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REDUCTION OF AROMATIC AZO-,AZOXY- AND NITRO-COMPOUNDS BY ULTRASONICALLY ACTIVATED NICKEL

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Abstract: Substituted hydrazobenzenes were obtained in excellent yields from reduction of the corresponding azo- or azoxy- compounds by hydrazine hydrate under the catalysis of ultrasonically activated nickel (UAN). Reduction of nitroarenes by UAN produced azoxyarenes as the major products.

Ultrasonically activated nickel (UAN), which is obtained by reduction of anhydrous nickelous chloride with ultrasonically dispersed potassium (UDP), is a new versatile reactive reagent for organic reduction, catalysis[1a] and coupling[1b] reactions. Recently we have found that it could also be prepared simply by irradiating ultrasonically the mixture of potassium and anhydrous nickelous chloride in toluene for 30 min. Herein we wish to report its new applications in

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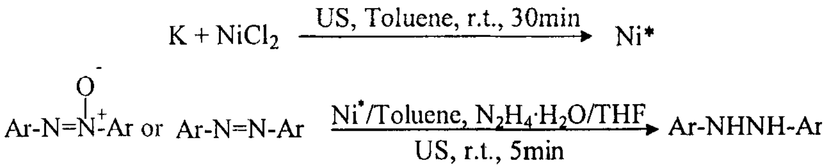
the preparations of hydrazobenzenes from azo- or azoxy arenes and azoxyarenes from nitroarenes.

Conversion of azo- and azoxy- arenes into the corresponding hydrazobenzenes could be carried out with a variety of reducing reagents[2] such as sodium borohydride and iodine system[2b], sodium dithionite with dioctylviologen[2c], aryltellurol[2d] or tributyltin hydride[2e] system or lithium aluminium hydride[2f, 2g]. Some of them, however, gave very poor yields or required strict conditions or expensive materials. In the present research, the azo or azoxy arenes were reduced to hydrazobenzenes by hydrazine hydrate in the presence of Ultrasonically activated nickel catalyst in nearly quantitative yields (**Scheme 1**). The mild reaction condition and high yields (**Table 1**) proved that UAN is an efficient promoter for the hydrogen transfer process. The reductions of 2-chloroazo- or azoxy- derivatives gave, however, rather poor yields. This implies that steric effect plays an important role in the reductions.

Scheme 1



$$K + NiCl_2 \xrightarrow{\text{US, Toluene, r.t., 30min}} Ni^*$$

$$\text{Ar-N=}\overset{\overset{O^-}{|}}{N^+}\text{-Ar or Ar-N=N-Ar} \xrightarrow[\text{US, r.t., 5min}]{\text{Ni}^*\text{/Toluene, } N_2H_4 \cdot H_2O\text{/THF}} \text{Ar-NHNH-Ar}$$

2(a-e) **3(a,b)** **4(a-e)**

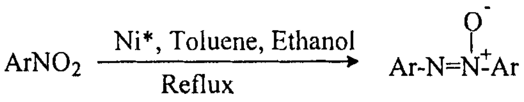
Although there are a great number of methods[3] available for the direct preparation of azoxy compounds from nitroarenes, no nickel has ever been used

Table 1. Hydrogenation of azo and azoxy arenes catalyzed by Ni*

Entry	Ar	2 or 3	Products	Yield (%)
1	C_6H_5	2a	4a	81.8
2	$4\text{-}ClC_6H_4$	2b	4b	93.6
3	$2\text{-}ClC_6H_4$	2c	4c	39.8
4	$4\text{-}BrC_6H_4$	2d	4d	98.2
5	$4\text{-}CH_3C_6H_4$	2e	4e	94.3
6	C_6H_5	3a	4a	90.3
7	$4\text{-}ClC_6H_4$	3b	4b	93.3

as reductant in the reactions. We found, however, Ultrasonically activated nickel that is not generally used as a reductant could reduce nitroarenes to azoxyarenes (**Scheme 2**). The yields are moderated (**Table 2**). Chlorine, bromine or iodine in the substrate is retained. Reductions of some nitroarenes such as alkylnitrobenzene or 4-nitroanisole gave, however, very complicated mixtures.

Scheme 2



1(b,d,f,g) **2(b,d,f,g)**

Table 2. The reduction of nitroarenes by Ni*

Entry	Ar	Nitroarenes	Products	Reaction Time (min)	Yield (%)
1	$4\text{-}ClC_6H_4$	1b	2b	60	59.0
2	$4\text{-}BrC_6H_4$	1d	2d	90	61.8
3	$4\text{-}IC_6H_4$	1f	2f	210	34.6
4	$3\text{-}ClC_6H_4$	1g	2g, 3c*	90	52.4 20.0

* 3,3'-dichlorazobenzene

In conclusion, UAN is an efficient reductant for both the reductions of azo and azoxy arenes to hydrazobenzenes and the reductions of nitroarenes to azoxyarenes. The UAN reagent has a wide of potential applications in organic reductive reactions.

