

## REVIEW

# Reduction of aromatic and heteroaromatic azo compounds with hydrazine hydrate

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**ABSTRACT:** The azo compounds have been reduced with hydrazine hydrate in the presence of a catalyst or without a catalyst. This reaction is an attractive alternate for the reduction of azo functional group to obtain new amines. In this review, the reduction of aromatic or heteroaromatic azo compounds with hydrazine hydrate have been reported.

**KEYWORDS:** Reduction, azo compounds, uncatalyzed reduction, hydrazine hydrate.

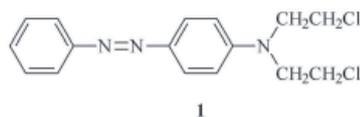
## 1. INTRODUCTION

Reduction of azo compounds to the amines is a useful chemical reaction for synthetic organic chemistry because of the fact that the amino group serves as a site for further derivatization. The amines are also essential in the production of many pharmaceuticals, polymers, photographic materials, dyes and pigments. The primary aromatic amines are generally prepared by reduction of aromatic nitro (1, 2, 3) or azo (4, 5, 6) compounds. Hydrazine hydrate has been commonly used for reduction of nitro group in the presence of catalysts (7, 8). The reduction of azo compounds have also been performed with hydrazine hydrate in presence of catalyst (9, 10). Pasha and Nanjundaswamy (11) demonstrated the reduction of azoarenes to aminoarenes with hydrazine hydrate in the presence of aluminium powder in ethanol. For the reduction of azo compounds, Ergenç and Rollas (Açikkol) (12-21) have already been using hydrazine hydrate without catalyst since 1972. Ross and Warwick (22) have shown that the azo derivatives reduced by hydrazine hydrate. However in this study, reduction product have not been isolated. To the best of our knowledge, Ergenç and Rollas were the first authors who reported reductive cleavage of azo compounds to give the corresponding amines without a catalyst. Recently, Zhang and Wang (23), Pasha and Nanjundaswamy (24), Koppes et al. (25) have also reported the reduction of azo compounds using hydrazine hydrate without catalyst. Certain aminophenyl substituted 1,2,4-triazoles and 1,3,4-thiadiazoles were synthesized from corresponding azo com-

pounds using hydrazine hydrate without catalyst by Rollas (26, 27). In this review, the reducing properties of hydrazine hydrate and the reductive cleavage of azo compound with hydrazine hydrate will be discussed.

## 2. THE REDUCTION OF AZO COMPOUNDS USING HYDRAZINE HYDRATE WITHOUT CATALYST

Hydrazine hydrate is a strong reducing agent. Generally, it has been used the reduction of nitro group (28). In the reduction of the azo compounds with hydrazine hydrate, Raney nickel has been used as a catalyst (9, 29). In 1955, Ross and Warwick (22) showed that the azo derivatives could be reduced by hydrazine hydrate. They reported the tumour-growth inhibitory activity of azo-derivatives of aromatic nitrogen mustards and the reduction of azo-linkage with hydrazine hydrate to correlate the ease of reduction of N,N-bis(2-chloroethyl)-4-(phenyldiazenyl)aniline (**1**) with its biological activity. Therefore the substituted derivatives of **1** have been prepared. Of the reducing agents examined, the most consistent results were obtained using hydrazine hydrate. However in this research, the reduction products, hydrazo-compounds or amines, have not been isolated.



**FIGURE 1.** N,N-bis(2-chloroethyl)-4-(phenyldiazenyl)aniline.

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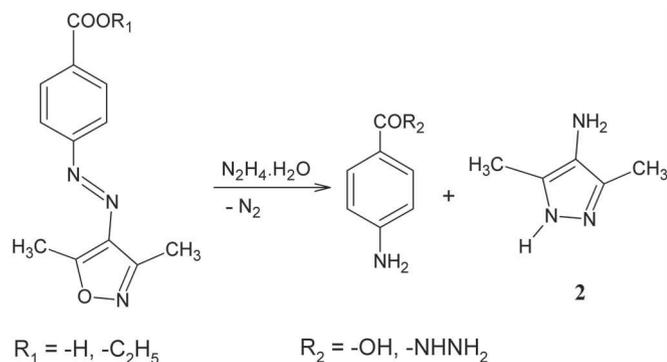
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Received:  
Dec 04, 2009

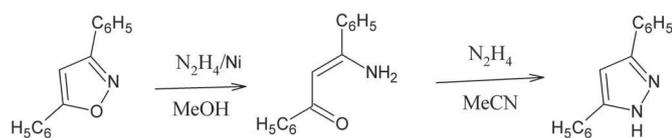
Accepted:  
Dec 31, 2009

In 1972, Ergenç and Açıklol (Rollas) (12) published the first report of the reductive cleavage of azo compounds with hydrazine hydrate without a catalyst for the synthesis of 4-amino-3,5-dimethylpyrazole **2**. In this reaction, isoxazole ring was observed to be converted to pyrazole ring while the azo function is reduced to amino group. (Scheme 1).



