



Reduction of Aromatic Nitrocompounds by Sodium Borohydride in Methanol in the Presence of Sodium Methoxide

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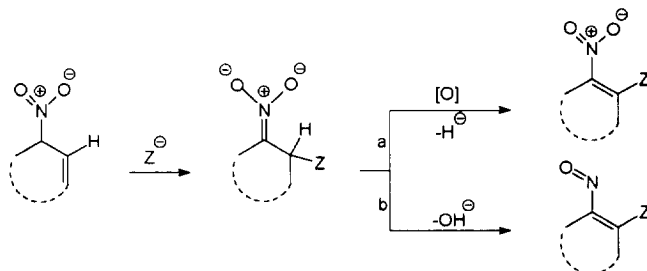
Abstract: The paper presents the results of the reduction of 4-nitroimidazoles, 4-nitropyrazoles and 3-nitropyridines by sodium borohydride or sodium borodeuteride in methanol in the presence of sodium methoxide. 1-Substituted 4-nitroimidazoles yield oximes of 4-imidazolidinones, the nitropyrazoles and nitropyridines yield respective azoxy compounds. The reaction mechanism proposed in the work makes allowances for catalytic effect of the system methanol-methoxide.
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The 1980s and 1990s brought about a considerable progress in the development of investigation and application potentials of the reactions of nitroarenes and nitroheteroarenes with nucleophiles. Within this time period, the reaction of vicarious nucleophilic substitution of hydrogen atom with alkyl, amino or hydroxy groups¹ had been worked out and investigated in detail. Also, a lot of attention had been paid to the process of electron transfer in the reactions of aromatic nitrocompounds with alkoxide anions². New reactions of ring transformations in nitroheteroarenes subjected to the attack of nucleophiles had been worked out too³. High reduction potential of nitroarenes results in the fact, that the reactions of nucleophilic substitution of hydrogen atom at the ring, as well as other nucleophilic reactions are quite frequently accompanied by the reduction of the nitro group.

As shown by the theory and ample experimental data, nitroarenes are attacked by nucleophiles, usually in the positions "ortho" and "para" to the nitro group, with the formation of respective Meisenheimer complexes^{3,4}. Relative rates of their formation and relative energies of the complexes depend both on the structure of reagents and on conditions of the experiments. The stabilization of the Meisenheimer complex may be affected, among others, by the intermolecular (a), or intramolecular (b) redox reactions, which, for the "ortho" complexes, are presented in Scheme 1.

The function of oxidizer in the intermolecular process may be assumed, among others, by the starting nitrocompound. Most of the reactions of aromatic nitrocompounds with nucleophiles are carried out in the

presence of strong bases (principally sodium or potassium alkoxides) in solvents such as alcohols or dimethylsulfoxide.



Scheme 1

The solvent has sometimes a dominant effect on the structure of final products of the reaction^{2,3}.

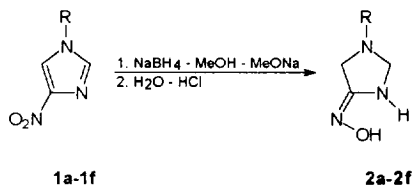
Sodium borohydride is, among others, the source of hydride anion, the simplest nucleophilic reagent. As the reagent in methanol solution, in the presence of sodium methoxide, sodium borohydride is relatively stable. It is very surprising that, according to our knowledge, no extensive investigations on the behaviour of aromatic nitrocompounds in the presence of this system have been undertaken recently. The present work aims to fill in this gap. 4-Nitro-1-phenylimidazole, 4-nitro-1-phenylpyrazole and a methoxy derivative of 3-nitropyridine have been selected by us as basic model systems. The work aims also to explain mechanisms of the reaction.

It is known, that sodium borohydride in methanol without of sodium methoxide⁵, and also sodium methoxide in methanol in the absence of sodium borohydride^{6,7} are capable of reducing some nitrocompounds. Due to the above, we have decided to investigate the behaviour of selected nitrocompounds also under these conditions.

RESULTS

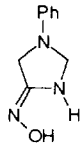
Introductory attempts to reduce 4-nitro-1-phenylimidazole (1c).

4-Nitro-1-phenylimidazole was tentatively subjected to hydride reduction under different conditions; the obtained results are presented in Table 1. The final product of reduction of 4-nitro-1-phenylimidazole (**1c**) by the system NaBH₄ - MeOH - MeONa was identified as (*Z*)-oxime of 1-phenyl-4-imidazolidinone (**2c**, R=Ph, scheme 2); the results were based on the elemental and spectroscopic data analysis, and were confirmed by the X-ray analysis of a single crystal⁸.



