

Notes

Reduction of Aromatic Nitro Compounds with Hydrazine in the Presence of Sodium Nitrate-Carbon

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Hydrazine has long been used as a specific reagent for reduction of aromatic nitro compounds to the corresponding amino derivatives in the presence of Pd-C, Pt-C, or Raney Ni.¹

The extended methods using hydrazine with FeCl₃-C², Graphite³, Montmorillonite⁴ afforded an elegant route for the preparation of aromatic amino compounds. However, these methods proved to be somewhat capricious and gave variable yields. In this letter, we wish to describe a mild and efficient reduction of aromatic nitro compounds to the amino compounds with hydrazine in the presence of sodium nitrate.

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

The obvious advantages over conventional methods are elimination of using expensive catalysts and improvements of reaction conditions.

A typical procedure is as follows: Under nitrogen, to a stirred mixture of sodium nitrate (0.85 g, 0.01 mol) and activated carbon (0.5 g) in ethanol (95%, 5 mL) was added all at once nitroarene (0.01 mol) and anhydrous hydrazine (1.9 mL, 0.06 mol). The resulting reaction mixture (slightly exothermic and effervescent) was refluxed until the reaction was complete as indicated by TLC analysis. Then the mixture was poured into ice-water and extracted with dichloromethane or benzene. The extract was dried over anhydrous calcium chloride.

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. Attempted reduction of aliphatic nitro compounds such as nitropropane or benzonitrile under same conditions resulted in recovery of the starting materials. Hydrazine alone did not effect a reduction nor did sodium nitrate alone in the case of nitrobenzene. However, activated carbon was critical to use as a reaction supporter. When nitrobenzene was reduced under

Table 1. Sodium Nitrate-Carbon Catalyzed Reduction of Nitroarenes with Hydrazine^a

Nitro compounds	Products	Time (hr)	Yields (%) ^b
C ₆ H ₅ -NO ₂	C ₆ H ₅ -NH ₂	2	87(50) ^c
<i>o</i> , <i>m</i> , <i>p</i> -CH ₃ C ₆ H ₄ -NO ₂	<i>o</i> , <i>m</i> , <i>p</i> -CH ₃ C ₆ H ₄ -NH ₂	3	85, 85, 87
<i>o</i> , <i>p</i> -HOC ₆ H ₄ -NO ₂	<i>o</i> , <i>p</i> -HOC ₆ H ₄ -NH ₂	2	85, 83
<i>o</i> , <i>m</i> , <i>p</i> -ClC ₆ H ₄ -NO ₂	<i>o</i> , <i>m</i> , <i>p</i> -ClC ₆ H ₄ -NH ₂	2	90, 95, 93
<i>p</i> -CH ₃ OC ₆ H ₄ -NO ₂	<i>p</i> -CH ₃ OC ₆ H ₄ -NH ₂	14	90
<i>p</i> -BrC ₆ H ₄ -NO ₂	<i>p</i> -BrC ₆ H ₄ -NH ₂	5	95
<i>p</i> -NH ₂ -C ₆ H ₄ -NO ₂	<i>p</i> -NH ₂ -C ₆ H ₄ -NH ₂	5	89
<i>p</i> -ClCH ₂ -C ₆ H ₄ -NO ₂	<i>p</i> -ClCH ₂ -C ₆ H ₄ -NH ₂	3	95
<i>o</i> -HOCC ₆ H ₄ -NO ₂	<i>o</i> -HOCC ₆ H ₄ -NH ₂	11	89
1-Nitronaphthalene	1-Aminonaphthalene	3	96
6-Nitroquinoline	6-Aminoquinoline	4	96
8-Nitroquinoline	8-Aminoquinoline	6	94
<i>p</i> -Nitroacetophenone	<i>p</i> -H ₂ NC ₆ H ₄ C(=O)NHNH ₂ CH ₃	5	89

^a All reactions were refluxed under nitrogen: Reduction reactions with large excess of sodium nitrate and carbon did not improve the yields (5% or less) significantly, ^b Isolated, ^c Without activated carbon.

same condition without activated carbon, only 50% of aniline along with unchanged nitrobenzene was obtained by GC. Also, with activated carbon-hydrazine without sodium nitrate under same condition, only 10% of aniline was produced in the case of nitrobenzene. Quantity of activated carbon for the reduction of nitrobenzene did not improve the yield significantly at any cases.

Reduction reaction also examined with other metal nitrate instead of sodium.

But only potassium nitrate gave the similar results. In summary, low cost, high yield and simplicity of workup are noteworthy of sodium nitrate-hydrazine system.

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