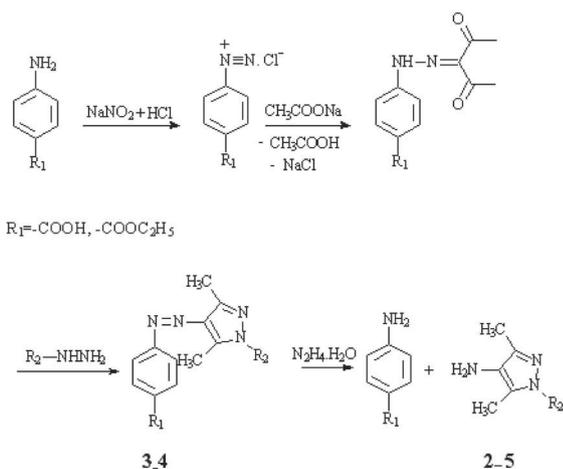
**SCHEME 1.** The reduction of azoisoxazoles with hydrazine hydrate.

Also, Sviridov et al. (30) reported the transformation of the isoxazole into the pyrazole with hydrazine hydrate in the presence of Raney nickel catalyst (Scheme 2).



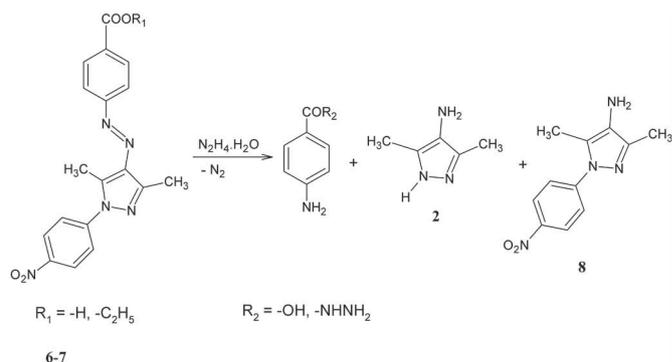
**SCHEME 2.** The conversion of 3,5-diphenylisoxazole to 3,5-diphenylpyrazole.

A method developed by Rollas (31) for the synthesis of substituted amines from the corresponding heteroaromatic azo compounds. Aryldiazonium salts can be coupled with active aliphatic CH compounds. Therefore the aryldiazonium salts were coupled with acetylacetone and the obtained hydrazones, which are stable form of the coupling products, were condensed with hydrazine or substituted hydrazines to form azopyrazoles. These azopyrazoles were heated with an excess amount of hydrazine in ethanolic solution on a steam bath until red or orange colour of the solution changed into pale yellow and also until nitrogen no longer evolved.



**SCHEME 3.** The reduction of azopyrazoles with hydrazine hydrate.

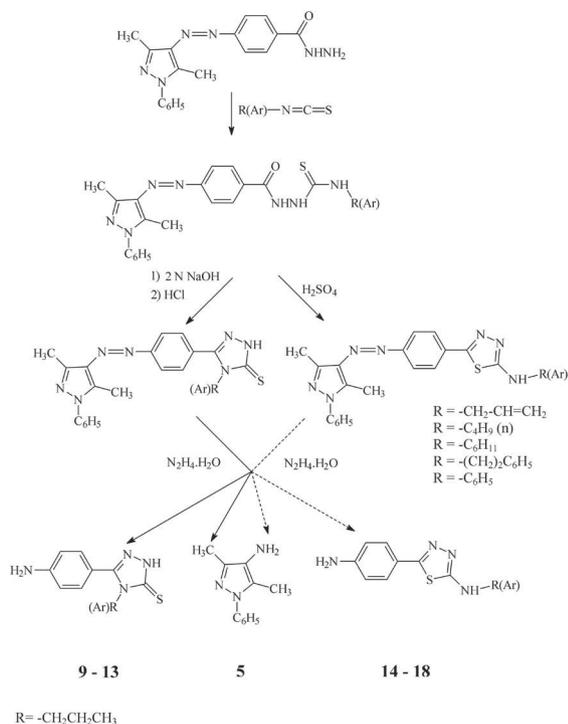
The reductive cleavage of **3** and **4** with hydrazine gave 4-amino-3,5-dimethylpyrazole **2** and the other amines, 4-aminobenzoic acid or 4-aminobenzoic acid hydrazide. In the experimental conditions the ester group have also been converted to hydrazide. The reduction of nitro group-containing azo compound, 3,5-dimethyl-4-(4-ethoxycarbonyl-phenylazo)-1-(4-nitrophenyl) pyrazole **7**, with hydrazine hydrate in ethanol without a catalyst is presented in Scheme 4. The carbon-nitrogen bond has also been reduced (14, 31).