EXPERIMENTAL SECTION:

IR spectra were taken on a IDP-440 spectrometer. ^{1}HNMR were recorded on a Jeol PMX-60SI spectrometer and chemical shifts were referred to TMS in $CDCl_3$. Ultrasonic was generated by a KQ-50 ultrasonic cleaner. Melting points were uncorrected. Toluene was distilled from sodium-benzophenone prior to use. Azo and azoxy compounds were commercial products or prepared according to known literature procedure[4].

Preparation of hydroazobenzene (4a) : General procedure for 4a-4e:

A suspension of potassium (0.23g, 6mmol) and anhydrous nickelous chloride (0.39g, 3mmol) in anhydrous toluene (10mL) was subjected to ultrasonic irradiation at room temperature under nitrogen for 30min until the black slurry metal was resulted.. Then azoxybenzene (0.50g, 2.5mmol) and hydrazine hydrate (85%, 0.6g, 10mmol) in 20mL THF were added. After stirred for 5min under ultrasonic the mixture was diluted with water (80mL) and extracted with ether (3 × 20mL). The organic layer were dried with anhydrous Na_2SO_4 and the solvents were removed under reduced pressure to give **4a** (0.38g, 81.8%). All operations should be carried as quickly as possible and then the product was pure enough for identification.

4a, hydroazobenzene: mp. 126-128°C (lit.[5] 126-127°C) ; IR: ν_{N-H}, 3300cm^{-1}; ^{1}H-NMR: δ4.6-5.6 (br.,2H) , δ6.7-7.7 (m,10H)

4b, 4,4'-dichlorhydroazobenzene: mp. 124-126°C (lit.[5] 120-122 °C) ; IR: ν_{N-H}, 3300cm^{-1}; ^{1}H-NMR: δ4.6-5.5 (br.,2H) , δ6.4-7.3 (m,8H)

4c, 2,2'-dichlorhydroazobenzene: mp. 84.5-87°C (lit.[5] 85-86°C) ; IR: ν_{N-H}, 3350cm^{-1}; ^{1}H-NMR: δ5.5-6.5 (br.,2H) , δ6.6-7.4 (m,8H)

4d, 4,4'-dibromohydroazobenzene: mp. 128-130°C (lit.[2f] 130-131°C) ; IR: ν_{N-H}, 3340cm^{-1}; ^{1}H-NMR: δ4.5-5.5 (br.,2H) , δ6.5-7.3 (m,8H)

4e, 4,4'-dimethylhydroazobenzene: mp. 127.5-130°C (lit.[5] 124-125°C) ; IR: ν_{N-H}, 3360cm^{-1}; ^{1}H-NMR: δ2.2 (s,6H) , δ3.8-4.6 (br.,2H) , δ6.5-7.1 (m,8H)

Preparation of 4,4'-dibromoazoxybenzene (2d) : General procedure for 2b, 2f and 2g

UAN (6mmol) was prepared with the same procedure as above. The reaction was quenched with 10mL ethanol. Then 4-bromonitrobenzene (0.4g, 2mmol) was added and the mixture was refluxed for 90 min. After cooling the reaction suspension was diluted with water (20mL) and acidified to pH<2 with 6M HCl. The resulted solution was extracted with ether (3 × 20mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvents were evaporated under vacuum. Then the crude product was chromatographed on a column of silica gel to give pure 2d, 0.22g Yield 61.8%.

2b, 4,4'-dichlorazoxybenzene: mp. 149-151°C (lit.[3d] 154-156°C) ; IR: ν_{Ph} 1580, 1480cm^{-1}, $\nu_{N=NO}$, 1410, 1330cm^{-1}; ^{1}H-NMR: δ7.3-8.5 (m,8H)

2d, 4,4'-dibromoazoxybenzene: mp. 171-173°C (lit.[3d] 173-175°C) ; IR: ν_{Ph} 1580, 1470cm^{-1}, $\nu_{N=NO}$, 1400, 1320cm^{-1}; ^{1}H-NMR: δ7.5-8.3 (m,8H)

2f, 4,4'-diIodoazoxybenzene: mp.192-194°C (lit. 208-210°C [3d], 199-200°C [6a]); IR: ν_{Ph} 1570, 1460cm^{-1}, $\nu_{N=NO}$, 1390, 1320cm^{-1}; ^{1}H-NMR: δ7.7-8.3 (m,8H)

2g, 3,3'-dichlorazoxybenzene: mp. 97-98°C (lit.[3d] 96-97°C) ; IR: ν_{Ph} 1550, 1470cm^{-1}, $\nu_{N=NO}$, 1420, 1300cm^{-1}; ^{1}H-NMR: δ7.3-8.5 (m,8H)

3c, 3,3'-dichlorazobenzene: mp. 102-104°C (lit.[6b] 103-104°C) ; IR: ν_{Ph} 1590, 1570, 1460cm^{-1}, $\nu_{N=N}$ Not observable for the symmetry; ^{1}H-NMR: δ7.4-8.0 (m,8H)

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