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GRAPHITE CATALYZED REDUCTION OF AROMATIC AND ALIPHATIC NITRO COMPOUNDS WITH HYDRAZINE HYDRATE

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Abstract. Aromatic and aliphatic nitro compounds were readily reduced to amino compounds in excellant yields with graphite and hydrazine hydrate.

Hydrazine has been used to reduce aromatic nitro compounds in the presence of PtO_2-C, Pt-C, Pd-C and Raney Ni.[1] The extended methods using $FeCl_3$-C,[2] Pd-C[3] with hydrazine afforded an elegant route for the preparation of aromatic amino compounds and partial reduction of dinitro aromatic compounds. However, the methodology described by these authors are inappropriate due to necessity of relatively expensive catalysts or long reaction time followed by tedious experiment procedure. We recently reported the high reduction ability of hydrazine hydrate in the presence of iron powder and activated carbon in ethanol to reduce nitroarenes under ultrasonic irradiation.[4] In our extended studies on the catalytic reduction of aromatic nitro compounds, we have discovered that graphite catalyzed aromatic nitro compounds to the corresponding aromatic amino compounds in quantitative yields in the presence of hydrazine hydrate.

Results of aromatic amino compounds prepared by this method are presented in Table-1.

The obvious advantages over conventional methods are elimination of use of expensive metals and improvements on reaction condition as well as yield. In a typical experiment, a 100 ml round bottom single neck flask was charged with 0.01 mol of aromatic nitro compound, 0.02 mol of hydrazine monohydrate, 3g of graphite and 10 ml of absolute ethanol. The mixture was refluxed for 2 hr under an stmosphere pressure of nitrogen. The contents was filtered and washed with ethanol or benzene to remove graphite. Removal of solvents by flash evaporation gave the corresponding amino compounds. Each product was characterized by comparison of their IR, NMR and mp with those of authentic samples. Hydrazine is the exclusive source of hydrogen was demonstrated when nitrobenzene was recovered quantitatively from a reaction mixture in which hydrazine was obmitted. The reduction capabilities of graphite-hydrazine to aliphatic nitro compound were also examined. Thus we found that nitroethane was reduced to ethylamine in 89% yield at same reaction condition.

Table-1. Graphite Catalyzed Reduction of Aromatic Nitro Compounds to Aromatic Amino Compounds with Hydrazine Hydrate in Ethanol[a]

Nitro compound	Amino compound	Yield(%, isolated)
C_6H_5-NO_2	C_6H_5-NH_2	95
o,m,p-$CH_3C_6H_4$-NO_2	o,m,p-$CH_3C_6H_4$-NH_2	96,95,98[b]
o,p-$CH_3OC_6H_4$-NO_2	o,p-$CH_3OC_6H_4$-NH_2	93,95[b]
o,p-HOC_6H_4-NO_2	o,p-HOC_6H_4-NH_2	86,89[b]
m-$HOOCC_6H_4$-NO_2	m-$HOOCC_6H_4$-NH_2	85
p-$NH_2C_6H_4$-NO_2	p-$NH_2C_6H_4$-NH_2	95
p-$HOCH_2CH_2SC_6H_4$-NO_2	p-$HOCH_2CH_2SC_6H_4$-NH_2	98
o,p-$CH_3CH_2CH_2OC_6H_4$-NO_2	o,p-$CH_3CH_2CH_2OC_6H_4$-NH_2	97,98[b]
2,4-Dinitrochlorobenzene	2,4-Diaminochlorobenzene	88[c]
6-Nitroquinoline	6-Aminoquinoline	95
8-Nitroquinoline	8-Aminoquinoline	96
1-Nitronaphthalene	1-Aminonaphthalene	92
4-Nitrodiphenylether	4-Aminodiphenylether	87

a. Reaction times are not optimized. All reactions were refluxed for 2 hr under nitogen atosphere. Graphite powder(325 mesh) was used. b. Para isomer yield

c. A 0.01 : 0.04 mol ratio of dinitro : Hydrazine hydrate was employed.

$CH_3CH_2NH_3Cl$, mp108-109°C(lit.[5] 109-110°C) was actually isolated after trapped with HCl in ether by fractional distillation from product mixture. The low cost, high yield and simplicity of workup are noteworthy of graphite-hydrazine system. We are presently exploring the ability of this system to a variety of fuctional group.

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