**SCHEME 4.** The reduction of azopyrazoles bearing nitro group.

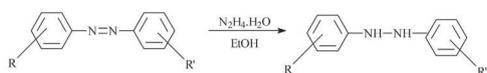
Recently, Rollas et al. (21) developed a new method for the synthesis of 4-amino-3,5-dimethylpyrazole. Aniline was used as the starting material instead of 4-aminobenzoic acid or ethyl 4-aminobenzoate. The reduction of the corresponding azo compound was afforded by lower amounts of hydrazine hydrate at room temperature. In this method, the separation of amines had been found easier than first method. Aniline was removed by extraction with diethyl ether. Since the reaction time was very long, the reduction of azo compounds was carried out with hydrazine hydrate (1:3) by refluxing in ethanol for 30 min to synthesize 4-amino-3,5-dimethylpyrazole (Rollas, unpublished data). Presence of excess hydrazine hydrate have been found unnecessary for the reduction.

The uncatalyzed reduction with hydrazine hydrate was applied to reduce different azo compounds containing 1,2,4-triazolin-5-thione and 1,3,4-thiadiazole rings by Rollas (32, 33). The synthetic pathway of the starting compounds which were obtained from the corresponding thiosemicarbazide derivatives (34) and target 1,2,4-triazolin-5-thiones **9-13** and 1,3,4-thiadiazoles **14-18** (26, 27) are presented in Scheme 5.



**SCHEME 5.** The reduction of azotriazoles and azothiadiazoles with hydrazine hydrate.

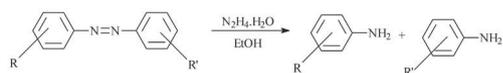
Zhang and Wang (23) reported the synthesis of certain hydrazo compounds starting from the azobenzene, substituted symmetric or nonsymmetric azobenzenes with the use of hydrazine hydrate in ethanol (Scheme 6).



R H 4-CH<sub>3</sub> 4-Cl 4-OCH<sub>3</sub> 4-Br 3,4-CH<sub>3</sub> 4-F 4-Cl 4-Br 4-CH<sub>3</sub> 3-Cl 4-NO  
R' H 4'-CH<sub>3</sub> 4'-Cl H 4'-Br 3',4'-CH<sub>3</sub> H H H H H H

**SCHEME 6.** The reduction of diazobenzenes to hydrazo compounds with hydrazine hydrate.

Pasha and Nanjundaswamy (24) described the synthesis of certain aromatic amines from the corresponding azoarenes with excess hydrazine hydrate without a catalyst in refluxing ethanol similar to Rollas's procedure (26, 27, 31).

