Notes

Reduction of Nitroarenes by Activated Metals

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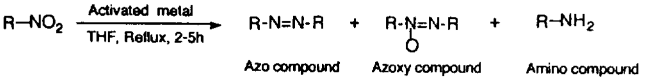
Recently, considerable interest has centered on the use of activated metals and their complexes as noble reagents in vast range of organic synthesis.[1] However, only a few examples for the use of activated metals (M*), such as Zn-Cu,[2] Ni-Zn,[3] Mo[4] with hydrazine monohydrate to reduce nitro group have been reported by our laboratory. In a series of our studies on the chemistry of activated metals, we have examined a broad range of metals that encompasses Mg*, Al*, Zn*, Ti*, W*, Nb* and Mo* for the reduction of nitroarenes.

The highly reactive metal powders such as Mg*, Al*, Zn*, Ti*, W*, Nb*, Mo* are readily prepared by the reaction of the corresponding anhydrous metal chloride with equivalent of lithium in freshly distilled tetrahydrofuran (THF) under nitrogen. The mixture is refluxed for 1-2 h to complete the reduction. When the refluxing is stopped, the very fine black metal particles are settled down (in most cases) in a black solution. Our results on the reduction of nitroarenes with the activated metals under various reaction conditions are presented in Table 1.



$$R{-}NO_2 \xrightarrow[\text{THF, Reflux, 2-5h}]{\text{Activated metal}} R{-}N{=}N{-}R + R{-}\underset{O}{\underset{|}{N}}{=}N{-}R + R{-}NH_2$$

Various kinds of nitroarenes were reduced to give the corresponding azo compounds exclusively in high yields and complete conversion using activated magnesium (run 1-2), zinc (runs 4, 5, 8) and aluminum (runs 9-13, 16-18) was achieved. Typical mol ratio of nitro compound versus activated metal was 1 : 2. However, commercially available zinc, magnesium and aluminum were inert for the reduction of nitroarenes, such as nitrobenzene (runs 1[e], 4[e], 10[f]). Several trends in reactivity for the activated metal are also apparent. For example, in contrast to the catalysis of the titanium which convert ketone or aldehyde into the corresponding coupled alkenes efficiently,[5] an activated titanium reduced *p*-nitrotoluene to give only 4,4′-dimethyl azoxybenzene in 9% yield after usual workup along with unreacted starting material (run 23) and nitrobenzene was reduced with activated titanium to give azobenzene in 29% and azoxybenzene in 40%, respectively, remaining starting material by GLC (run 24). It should also be noted that the reaction conditions were extremely important in some cases. For example, when a mixture of *p*-chloronitrobenzene and activated aluminum was refluxed for 5 h, dechlorination reaction occurred to form azobenzene in 4% yield and 4-chloroazobenzene in 16% yield along with 4,4′-dichloroazobenzene in 80% (run 16). However, when the same reaction was carried out for 1.5 h, 4,4′-dichloroazobenzene was formed exclusively in 88% yield (run 15). We also investigated the effects of sonication with Han's cup[6] on the reduction of nitroarenes (runs 2, 5, 7, 13, 20, 21). We found that nitro compounds were reduced to give the corresponding azo, azoxy and amino compound (runs 2, 5, 7, 13, 20, 21). This apparent discrepancy to heating is probably due to the local heating effect.[7] Unexpectedly, completely reduced aminoarenes were found in some cases under sonic irradiation for the reduction of nitroarenes using acivated magnesium (run 2), aluminum (runs 13, 20), indium (run 21). For example, when 1-nitronaphthalene was sonicated with activated aluminum powder prepared from the reduction of aluminum chloride with lithium in THF under sonic irradiation for 2 h, 1-aminonaphthalene was isolated in 87% yield (run 20). THF probably provides a unique hydrogen source in such reaction conditions. It has been observed that the reaction under sonic irradiation gave different results from heating with stirring.[8] When the other activated metals were examined for the reduction of nitro group, we have found that activated tungsten, zirconium and molybdenum were inactive for the reduction (runs 27-30). We have also studied the reduction of aliphatic nitro compound, such as 1-nitrodecane, with activated aluminum, magnesium or zinc. However, all attempts to apply this reagents to 1-nitrodecane gave only denitrated product, decane. In summary, high reactive metal powder is easily and safely prepared by lithium reduction of the corresponding metal salt either under heating or sonication and this activated metal powders, such as magnesium, zinc and aluminum were able to reduce nitroarenes. Work is now in progress to use of these activated metals to the other functional group transformation and we will report on them in due course.

