B. Analysis of the Extent of Immobilization

The dried resin was analyzed for diazonium ion content by reductometric titration procedure using 57% hydroiodic acid [19, 20] where the liberated iodine was titrated with standardized sodium thiosulphate solution using starch as indicator. This experiments were done with the diazonium ions obtained from different aromatic amines (table-I) and the average capacity was found to be 2.26 m. eqv. of  $\text{ArN}_2^+$  per gram of the resin. The dry resin was stored at  $5^\circ\text{C}$  and the diazonium ion content was found to remain constant over a period of six months. Immobilization of diazonium ions on cation exchange resin proves to be an excellent method for their stabilization and hence various solid phase reactions on them.

**Table I: Diazonium ion content in the loaded resin**

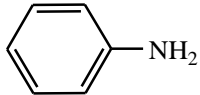
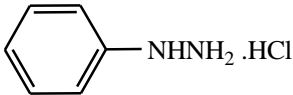
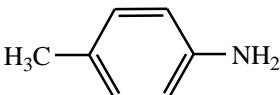
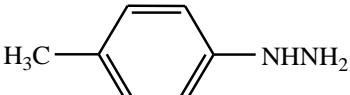
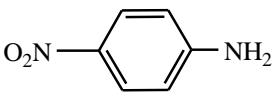
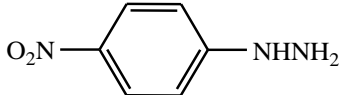

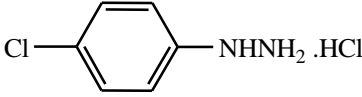
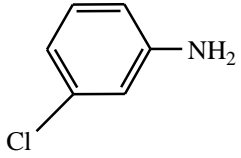
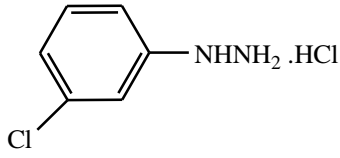
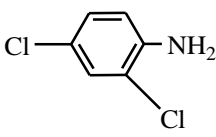
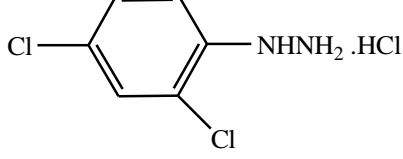
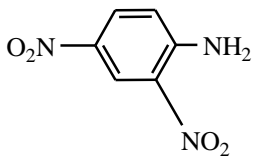
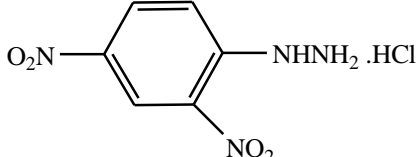
Resin immobilized diazonium ions obtained from	Diazonium ion content*	Average capacity*
4-nitroaniline	2.18	2.26
4-chloroaniline	2.11	
2,4-dinitroaniline	2.36	
2,4-dichloroaniline	2.40	

\*m.eqv.per gram of the resin

#### III.C. General Procedure for Solid Phase Reduction of Resin Immobilized Diazonium ions

To a 100 mL solution of 2% aqueous  $\text{NaBH}_4$  were added 15 g diazonium ion immobilized beads with constant stirring at room temperature. The reaction occurred instantaneously as evident from the change in colour of the solution followed by the beads. Stirring was continued for 3-4 hours. The blackened beads were recovered and washed several times with water and then dried. The products were extracted from the dried beads with 95% (v/v) ethanol and reduced pressure removal of the solvent gave the desired hydrazines. The products were also obtained as their hydrochloride salts in some cases on passing HCl-gas through their ethanol extracts. Since the target compounds chosen were those that have already been synthesized earlier, the identification of them was mainly done by comparing their melting points and the hydrazone derivatives of a particular carbonyl compound. The physical characteristics of the hydrazines obtained are given in table-II.

**Table II: List of Hydrazines prepared and their physical characteristics**

Sl. No.	Aromatic amines used	Arylhydrazines produced	Reaction time (hrs.)	M.P. (°C)		*Yield (%)
				Obs.	Lit.	
1.			3.5	238	240d	85
2.			3.0	67	65	78
3.			4.0	156	158	89
4.			4.0	210	216d	75
5.			4.0	240	242d	70
6.			3.5	200	217d	75
7.			4.0	189	192d	88

### III.D. Conversion of the hydrazines to the Hydrazine [21] derivatives of benzophenone

#### 1) Phenylhydrazone :

0.5 g of phenylhydrazine hydrochloride prepared was dissolved in 5 mL water containing 0.8 g sodium acetate. To it, an ethanolic solution of 0.3 g of benzophenone was added and shaken well to get a clear solution. The mixture was warmed on a water bath for 10-15 minutes and cooled. The crystalline derivative was filtered off and recrystallized from dilute ethanol. The observed melting point was 138<sup>0</sup>C (Lit. 137<sup>0</sup>C).