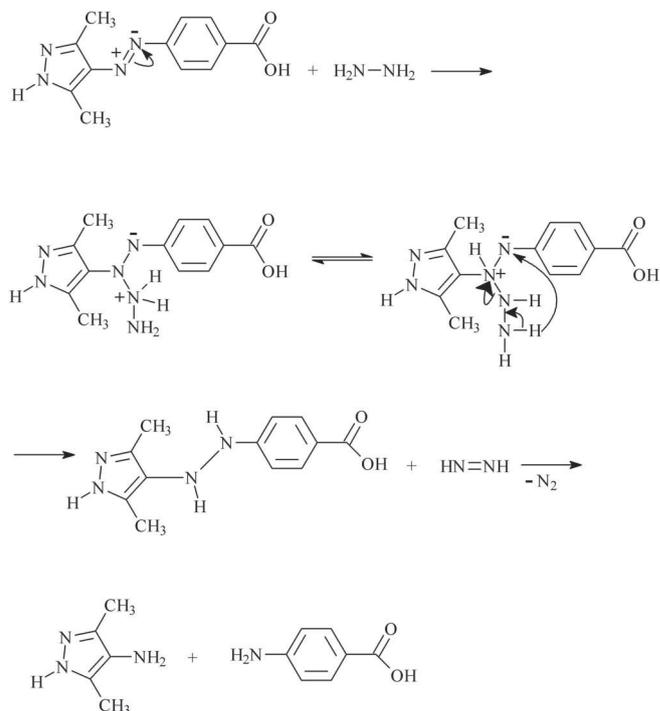


R H 2-CH<sub>3</sub> 3-CH<sub>3</sub> 3-OCH<sub>3</sub> 2-OH 2-Cl 2-OH 2-COOH 4-COOH 4-NH<sub>2</sub>  
R' H 2'-CH<sub>3</sub> 3'-CH<sub>3</sub> 3'-OCH<sub>3</sub> 2'-OH 2'-Cl H 4'-N(CH<sub>3</sub>)<sub>2</sub> H H

**SCHEME 7.** The reduction of diazobenzenes to amines with hydrazine hydrate.

A mechanism for the reduction of azo groups by hydrazine hydrate without using a catalyst is suggested as shown in Scheme 8. The proposed hypothesis may be supported by Koppes et al. (25). They reported that the reduction of azo compounds had been carried out via diimide. The production of

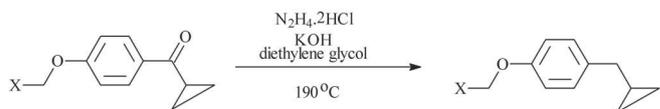
diimide from hydrazine hydrate could be obtained by an oxidant agent. Diimide could be produced by air oxygen. However Koppes et al. also reduced azo compounds to hydrazo compounds in anaerobic conditions by protecting from the air oxidation. In the hydrazine hydrate reduction, azo group may act as an oxidant. According to the procedure reported by Koppes et al., the minimum amount of hydrazine hydrate was used therefore, azo compounds were only reduced to hydrazo compounds and the further reduction has not been occurred. We thought that the mechanism of reduction is unclear.



**SCHEME 8.** The proposed mechanism of the reduction of azo compounds with hydrazine hydrate.

### 3. OTHER REDUCTIONS WITH HYDRAZINE HYDRATE

Hydrazine hydrate has been used in the reduction of ketones. The Wolff-Kishner reduction is usually carried out by heating the ketone with hydrazine and alkali. In this procedure, hydrazone is not isolated. The mechanism of reduction involves base-catalyzed tautomerization of the hydrazone followed by loss of nitrogen. Dwivedi et al. (35) used phenyl cyclopropyl ketones as starting material for the reduction of ketones to methylene groups (Scheme 9).

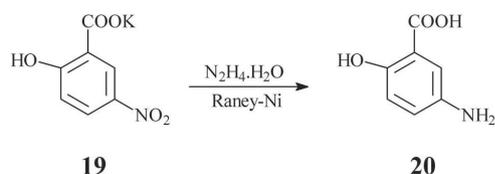


**SCHEME 9.** The reduction of cyclopropylketones with hydrazine hydrate (Wolff-Kishner reduction)

Many amines have been prepared by the reduction of corresponding nitro compounds. A large number of reducing agents have been used for the reduction of nitro group. One of the good reducing agents is hydrazine hydrate that has been used

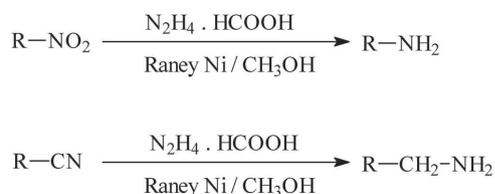
in the presence of heterogeneous catalyst. Vass et al. (36) described solvent-free reduction of aromatic nitro compounds with hydrazine hydrate supported on solid material, alumina, in the presence of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  under microwave irradiation. Kumbhar et al. (37) reduced aromatic nitro compounds with hydrazine hydrate in the presence of oxide-MgO catalyst prepared from a Mg-Fe hydrotalcite precursor. It is reported that the catalyst was found to be highly active and selective.

Breviglieri et al. (38) reported the reduction of 5-nitrosalicylic acid potassium salt **19** to 5-aminosalicylic acid **20** with hydrazine hydrate in the presence of Raney nickel that has been used as a catalyst with hydrogen donor hydrazine.