Scheme 2

Table 1. Reaction of 4-Nitro-1-phenylimidazole (1c) with Borohydrides in the Methanol Solution

Reducing system	temp.	time	product	yield %
NaBH ₄ - MeOH	25°C	120 h	low conversion, no stable products	
MeOH - MeONa	25°C	24 h	no reaction	
MeOH - MeONa	65°C	3 h	Ph-NH-COOCH ₃ + others*	
NaBH ₄ - MeOH - MeONa	25°C	3 h		94%
NaBH ₃ CN - MeOH - MeONa	25°C	72 h	aniline, N-methylaniline, N,N-dimethylaniline and others	
NaBH ₃ CN - MeOH-H ₂ O, pH=3	25°C	24 h	no reaction	

*)The reaction proceeded only in the solution whereof the sodium methoxide concentration was four times higher than in the standard solution. In the standard solution (1.2g Na in 50 ccm methanol - 1.04 mol/dm³), the reaction did not proceed.

Replacing the solution MeOH - MeONa with other alcohol-sodium alkoxide solutions resulted in the decrease of the oxime yield, with aniline being the main product (Table 2). In view of these results, further reduction attempts using NaBH₄ were carried out always in methanol in the presence of sodium methoxide.

Table 2. Reaction of 4-Nitro-1-phenylimidazole (1c) with the Systems NaBH₄-R'OH -R'ONa at 25°C.

R'	Products		
	oxime 2	aniline	others
CH ₃	94 %	traces	-
CH ₃ CH ₂	6 %	> 90 %	-
(CH ₃) ₂ CH	2 %	> 90 %	-
(CH ₃) ₃ C	-	ca. 20 %	ca. 80 %

Reduction of 4-nitroimidazoles (1a-h).

The attempts to reduce 1-*H*-4(5)-nitroimidazole, yielded no imidazole derivatives. A substituent at the position 1 turned out to be indispensable for the reaction to be successful. In the case of 1-substituted 4-nitroimidazoles **1a-f** having no other substituents at the ring carbon atoms, we obtained only the oximes of respectively 1-substituted 4-imidazolidinones **2 a-f** (Scheme 2, Table 3).

The introduction of methyl group into the position 2 of 4-nitroimidazoles resulted in the formation of mixtures of oximes. For example, the reduction of 2-methyl-4-nitro-1-phenylimidazole (**1g**) gave a mixture of the expected oxime **2g** with 2-methyl-5-methoxy-1-phenyl-4-oximinoimidazoline (**3g**). The methyl group in 5-methyl-4-nitro-1-phenylimidazole (**1h**) in the presence of MeONa (and also of other strong bases) undergoes deprotonation, and the compound decomposes both in the presence and in the absence of NaBH₄. In ethylene glycol, NaBH₄ does not react with **1h**, even at increased temperature. The unchanged starting

material is regained. Under similar conditions, **1c** is reduced to **2c**, though the maximum yield of the product is lower (about 60%) as compared with reduction by the system $\text{NaBH}_4\text{-MeOH-MeONa}$.

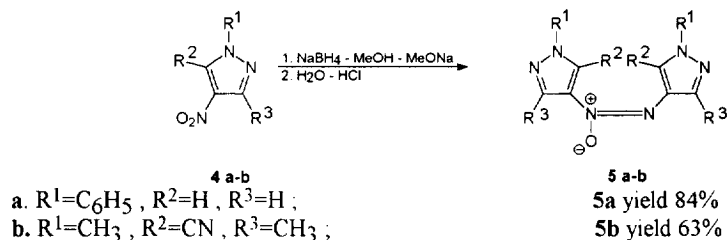
Table 3. Reduction of 1-Substituted 4-Nitroimidazoles (**1a-f**) by the System $\text{NaBH}_4\text{-MeOH-MeONa}$ at 25°C

Starting nitroimidazole		Product	
No. of compound	R	No. of compound	oxime yield (%)
1a	$\text{CH}_3\text{-}$	2a	30 *
1b	$\text{C}_6\text{H}_5\text{-CH}_2\text{-}$	2b	50
1c	$\text{C}_6\text{H}_5\text{-}$	2c	94
1d	$p\text{-CH}_3\text{-C}_6\text{H}_4\text{-}$	2d	73
1e	$p\text{-Cl-C}_6\text{H}_4\text{-}$	2e	70
1f	1'-phenyl-4'-imidazolyl	2f	54

*) at 0°C; product unstable at higher temperatures

Reduction of 4-nitropyrazoles (**4a-b**).