Spectral data : Found : C,83.72; H,5.90; N,10.31; Calc. : C,83.82, H,5.88; N,10.29  
IR : 1660 (C=N str.)  
<sup>1</sup>NMR :d 4.1 (s, 1H), 7.7-7.9 (m, 15H)

**2) 4-methylphenylhydrazone :**

The same procedure was followed as in the case of (1).

The observed melting point was 158<sup>0</sup>C (Lit. 161<sup>0</sup>C).

**3) 4-nitrophenylhydrazone :**

The same procedure was followed as in the case of (1).

The observed melting point was 153<sup>0</sup>C (Lit. 155<sup>0</sup>C).

**4) 4-chlorophenylhydrazone :**

The same procedure was followed as in the case of (1).

The observed melting point was 110<sup>0</sup>C (Lit. 106<sup>0</sup>C).

**5) 3-chlorophenylhydrazone :**

The same procedure was followed as in the case of (1).

The observed melting point was 125<sup>0</sup>C (Lit. 127<sup>0</sup>C).

**6) 2,4-dichlorophenylhydrazone :**

The same procedure was followed as in the case of (1).

The observed melting point was 146<sup>0</sup>C (Lit. 145<sup>0</sup>C).

**7) 2,4-dinitrophenylhydrazone :**

To a solution of 0.25 g benzophenone in minimum volume of ethanol was added a solution of 0.5 g 2,4-dinitrophenylhydrazine hydrochloride in ethanol having few drops conc. sulphuric acid and warmed on water bath. The orange yellow solid so separated was filtered off and recrystallized from dilute ethanol. The observed melting point was 238<sup>0</sup>C (Lit. 238<sup>0</sup>C).

Spectral data : Found : C,66.29; H,4.07; N,12.22; Calc. : C,66.27, H,4.06; N,12.20  
IR : 1622 (-NO<sub>2</sub> str.), 1660 (C=N str.)  
<sup>1</sup>NMR :d 9.4 (s, 1H), 7.1-8.4 (m, 13H)

#### IV. CONCLUSION

The study reveals the synthetic utility of resin immobilized diazonium ions in the simple synthesis of arylhydrazines in solid phase. In this study, aryl diazonium ions prepared by the conventional method were immobilized and stabilized on a cation exchange resin and solid phase reduction was carried out using aqueous sodium borohydride to give corresponding arylhydrazines under biphasic condition. The reduction of immobilized diazonium ions to produce hydrazines by this procedure is noteworthy. Simplicity of work up procedure is an added advantage.

#### REFERENCES

- [1] Ridd, J. H. 1961. Quart. Rev., 15, 418.
- [2] Zollinger, H. 1967. Azo & Diazo Chemistry, Interscience, New York, pp. 1-37.
- [3] Sidgwick, R. 1966. The Organic Chemistry of Nitrogen, Oxford Press, by Millar and Springall, 3rd Edn., Ch. 16 & 17.
- [4] Schraube, C., Schmidt, C. 1894. Chem. Ber., 27, 514.

- [5] Forster, M. O. 1920. J. Chem. Soc., 117, 1157.
- [6] Davies, W. 1922. J. Chem. Soc., 121, 715.
- [7] Thompson, L. 1921. J. Soc. Dyers Colourists, 37, 7.
- [8] Pfannstiel, K. 1942. J. Janecke, Ber, 75, 1096.
- [9] Horner, L., Stohr, H. 1953. Chem. Ber., 86, 1073.
- [10] Patai, S. 1978. The Chemistry of Diazonium And Diazo Groups, Part I, Wiley & Sons, New York, p-153.
- [11] Das, P. J., Khaound, S. & Dutta, J. 1995. Ind. J. Chem., 34B, 161-163.
- [12] Das, P. J. & Khaound, S. 1998. Ind. J. Chem., 37B, 155-157.
- [13] Das, P. J. & Khaound, S. 1994. Tetrahedron, 50, 9107-9112.
- [14] Das, P. J. & Khaound, S. 1997. Tetrahedron, 53, 9749-9754.
- [15] Sikdar, A. P., Chetri, A. B., Das, P. J. 2003. Indian J. Chem., 42B, 2878.
- [16] Sikdar, A. P., Chetri, A. B., Das, P. J. 2003. Synth. Commun. 33, 3147.
- [17] Sikdar, A. P., Das, P. J. 2005. J. Assam Sc. Soc., 46, PP 01-03.
- [18] Sikdar, A. P., Das, P. J. 2007. Indian J. Chem., 46B, 1208.
- [19] Aldrovandi, R., Lorenzi, F. De 1952. Chem. Abstr., 46, 10051h.
- [20] Patai, S. 1978. The Chemistry of Diazonium And Diazo Groups, Part I, Wiley & Sons, New York, p-153.
- [21] Vogel, A. I. 1989. Text Book Of Practical Organic Chemistry, ELBS 5th ed., p. no. 1257-58.