Activated Molybdenum Promoted Reduction of Nitroarenes with Hydrazine monohydrate

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Received July 18, 1994

Hydrazine has been used to reduce aromatic nitro compounds in the presence of PtO_2-C, Pt-C, Pd-C or Ni[1]. The extended methods using $FeCl_3$[2], Pd-C[3], graphite[4], montmorillonite[5], S[6], Fe-C[7], or $NaNO_3$[8] with hydrazine provided elegant routes for the preparation of aromatic amino compounds. We recently reported the reduction of nitroarenes with activated copper-zinc[9] or nickel-zinc[10] in the presence of hydrazine monohydrate. In continuation of our work on the reduction of nitro group[4-10], we found that nitroarenes were reduced to the corresponding aminoarenes in good yields with activated molybdenum and hydrazine monohydrate. Our results on the reduction of nitroarenes with these reagents are presented in Table 1.

$$R\text{-}NO_2 \xrightarrow[\text{DME, reflux, 2 h}]{\text{Activated Mo/}NH_2NH_2H_2O} R\text{-}NH_2$$

R = C_6H_5, *o,m,p*-$CH_3C_6H_4$, *o,m,p*-ClC_6H_4, *p*-BrC_6H_4, *p*-$CH_3OC_6H_4$, *p*-HOC_6H_4, *p*-$NH_2C_6H_4$, *p*-$N{\equiv}CC_6H_4$, 1-naphthyl, 6-quinolinyl

Various nitroarenes were reduced to aminoarenes exclusively followed by complete conversion (run 1-10). The obvious advantages over conventional methods are the elimination of use of expensive metals, reuseability of activated molybdenum and simple workup procedure as well as yield. However, reduction of nitrobenzene with a mixture of commercially available molybdenum powder, anhydrous zinc chloride and hydrazine monohydrate did not take place nor did zinc chloride alone with hydrazine monohydrate. Interestingly, when nitrobenzene was treated with a commercially available molybdenum powder and a large excess of hydrazine monohydrate in dry DME and heated to reflux under nitrogen for 15 h (run 1, c), 88% of aniline was formed by GLC along with unreacted nitrobenzene (after heated to reflux for 3 h, only 17% of aniline was formed). When nitrobenzene was also treated with other activated metals prepared from metal chlorides (such as Nb, W, Ti, Zr) with stoichiometric amount of zinc or lithium and hydrazine monohydrate in dry DME and refluxed for 15 h, aniline was formed in only 0-50%. On the other hand, reduction of nitrobenzene using activated molybdenum powder prepared by the reaction of molybdenum chloride with magnesium or lithiumun in the presence of a large excess of hydrazine monohydrate in dry DME under reflux for 5 h, afforded 80-95% of aniline with remaining nitrobenzene by GLC. In the absence of activated molybdenum, the reaction of *p*-nitrotoluene with zinc powder-hydrazine monohydrate in DME and heated to reflux under nitrogen for 15 h produced 79% of *p*-toluidine, 3% of 4,4'-dimethylazobenzene and 3% of 4,4'-dimethylazoxybenzene with unreacted starting material.

Table 1. Activated Molybdenum Catalyzed Reduction of Nitroarenes with Hydrazine Monodydrate in Dimethoxyethane[a]

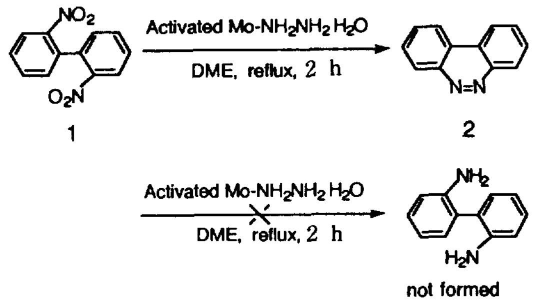
Run	Nitro compounds	Products	Yield (%)[b]
1	C_6H_5-NO_2	C_6H_5-NH_2	87(88)[c]
2	*o,m,p*-$CH_3C_6H_4$-NO_2	*o,m,p*-$CH_3C_6H_4$-NH_2	83,85,88
3	*o,m,p*-ClC_6H_4-NO_2	*o,m,p*-ClC_6H_4-NH_2	86,88,90(38)[d]
4	*p*-BrC_6H_4-NO_2	*p*-BrC_6H_4-NH_2	92
5	*p*-NCC_6H_4-NO_2	*p*-NCC_6H_4-NH_2	90
6	*p*-$CH_3OC_6H_4$-NO_2	*p*-$CH_3OC_6H_4$-NH_2	88
7	*p*-HOC_6H_4-NO_2	*p*-HOC_6H_4-NH_2	85
8	*p*$NH_2C_6H_4$-NO_2	*p*-$NH_2C_6H_4$-NH_2	83
9	1-Nitronaphthalene	1-Aminoaphthalene	85
10	6-Nitroquinoline	6-Aminoquinoline	90

[a] Activated molybdenum was first prepared by mixing of 1.4 mmol of $MoCl_5$ and 3.5 mmol of Zn in 10 m*l* of DME and the mixture was heated to reflux under nitrogen for 1 h. After cooled to room temperature, 1.2 mmol of nitroarenes and 20.6 mmol of $NH_2NH_2H_2O$ were added and heated to reflux under nitrogen for 2 h. [b] Isolated. [c] Commercially available molybdenum was used. [d] 10 mmol of $NH_2NH_2H_2O$ was employed and heated to reflux for 4 h.