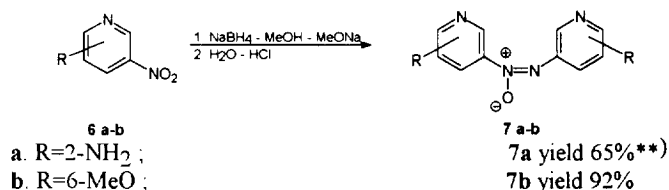
4-Nitro-1-phenylpyrazole (**4a**) underwent hydride reduction at 25°C, only in the presence of the $\text{NaBH}_4\text{-MeOH-MeONa}$ system. In this case, the only product isolated after work-up was 4,4'-azoxy-1,1'-diphenylpyrazole (**5a**). Also, the reduction of 5-cyano-1,3-dimethyl-4-nitropyrazole (**4b**) yielded only a respective azoxycompound **5b** (Scheme 3). The cyano group remained unchanged in the reaction.



Scheme 3

Reduction of 3-nitropyridines^{*)} (**6a-b**) and azine *N*-oxides.

In the absence of MeONa at temp. 25°C, 3-nitropyridines **6a-b** were not reduced by NaBH_4 . In the presence of MeONa, respective azoxycompounds **7a-b** were formed (Scheme 4), despite the fact that electron-donating substituents were present at the positions 2 or 6 of the substrates. The reactions required long time periods.



Scheme 4

*)Both compounds **6a** (2-amino-3-nitropyridine) and **6b** (2-methoxy-5-nitropyridine) are treated here as 3-nitropyridine derivatives to emphasize relative positions of the ring nitrogen atom and the nitro group. **) The yield of crude **7a** (unstable)

The system $\text{NaBH}_4\text{-MeOH-MeONa}$ also reduced the N-oxides of 4-picoline and quinoline, to 4-picoline and quinoline respectively. These reactions also occurred very slowly. The reduction of 4-nitropyridine N-oxide proceeded much faster, but in this case, a complex mixture of unidentified products was formed.

Reduction of nitroarenes.

Nitrobenzene at 25°C is reduced neither by NaBH_4 nor MeONa in methanol, nor by their mixture. At the boiling point of concentrated nitrobenzene solutions in methanol, in the presence of MeONa , azoxybenzene is formed with moderate yield.

1,3-Dinitrobenzene reduced by the $\text{NaBH}_4\text{-MeOH-MeONa}$ system at 25°C gives 3,3'-dinitroazoxybenzene with good yield. Under the same conditions, 1,4-dinitrobenzene turns into 4-nitroanisole that does not undergo further transformations. Both 1-nitronaphthalene and 2-nitronaphthalene at 25°C are reduced only by the system $\text{NaBH}_4\text{-MeOH-MeONa}$. 1-Nitronaphthalene yields the mixture of 1,1'-azonaphthalene (60%), 1-aminonaphthalene (14%) and naphthalene (1%); lowering the temperature to 0°C did not affect the structure and proportions of the products. 2-Nitronaphthalene yielded the mixture of 2,2'-azoxynaphthalene (54%) and 2,2'-hydrazonaphthalene (35%). Neither 9-nitroanthracene nor 1-nitropyrene have been changed at 25°C .

Reduction of 4-nitro-1-phenylimidazole (1c) and 4-nitro-1-phenylpyrazole (4a) by NaBD_4 in the presence of MeONa in MeOH at 25°C .

The reduction of **1c** by NaBD_4 yields the oxime **2c** partially deuterated at the heterocyclic ring. The signal of 2-methylene group in the ^1H NMR spectrum of this product occurs as a singlet at $\delta=5.50$ ppm, with the relative intensity corresponding to one proton; the signal of 5-methylene group occurs also as a singlet (slightly widened) at $\delta=3.84$ ppm, with the intensity corresponding approximately to a half of the proton.

The reduction of **1c** carried out by the $\text{NaBD}_4\text{-MeOD-MeONa}$ system with consecutive acidification of the mixture with the DCl solution in D_2O decreases the signal intensity of $=\text{NOH}$ and $-\text{NH}$ groups, practically not influencing relative signal intensities of the methylene groups and phenyl substituent, as compared with the reduction in MeOH . No exchange of hydrogen by deuterium in the methylene groups of **2c** affected by MeOD-MeONa at 25°C has been observed.

The reduction of 4-nitro-1-phenylpyrazole (**4a**) by the $\text{NaBD}_4\text{-MeOH-MeONa}$ system at 25°C leads to the azoxycompound **5a** partially deuterated in both pyrazole rings. In the ^1H NMR spectrum of the product, all signals of pyrazole protons occur as singlets having the following chemical shifts: δ [ppm] = 8.36 (3-H), 8.45 (3'-H), 9.30 (5-H) and 9.35 (5'-H). The intensities of signals at $\delta=9.30$ and 9.35 ppm vary, and they are much weaker than in the product obtained by the reduction of **4a** using NaBH_4 . The signal at $\delta=9.30$ ppm corresponds approximately to a half of a proton; the signal at $\delta=9.35$ ppm corresponds approximately to a third of a proton (as compared to the intensity of ten protons of two phenyl substituents).

