

CATALYTIC REDUCTION OF AROMATIC NITRO COMPOUNDS WITH HYDRAZINE  
IN THE PRESENCE OF IRON(III) CHLORIDE AND ACTIVE CARBON

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A catalytic reduction of aromatic nitro compounds to aromatic amino compounds with hydrazine in the presence of Fe(III) chloride and active carbon was studied. The corresponding amino compounds were obtained with excellent purities and in good yields. The method was also applied to the partial reduction of dinitro compounds.

It is well known that hydrazine reduces aromatic nitro group to the amino group<sup>1)</sup> in the presence of Pd-C, Pt-C, or Raney Ni. In these methods side reaction products were often accompanied and large excess of hydrazine was required to complete the reduction. A new method was found, in which the reaction is conducted at temperature ranging from r.t. to 80°C in the presence of Fe(III) chloride and active carbon.

An example of the reduction is as follows; The reduction of m-nitrobenzonitrile(I).

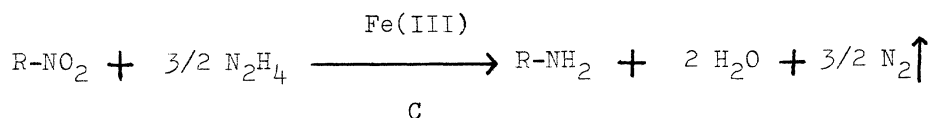
The mixture of I (14.8g, 0.1 mol), active carbon ( 2.2g, KV-0, 250 mesh Futamura Chemical Co.), FeCl<sub>3</sub>·6H<sub>2</sub>O (160.7mg), and methanol (50ml) was refluxed for ten min with stirring and then to the mixture was added dropwise hydrazine hydrate (96.5% purity, 8g, 0.154 mol) within 1 hr. The mixture was stirred for additional 3 hr under refluxing until I was disappeared, and was filtered to remove active carbon.

From the filtrate colorless needles of m-aminobenzonitrile were obtained.

Yield 10.8g ( 91.5% ), mp. 52.5-53°C.

Similar results were obtained in the cases of various nitro compounds. On the application of the method to the partial reduction of dinitro compounds to the corresponding amino-nitro compounds similar results were obtained. These results were summarised in the table 1.

The reaction is expressed as follows.



The corresponding hydroxylamine, RNHOH, was detected as an intermediate and the evolution of nitrogen gas was observed. The mechanism is now being investigated and will be reported in future. The products were identified with authentic compounds by means of elemental analysis, melting point, IR, NMR, and Mass spectra.

Table 1. Reaction condition and result of the hydrazine reduction

Nitro compound	Condition			Amino compound	
	Fe(mg)/C(g) per 0.1 mol R-NO <sub>2</sub>	Temp.(°C)	hr	Yield (%)	mp.(°C) (bp.)
p-nitrotoluene	20.6/2	reflux*	5	93.9	43.0 - 3.5
m-nitroanisole	18.5/2	reflux	5	96.0	(81 - 6)
p-nitroanisole	20.1/1	reflux	5	93.0	58.0 - 9
o-nitroanisole	21.3/1	reflux	5	97.5	(89. - 92)
3,4-dimethylnitrobenzene	52.1/1.1	reflux*	8	99.0	49.5- 50
p-nitroacetanilide	136.7/2	reflux	3	91.3	165.0- 66
4-nitrodiphenyl ether	23.4/1	reflux	5	93.0	33.5- 4.0
4,4'-dinitrodiphenyl ether	375.2/5	reflux	5	97.6	189.0- 9.5
2,5-diethoxy-4-nitrobenzanilide	195.0/4	53-60	13	93.0	100.0- 1
5-chloro-2,4-dimethoxynitrobenzene	47.0/1.4	50-55	26	87.0	91.0- 2
4-methoxy-3-nitroacetanilide	205.0/2.2	reflux	23	93.5	110.0-10.5
4-methoxy-4'-nitrodiphenylamine	100.0/5	reflux	14	90.5	101.5- 2
Partial reduction					
m-dinitrobenzene	102.3/2.4	45-43	6	97.4 <sup>α)</sup>	112.5 - 3.5
2,4-dinitroanisole	106.4/2.4	25-30	3	66.0 <sup>β)</sup>	112. - 4
2,4-dinitrophenol	300.0/4.2	55-53	9	39.0 <sup>γ)</sup>	176. - 7

C: Active carbon. Fe: FeCl<sub>3</sub>·6H<sub>2</sub>O. Solvent: Methanol (\* Ethanol ).

α) m-nitroaniline. β) 5-nitro-o-anisidine. γ) 2-amino-4-nitrophenol.

## Reference

- 1) A. Furst, Chem. Rev., 65, 51 (1965).

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