When hydrazine was omitted, nitrobenzene was recovered quantitively from a reaction mixture. As a solvent, we have found that DME was superior to tetrahydrofuran (THF), diethyl ether or benzene. THF led side products from decomposition of itself by activated molybdenum. In case of using benzene or diethyl ether as a solvent, reduction of nitroarenes did not lead to complete (5 h, <90%). We have studied the recycle ability of activated molybdenum and found that activated molybdenum can be recycled many times. For example, we recovered the activated molybdenum almost quantitatively by decanting the product mixture from the reaction flask, washing with dry DME, recharged the vessel with nitroarenes, hydrazine monohydrate and DME, and reused the activated molybdenum several times (we tested 5 times) without significant loss of activity.

While systematic rate data were not taken, it was observed that the reactions proceeded up to 90% after 1 h. Two hours was usually enough to complete reduction.

In an extension of this work, we have studied the reduction of 2,2-dinitrobiphenyl (1). Using our reagents in DME under reflux for 2 h, benzo[c]cinnoline (2) was isolated in 88% yield. However, Benzo[c]cinnoline was not further reduced with our reagents.



Unfortunately, aliphatic nitro compounds, such as nitrobutane or nitrocyclohexane, were not reduced by this reducing system. Also, attempted hydrogenation of olefins, such as stilbene or reductiin of benzonitrile with our reagents resulted in recovery of the starting materials respectively. The source of this unexpected reactivity of activated molybdenum powder for the reduction of nitroarenes may be from the high surface area, some unique surface species which we are currently under investigation. In conclusion, the high yields, short reaction times, mild conditions and simplicity of workup are noteworthy of this system. We are presently exploring the scope of activated molybdenum to a variety of functional group transformation.

Experimental

Commercial nitro compounds (Aldrich, Junsei, Yakuri) and solvents were purified and dried prior to use when deemed necessary. Anhydrous molybdenum (V) chloride and zinc dust (−325 mesh) were purchased from Aldrich chemical and used without any further treatment. Hydrazine monohydrate was purchased from Junsei Chemicals. Dimethoxyethane (DME) was distilled over sodium. Amino compounds were identified by comparison of their physical and chemical properties with those of authentic samples.

General procedure for the preparation of activated molybdenum powder. A typical preparation of activated molybdenum powder is as follows. Into a 100 m*l* of two-necked round bottom flask equipped with nitrogen septum inlet and condenser were placed anhydrous molybdenum chloride (0.38 g, 1.4 mmol), zinc (0.23 g, 3.5 mmol) and dry DME (10 m*l*). The exothermic reaction took place immediately and dark red solution turned to black. The mixture was then heated to reflux for 1h to complete reduction. When the heating was stopped, the very finely divided black metal powder was settled down in a black solution. This slurry was ready for this investigation without any further treatment after cooled to room temperature.

General procedure of reduction of nitroarenes with activated metal powder. Nitroarenes (1.2 mmol) and hydrazine monohydrate (1 m*l*, 20.6 mmol) were added to the stirred slurry. After initial effervescence had ceased, the resulting reaction mixture was then heated to reflux for 2 h. The dark solution mixture became clear and dark powder (presumably activated molybdenum) was settled down. Product isolation was straightforward. After filtration, solvent removal, and flash chromatography on a short silica gel column (4 cm×1.5 dia.) using methylene chloride or methylene chloride-ethanol (8 : 2, v/v) as a eluant, the expected aminoarenes were obtained in 83-92% (see Table 1). Assignments of the simple amino compounds are based on NMR, IR and GLC-Mass spectral data.

Benzo[c]cinnoline was isolated as followed; after filtration and evaporation of solvent, silica gel column chromatography of the residue using ethyl acetate-hexane (1 : 1) as eluent provided benzo[c]cinnoline as reddish yellow crystalline solid. mp. 155-156 ℃ (lit.[11], mp. 157-158 ℃): ^1H NMR ($CDCl_3$) δ 7.78-7.90 (m, 4H)., 8.43-8.76 (m, 4H); MS (m/z): 180 (m^+).

Acknowledgment. This work was supported in part by Non Directed Research Fund from the Korea Research Foundation (1993) and a Basic Science Research Institute Program from the Ministry of Education (1994) of the Republic of Korea.

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Hydride Reduction of diag-(η^5-C_5H_5)Re$(CO)_2Br_2$: Ring Attack vs. Metal-Halogen Exchange

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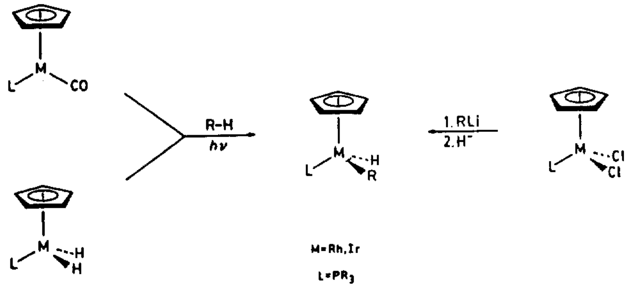
Received July 21, 1994

The activation of alkanes by soluble cyclopentadienyl metal complexes has been shown to afford stable hydrido (alkyl) metal complexes in the case of rhenium, rhodium, and iridium systems.[1-3] The same products of these intermolecular oxidative addition reactions have also been independently prepared from the corresponding cyclopentadienyl rhodium and iridium dihalides by sequential halide reduction (Scheme 1).[4] In contrast, the reaction of reducing agents with analogous cyclopentadienyl rhenium dihalides has not been extensively studied.[5-7] This paper reports the results on the reaction of diag-CpRe$(CO)_2Br_2$(**1**: diag=diagonal; Cp=η^5-C_5H_5)



Scheme 1.