Experimental

Commercial nitro compounds (Aldrich, Junsei, Yakuri) and solvents were purified and dried prior to use when deemed necessary. Tetrahydrofuran (THF) was distilled over sodium. Anhydrous metal chlorides, lithium dispersion and lithium wire were purchased from Aldrich Chemical. Melting points were determined with an electrothermal apparatus (ENG, LTD. NO F-01265) and were uncorrected. ^{1}H NMR (Bruker AC 80 spectrometer) was used for identification of the amino compounds. TLC was performed on precoated aluminum plates with Merck silica gel 60 F-254 as the adsorbent (layer thickness 0.2 mm). The developed plates were air dried and irradiated with UV light. Column chromatography was carried out on Merck silica gel 60 (70-230 mesh). Mass spectra (70 eV electron impact) were taken on a Finingan 4510 instrument equipped with a Finingan-incos data system. GLC-Mass analysis was performed on a Hewlett-Packard MSD 5890 series equipped with a capillary column (HP1, 25 m). GLC was done with a Varian 3300 instrument equipped with a FID detector and a stainless steel column packed with

Table 1. Reduction of Nitroarenes by Activated Metals at Various Reaction Conditions[a]

Run	Activated Metal	Metal halide	Reducing agent	R	Solvent	Reaction condition, h[c] (h[d])	Product (%)[b] Azo compound	Azoxy compound	Amino compound
1	Mg	$MgCl_2$	Li	C_6H_5	THF	Reflux, 1h (5h)	90 (0[e])		
2	Mg	$MgCl_2$	Li	*p*-$CH_3C_6H_4$	THF	Ultrasound, 1h (2h)	70		20
3[f]	Mg	$MgCl_2$	Li	*p*-ClC_6H_4	THF	Reflux, 1h (5h)	60	40	
4	Zn	$ZnCl_2$	Li	C_6H_5	THF	Reflux, 1h (5h)	85 (0[e])		
5	Zn	$ZnCl_2$	Li	C_6H_5	THF	Ultrasound, 1h (5h)	80	12	
6	Zn	$ZnCl_2$	Li	*m,p*-$CH_3C_6H_4$	THF	Reflux, 1h (5h)	52, 85	41, 3	
7	Zn	$ZnCl_2$	Li	*p*-$CH_3C_6H_4$	THF	Ultrasound, 1h (2h)	75	18	
8[f]	Zn	$ZnCl_2$	Li	*p*-ClC_6H_4	THF	Reflux, 1h (5h)	79 (14, 7)[g]		
9	Al	$AlCl_3$	Li	C_6H_5	THF	Reflux, 2h (3h)	90 (0[e])		
10	Al	$AlCl_3$	Li	*o,m,p*-$CH_3C_6H_4$	THF	Reflux, 2h (5h)	83, 88, 85		
11	Al	$AlCl_3$	Li	*p*-$CH_3OC_6H_4$	THF	Reflux, 2h (5h)	92		
12	Al	$AlCl_3$	Li	*o*-ClC_6H_4	THF	Reflux, 2h (3.5h)	85		
13[f]	Al	$AlCl_3$	Li	*p*-ClC_6H_4	THF	Ultrasound, 2h (2h)	44	26	10
14	Al	$AlCl_3$	Li	*m*-ClC_6H_4	THF	Reflux, 2h (1.5h)	57	26	
15	Al	$AlCl_3$	Li	*p*-ClC_6H_4	THF	Reflux, 2h (1.5h)	88		
16	Al	$AlCl_3$	Li	*p*-ClC_6H_4	THF	Reflux, 2h (2h)	80 (16, 4)[g]		
17	Al	$AlCl_3$	Li	*p*-BrC_6H_4	THF	Reflux, 2h (2h)	70 (25, 5)[g]		
18	Al	$AlCl_3$	Li	*p*-CNC_6H_4	THF	Reflux, 2h (1.5h)	88		
19	Al	$AlCl_3$	Li	1-Naphthyl	THF	Reflux, 2h (2h)	45		48
20	Al	$AlCl_3$	Li	1-Naphthyl	THF	Ultrasound, 2h (2h)			87
21[f]	In	$InCl_3$	Li	C_6H_5	THF	Ultrasound, 1h (3h)	7	18	13
22[f]	In	$InCl_3$	Li	C_6H_5	THF	Reflux, 1h (5h)	38	35	6
23[f]	Ti	$TiCl_3$	Li	*p*-$CH_3C_6H_4$	THF	Reflux, 1h (5h)		9	
24[f]	Ti	$TiCl_3$	Li	C_6H_5	THF	Reflux, 1h (5h)	29	40	
25[f]	Nb	$NbCl_5$	Li	C_6H_5	THF	Reflux, 1h (5h)	85	3	
26[f]	Nb	$NbCl_5$	Li	*p*-$CH_3C_6H_4$	THF	Reflux, 1h (5h)	36		
27	W	WCl_6	Li	C_6H_5	DME	Reflux, 1h (5h)	no reaction		
28	Zr	$ZrCl_4$	Zn	C_6H_5	THF	Reflux, 1h (5h)	no reaction		
29	Mo	$MoCl_5$	Li	C_6H_5	THF	Reflux, 1h (5h)	no reaction		
30	Mo	$MoCl_5$	Li	C_6H_5	DME	Reflux, 1h (5h)	no reaction		