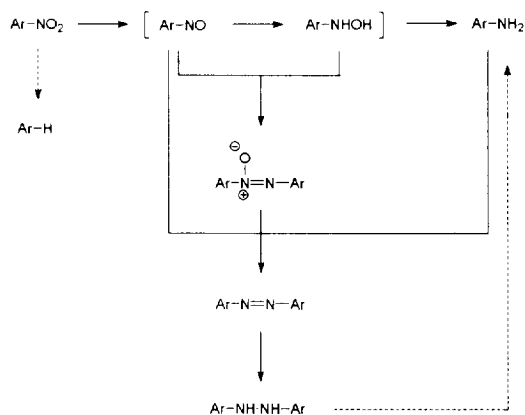
Reduction of 3-nitropyridine derivative 6b by the $\text{NaBD}_4\text{-MeOH-MeONa}$ system at 25°C .

The reduction took about 7 days and led to the acquisition of azoxypyridine **7b** deuterated in over 80% at the positions 2 and 2'. Eight signals grouped into four pairs can be observed in the ^1H NMR spectrum of the non-deuterated compound **7b**. One pair stands for the signals of methoxy groups, and the remaining three

pairs stand for the signals of pyridine protons. The spectrum of deuterated product is more simple. The signals of protons 2 and 2' ($\delta=9.06$ and 9.04 ppm) are very weak, and the signals of protons 4 and 4' are being simplified from doublets of doublets ($J_d = 9\text{Hz}$ and 3Hz in the spectrum of **7b** having no deuterium) to doublets ($J_d = 9\text{Hz}$). The other signals remain practically unchanged.

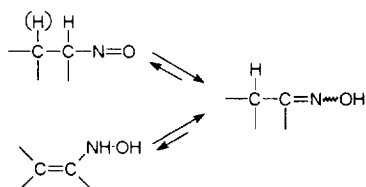
DISCUSSION OF THE RESULTS

Basing on a generally accepted viewpoint supported by ample experimental data gathered in the course of several investigations, the reduction of aromatic nitrocompounds in the presence of bases (hydroxides, alkoxides) may be generally presented by the scheme 5. Scheme 5 may be complemented by products of the reduction of the aromatic ring⁹, including also oximes of cyclic carbonyl compounds. Prior to these investigations, the only known example of the reduction of an aromatic nitrocompound to oxime had been the reduction of 2-methyl-4-nitro-1-phenoxy-carbonylimidazole with hydrogen¹⁰.



Scheme 5

It is worth while indicating that oximes may be normally formed both from nitroalkanes containing hydrogen atom at the α -carbon atom, and from α,β -unsaturated hydroxylamines, due to tautomeric interconversions (Scheme 6).



Scheme 6

The structure of final (isolated) reduction products of nitrocompounds, as well as their proportions depend on relative rates of particular reactions presented in the schemes 5 and 6.

The multidirectional course of the reduction of nitrocompounds makes it difficult to investigate in detail mechanisms of this process. In order to explain the mechanism of hydride reduction of aromatic nitrocompounds in MeOH in the presence of MeONa, the present work presents the investigations on the distribution of deuterium in the products obtained as a result of the reduction of 4-nitro-1-phenylimidazole, 4-nitro-1-phenylpyrazole and 6-methoxy-3-nitropyridine by means of NaBD₄. High yields of the products, their different structures and very clear ¹H NMR spectra made it possible to come to the following conclusions. In the all investigated cases, the reactions begin with nucleophilic attack of deuterium anion on carbon atoms in the positions 5 of the imidazole and pyrazole derivatives, or in the positions 2 of the 3-nitropyridine derivative **6b**. The Meisenheimer complexes I afford the mixture of respective nitrosoimidazoles, nitrosopyrazoles, nitrosopyridine and their 5 (imidazole, pyrazole) or 2 (pyridine) deuterated derivatives. The next attack of deuterium anion takes place again on the position 5 (or 2), with the formation of reduced Meisenheimer complexes II. The subsequent course of the reaction is different for nitro derivatives of imidazoles and different for pyrazoles or the pyridine. In the imidazole Meisenheimer complex, the endocyclic double bond C₍₂₎=N₍₃₎ is reduced, thereby giving of 4-oximinoimidazolidinones (Scheme 7). The pyrazole (and pyridine) Meisenheimer complex II undergoes aromatization, due to the migration of a hydrogen or deuterium atom to the exocyclic nitrogen atom, and the this formed anion of hydroxylamine derivative undergoes condensation with nitrosopyrazole (nitrosopyridine) or its deuterated derivative to azoxycompounds (Scheme 8).