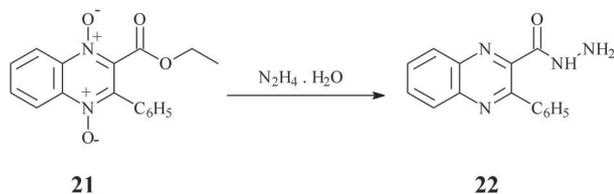
**FIGURE 2.** The reduction of 5-nitrosalicylic acid potassium salt to 5-aminosalicylic acid with hydrazine hydrate

Gowda S. and Gowda D.C. (39) reported the reduction of aliphatic and aromatic nitro compounds and nitriles to corresponding amines in the presence of Raney nickel and hydrazinium monoformate. The application of hydrazinium monohydrate/Raney nickel is a new system of the reduction of nitro and nitrile groups (Scheme 10). Majid et al. (40) reported the reduction of an intermediate nitroso compound to amine by hydrazine hydrate without a catalyst.



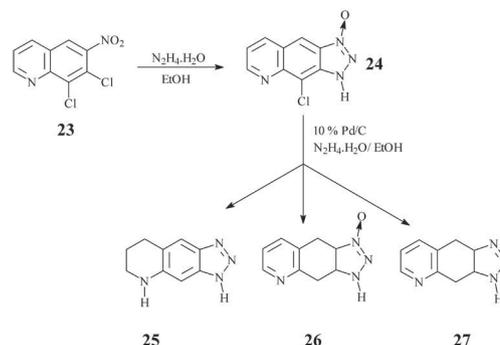
**SCHEME 10.** The reduction of nitro and nitrile groups.

Lima et al. (41) reported the reduction of ethyl 3-phenylquinoxaline-2-carboxylate 1,4-di-N-oxide **21** to 3-phenyl-2-quinoxalinecarbohydrazide **22** with hydrazine hydrate.



**FIGURE 3.** The reduction of ethyl 3-phenylquinoxaline-2-carboxylate 1,4-di-N-oxide.

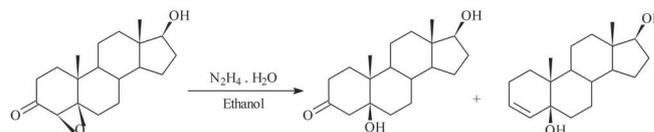
Carta and Paglietti (42) reported the synthesis of compound **24** starting from **23** in the presence of excess hydrazine hydrate in ethanol. In the further reduction of **24**, while the chlorine and N-oxide reduced by hydrazine hydrate and Pd/C catalyst, pyridine and benzene rings of quinoxaline reduced to dihydro or tetrahydro products **25-27**.



**SCHEME 11.** The reduction of chlorine and N-oxide by hydrazine hydrate.

The reduction of carbon-carbon double bond is very important in organic synthesis to obtain new compounds. The reduction of double bond has also been carried out with hydrazine hydrate over a diimid ( $\text{HN}=\text{NH}$ ) intermediate (43). Rollas's method (26, 27) gave also the reduced azo products along with the reduced allyl group compound **9** and compound **14** (Scheme 5). In the presence of azo group or air oxygen, diimide has been produced from hydrazine hydrate. Therefore, allyl group is reduced to propyl group. However in the presence of small amount of hydrazine hydrate, the reduction of allyl group to propyl does not occur (Rollas's modified reduction procedure, unpublished data). The azo group was reduced to amines.

The reduction of  $\alpha,\beta$ -epoxy ketones to the corresponding  $\beta$ -hydroxy ketones is very important process in the structure elucidation of natural products. Salvador et al. (44) gained  $\beta$ -hydroxyketones by reductive cleavage of the steroidal epoxy ketones under mild conditions using hydrazine hydrate in ethanol (Scheme 12).



**SCHEME 12.** The reduction of  $\alpha,\beta$ -epoxy ketones to the corresponding  $\beta$ -hydroxy ketones.

#### 4. CONCLUSION

The reduction reactions performed by the use of hydrazine hydrate with or without a catalyst have been discussed here and versatile methods for the synthesis of aromatic or heteroaromatic primary amines has been instructed. The advantage of this proposed method is that primary amines can be prepared in good yields. Particularly, this review is focused on uncatalyzed reductive cleavage of azo compounds with hydrazine hydrate.

## Aromatic ve heteroaromatic bileşiklerin hidrazin hidratla redüksiyonu

**ÖZET:** Azo bileşikleri hidrazin hidratla katalizörsüz veya çeşitli katalizörler varlığında indirgenmektedir. Bu redüksiyon, azo işlevli grubu içeren bileşiklerden yeni aminlerin elde edilmesi için uygulanabilir bir yöntemdir. Derleme esas olarak aromatik veya heteroaromatik azo bileşiklerinin hidrazin hidratla indirgenmesini kapsamaktadır.

**ANAHTAR KELİMELER:** indirgenme, azo bileşikleri, katalizörsüz redüksiyon, hidrazin hidrat.

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