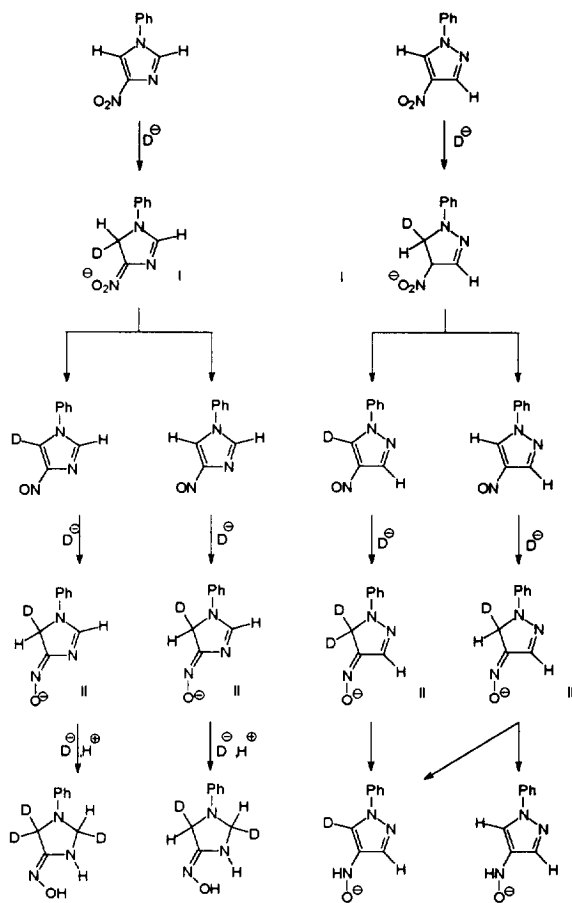
According to the scheme 7, deuterium atoms in the reduction product of 4-nitro-1-phenylimidazole are at the positions 2 and 5 of the oximes being formed, whereas in the reduction product of 4-nitro-1-phenylpyrazole, they are exclusively at the carbon atoms 5 and 5' of the pyrazole rings (Schemes 7 and 8).

The integration of signals in ¹H NMR spectrum of the partially deuterated products indicates that there is no primary isotope effect of the deuterium observed in the nitroazoles reduction processes. The occurrence of the isotope effect would have led to higher content of deuterium at the carbon atom 5 in 4-oximino-1-phenylimidazolidine and at the carbon atoms 5 and 5' in 4,4'-azoxy-1,1'-diphenylpyrazole, as compared to the content observed in the experiments. Also no couplings between geminal hydrogen and deuterium atoms in the spectrum of oxime **2c** have been observed, which indicates that geminal coupling constants J_{H,D} are in this case close to zero.

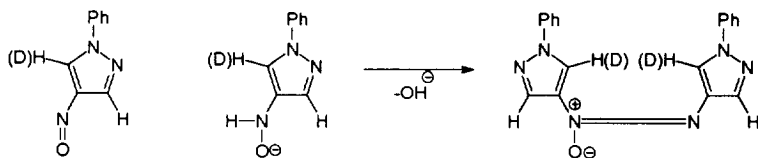
The situation is slightly different in the reduction of **6b** with NaBD₄. In the azoxy pyridine **7b**, being the product of this reaction, practically a full exchange of hydrogen into deuterium atoms at the positions 2 and 2' has been observed. This result may be explained by assuming high selectivity of the attack of deuterium anion on the carbon atom in the position 2 of the starting compound **6b** (and the intermediated nitroso derivative), and by assuming the occurrence of high (k_H : k_D >5) primary isotope effect in further stages of the reaction. The indispensably long time of the reaction (about 7 days at 25°C) justifies the acceptance of the above explanation, assuming that the reduction steps of **6b** to **7b** are analogous to the reduction steps of **4a** to **5a**.

As it has been presented in the discussion of the results, NaBH₄ in MeOH in the absence of MeONa at 25°C reduce neither 4-nitroimidazoles nor 4-nitropyrzoles, what indicates the participation of sodium methoxide in the reduction process. The most probable mechanism for transforming the Meisenheimer complex I to the nitrosocompound has been shown in the scheme 9, on the example of the reduction of 4-nitro-1-phenylimidazole. We assume in the suggested reaction mechanism, that apart from hydride anion,

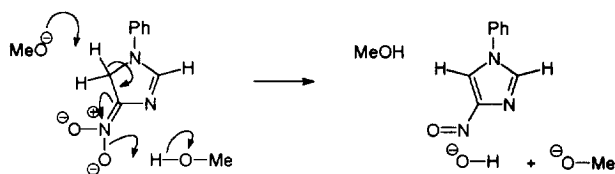
both methoxide anion and methanol take part in the reduction process (Scheme 9), what agrees not only with the results of nitrocompounds reduction discussed in the present work, but also with the formerly observed effect of the solvent on the reaction course of 4-nitroimidazoles with nucleophiles³.



Scheme 7



Scheme 8



Scheme 9

CONCLUSIONS

The reduction of nitrocompounds by the $\text{NaBH}_4\text{-MeOH-MeONa}$ system probably occurs in a similar way, independently of whether the starting nitrocompound is aromatic or heteroaromatic. The reaction starts with the nucleophilic attack of hydride anion on the carbon atom β (or δ in some cases) with respect to the nitro group. The next, key step of the reduction consists in the 1,3 elimination (from Meisenheimer complex) of the hydrogen atom linked to the carbon atom β (or δ), and of one of oxygen atoms of the nitro group. The elimination occurs under the catalytic influence of methoxide anion and methanol. In the formed nitroso compound, the direct attack of the hydride anion on the nitroso nitrogen atom is not observed; the hydride anion again attacks the carbon atom β (or δ) of the aromatic ring. The differences in the behaviour of addition products of hydride anion to nitroso derivatives of imidazoles and pyrazoles or pyridines (Meisenheimer complexes II, Scheme 8) are not quite clear. One of the possible explanations lies in the differences in aromaticity (resonance energies) of the imidazole and pyrazole or pyridine rings, the latter two being more aromatic. Unfortunately, respective data are available only for the unsubstituted compounds and some of their simple derivatives. The problem will be investigated later including quantum chemical calculations.

EXPERIMENTAL

1-Aryl-4-nitro- and 1-aryl-2-methyl-4-nitroimidazoles (4-nitro-1-phenylimidazole (**1c**, m.p. 201-203°C, lit. 200-202°C); 1-(4'-methylphenyl)-4-nitroimidazole (**1d**, m.p. 169-170°C, lit. 171-173°C), 1-(4'-chlorophenyl)-4-nitroimidazole (**1e**, m.p. 199-200°C, lit. 200-202°C), 2-methyl-4-nitro-1-phenylimidazole (**1g**, m.p. 141-143°C, lit. 139-140°C) were obtained in the reaction of 1,4-dinitro- or 2-methyl-1,4-dinitroimidazole with respective aromatic amines¹¹. 1-Methyl-4-nitroimidazole (**1a**, m.p. 125-126°C, lit. 126-127°C) was obtained by the alkylation of sodium salt of 4(5)-nitroimidazole with dimethyl sulphate¹². 1-Benzyl-4-nitroimidazole (**1b**, m.p. 73-74°C lit 76°C) was prepared by the alkylation of sodium salt of 4(5)-nitroimidazole with benzyl bromide¹³. 4-Nitro-1-phenylpyrazole (**4a**, m.p. 129-130°C, lit. 126-127°C) was obtained by the condensation of phenylhydrazine hydrochloride with sodium salt of 2-nitro-1,3-propanal¹⁴. The synthesis of 4-nitro-1-(1'-phenyl-4'-imidazolyl)imidazole (**1f**) will be presented by us elsewhere. The

structures and purity of the synthesized starting materials were confirmed by spectroscopic methods and TLC analyses. The other substrates were commercial compounds. ^1H NMR spectra were measured on the spectrometer Tesla BS-587 (80 MHz) or Varian XL-300, using TMS as an internal standard. Mass spectra were recorded by means of a Shimadzu GCMS QP-2000 or Finnigan MAT 95. The properties of the obtained products are presented below. The melting points given in the work were not corrected.

Reduction of nitrocompounds by the system $\text{NaBH}_4\text{-MeOH-MeONa}$ (general procedure).

50ccm of methanol and 1.2 g of metallic sodium was introduced to the flask with stirring. After the sodium dissolved, 2 mmoles of a nitrocompound and 0.6g (15.9 mmol) of sodium borohydride were added to the solution. The reaction was carried out at 25°C until the substrate spot on TLC disappeared (from 1.5 h to 7 days, TLC benzene-ethyl acetate 4:1 or 3:2). The reaction mixtures were neutralized with concentrated hydrochloric acid until pH~7 (in the case of nitronaphthalene reduction until pH=4) and then they were condensed under reduced pressure at about 40°C. The remaining part was poured into 150 ccm of cold water. The precipitation was filtered off and recrystallized. When there was no precipitation, the solution was extracted with chloroform five times. The extract was dried over anhydrous magnesium sulphate and evaporated until dry under reduced pressure at about 40°C. The residue was recrystallized, separated chromatographically, or it was directly analyzed using GCMS and ^1H NMR methods.

1-Methyl-4-oximinoimidazolidine (2a).

Unstable oil, MS 70eV (m/e, %) M^+ = 115 (40.1), 114 (23.3), 98 (22.5), 58 (31.5), 57 (35.0), 44 (100.0), 42 (95.2), 30 (36.5), 28 (30.6), 17 (33.9), 16 (48.6).

1-Benzyl-4-oximinoimidazolidine (2b).

M.p. 124-125°C (dichloroethane), ^1H NMR δ (ppm) (DMSO- d_6): 8.71 (s, 1H, OH), 7.39-7.21 (m, 5H, Ph), 6.54 (br s, 1H, NH), 3.87 (s, 2H, 4- CH_2), 3.67 (s, 2H, 2- CH_2), 3.17 (s, 2H, Ph- CH_2), MS 70eV (m/e, %): M^+ = 191 (4.8), 100 (23.7), 91 (100.0), 65 (22.2), 42 (39.7), 30 (16.3), 28 (15.0). Found: C 62.54, H 7.01, N 21.74; $\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}$ requires: C 62.81, H 6.85, N 21.97.

4-Oximino-1-phenylimidazolidine (2c).

M.p. 230°C dec. (methanol), ^1H NMR δ (ppm) (DMSO- d_6): 8.94 (s, 1H, OH), 7.31-6.38 (m, 6H, Ph+NH), 4.56 (s, 2H, 4- CH_2), 3.88 (s, 2H, 2- CH_2), MS 70eV (m/e, %): M^+ = 177.1 (100.00), 176.1 (20.63), 160.1 (12.96), 106.1 (95.15), 105.1 (38.15), 104.1 (23.01), 77 (27.18). Found: C 60.24, H 6.35, N 39.58; $\text{C}_9\text{H}_{11}\text{N}_3\text{O}$ requires: C 61.00, H 6.26, N 23.71.

1-(4'-Methylphenyl)-4-oximinoimidazolidine (2d).

M.p. 239°C dec. (methanol), ^1H NMR δ (ppm) (DMSO- d_6): 8.94 (s, 1H, OH), 7.19-6.38 (m, 5H, Ar + NH), 4.44 (s, 2H, 4- CH_2), 3.81 (s, 2H, 2- CH_2), 2.19 (s, 3H, CH_3), MS 70eV (m/e, %): M^+ = 191 (67.9), 174 (13.4), 146 (12.9), 120 (100.0), 119 (57.7), 118 (33.7), 91 (56.4), 77 (11.0), 65 (26.9), 51 (10.7). Found: C 62.59, H 6.82, N 22.09; $\text{C}_{10}\text{H}_{13}\text{N}_3\text{O}$ requires: C 62.81, H 6.85, N 21.97.

1-(4'-Chlorophenyl)-4-oximinoimidazolidine (2e).

M.p. 254°C dec. (methanol), ^1H NMR δ (ppm) (DMSO- d_6): 8.96 (s, 1H, OH), 7.33-6.50 (m, 4H, Ar), 7.04 (br s, 1H, NH), 4.58 (s, 2H, 4- CH_2), 3.87 (s, 2H, 2- CH_2), MS 70eV (m/e, %): M^+ = 213 (15.6), 211 (47.0), 166 (11.8), 142 (28.7), 141 (22.5), 140 (100.0), 139 (47.8), 138 (34.7), 127 (12.8), 113 (12.0), 111 (33.9),

77 (12.9), 75 (29.4), 55 (18.3), 42 (28.7), 30 (25.7), 28 (30.9). Found: C 50.79, H 4.82, N 19.87, C₉H₁₀N₃OCl requires: C 51.07, H 4.76, N 19.85.

4-Oximino-1-(1'-phenyl-4'-imidazolyl)imidazolidine (2f).

M.p. 183°C dec. (methanol), ¹H NMR δ (ppm) (DMSO-d₆): 8.93 (s, 1H, OH), 8.06 (s, 1H, 5'-CH), 7.65-7.28 (m, 5H, Ph), 7.00 (s, 1H, 2'-CH), 6.90 (br s, 1H, NH), 4.50 (s, 2H, CH₂), 3.78 (s, 2H, CH₂), MS 70eV (m/e, %): M⁺= 243 (33.7), 242 (39.4), 226 (19.0), 172 (70.1), 171 (28.9), 170 (20.7), 104 (86.4), 77 (100.0), 51 (45.1), 30 (20.4), 28 (41.4), 27 (32.5). Found: C 58.91, H 5.41, N 28.97; C₁₂H₁₃N₅O requires: C 59.25, H 5.39, N 28.79.

2-Methyl-4-oximino-1-phenylimidazolidine (2g).

M.p. 184-185°C (dichloroethane), ¹H NMR δ (ppm) (DMSO-d₆): 8.96 (s, 1H, OH), 7.31-6.52 (m, 6H, Ph+NH), 5.12 (q, 1H, J_d=7.1 Hz, Me-C-H), 3.91 (dd, 2H, J_d=14.3 Hz, CH₂), 1.25 (d, 3H, J_d=14.3 Hz, CH₃), MS 70eV (m/e, %): M⁺= 191 (28.6), 176 (45.3), 106 (100.0), 77 (74.6), 51 (39.9), 42 (31.5), 28 (39.2), 15 (20.2). Found: C 62.73, H 6.50, N 21.62; C₁₀H₁₃N₃O requires: C 62.81, H 6.85, 21.97.

2-Methyl-5-methoxy-4-oximino-1-phenylimidazoline (3g).

M.p. 141-143°C (dichloroethane, DMF), ¹H NMR δ (ppm) (DMSO-d₆): 2.08 i 2.09 (2 s, 3H, CH₃); 3.09 i 3.12 (2 s, 3H, CH₃O); 5.88 i 6.25 (2 s, 1H, CH); 7.40 (br s, 5H, C₆H₅); 10.23 i 10.30 (2 s, 1H, OH), MS 70eV (m/e, %): M⁺= 219 (12.8), 189 (39.2), 130 (20.3), 118 (85.7), 104 (35.8), 77 (100.0), 67 (21.8), 51 (51.2). Found: C 60.53, H 6.03, N 19.28; C₁₁H₁₃N₃O₂ requires: C 60.26, H 5.98, N 19.17.

4,4'-Azoxy-1,1'-diphenylpyrazole (5a).

M.p. 201-202°C (acetic acid), ¹H NMR δ (ppm) (DMSO-d₆): 9.32 (s, 1H, 5-CH), 9.25 (s, 1H, 5'-CH), 8.38 (s, 1H, 3-CH), 8.31 (s, 1H, 3'-CH), 8.00-7.78 (m, 5H, Ph), 7.55-7.30 (m, 5H, Ph'), MS 70eV (m/e, %): M⁺= 330 (54.3), 314 (8.5), 157 (17.6), 130 (100.0), 129 (15.7), 104 (25.6), 77 (63.4), 51 (31.1). Found: C 65.31, H 4.20, N 25.37, C₁₈H₁₄N₆O requires: C 65.45, H 4.27, N 25.44.

4,4'-Azoxy-5,5'-dicyano-3,3'-dimethylpyrazole (5b).

M.p. 248-249°C (methanol), ¹H NMR δ (ppm) (DMSO-d₆): 4.03 (s, 6H, N-CH₃), 2.33 (s, 6H, C-CH₃), MS 70eV (m/e, %): M⁺= 284 (13.2), 268 (6.2), 93 (14.9), 67 (35.6), 66 (25.7), 43 (25.4), 42 (100.0), 28 (11.2), 15 (46.4). Found: C 50.49, H 4.47, N 39.58; C₁₂H₁₂N₈O requires: C 50.70, H 4.25, N 39.42.

2,2'-Diamino-3,3'-azoxy pyridine (7a).

Redish solid unstable in organic solvents, all attempts to purify the compound or to record its NMR spectrum have failed; MS 70eV (m/e, %) M⁺= 230 (54.3), 124 (48.3), 107 (82.5), 94 (46.7), 93 (93.1), 80 (57.1), 66 (50.9), 53 (83.3), 43 (45.7), 39 (100.0), 28 (92.2), 27 (58.2).

5,5'-Azoxy-2,2'-dimethoxy pyridine (7b).

M.p. 133-134°C (methanol), ¹H NMR δ (ppm) (DMSO-d₆): 9.06 (d, 1H, J_d=3 Hz, 2-H), 9.04 (d, 1H, J_d=3 Hz, 2'-H), 8.59 (dd, 1H, J_d=3 Hz, 9 Hz, 4-H), 8.52 (dd, 1H, J_d=3 Hz, 9 Hz, 4'-H), 7.04 (d, 1H, J_d=9 Hz, 5-H), 7.01 (d, 1H, J_d=9 Hz, 5'-H), 3.97 (s, 3H, OCH₃), 3.94 (s, 3H, OCH₃'), MS 70eV (m/e, %): M⁺= 260 (21.0), 244 (8.8), 217 (14.9), 122 (18.0), 108 (48.2), 95 (18.5), 93 (18.7), 81 (20.3), 80 (100.0), 66 (14.4), 53 (16.7), 52 (31.0), 39 (22.1), Found: C 55.45, H 4.84, N 21.56; C₁₂H₁₂N₄O₃ requires: C 55.38, H 4.65, N 21.53.

Products of the reduction of nitroarenes.

The azoxy, azo, hydrazo or amino products were characterized by their MS spectra and compared with authentic samples.

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(Received in UK 18 March 1996; revised 20 May 1996; accepted 23 May 1996)