[a] Equivalent mole ratio of metal chloride: lithium was employed and typical mole ratio of nitro compound versus activated metal was 1 : 2. [b] Isolated otherwise cited. [c] Activation time. [d] Reduction time (See, experimental section). [e] Using commercially available metal powder. [f] GLC yields and rest was starting material. [g] 14% of 4-chloroazobenzene and 7% of azobenzne on Run 8, 16% of 4-chloroazobenzene and 4% of azobenzne on Run 16 and 25% of 4-bromoazobenzene and 4% of azobenzene were formed on Run 17 by GLC.

10% OV-101, Chromosob W HP 80/100 (2 m×1/8 in).

General procedure for the preparation of activated metal powders. An example of a typical preparation for activated aluminum powder is as follows. 0.084 g (12 mmol) of lithium dispersion, 0.53 g (4 mmol) of anhydrous aluminum chloride, and 15 mL of THF were placed in a dry 100 mL, two-necked, round-bottomed flask equipped with a septum inlet, magnetic stirring, nitrogen atmosphere, and condenser. The mixture is stirred and heated to reflux for 1-2 h. After cooled to room temperature for 0.5 h, the very fine black particles settled out in a black solution above the black powder (in most cases). This slurry is ready to use for this investigation without any further treatment.

Gneral procedure for the reduction of nitroarenes with activated metal powders. 1.5 mmol of nitroarenes was injected to this slurry (above description). The mixture was refluxed for 2 h. Product isolation was straightforward: removal of solvent under reduced pressure and extraction with methylene chloride and chromatography with silica gel. Evaporation of solvent from eluants gave over 95% pure product (by GLC and NMR). The yields are based on quantities obtained after this step. Some physical properties of the products are recorded below. Azobenzene: mp 68-69 ℃ (lit.,[9] 68-69 ℃); MS (m/z); 182 (M^+). Azoxybenzene: mp 35.5-36 ℃ (lit.,[9] 35-36 ℃); MS (m/z); 198 (M^+). 2,2′-Dimethylazobenzene: mp 53-54 ℃ (lit.,[10] 53-54 ℃); MS (m/z); 210 (M^+). 2,2′-Dimethylazoxybenzene: mp 57-58 ℃ (lit.,[11] 60℃); MS (m/z); 226 (M^+). 4,4′-Dimethylazobenzene: mp 141-142 ℃ (lit.,[12] 144-145 ℃); MS (m/z); 210 (M^+). 4,4′-Dimethylazoxybenzene: mp 67-68 ℃ (lit.,[9] 60 ℃); MS (m/z); 226 (M^+). 3,3′-Dimethylazobenzene: mp 52-54 ℃ (lit.,[13] 54-55 ℃); MS (m/z); 210 (M^+). 3,3′-Dimethylazoxybenzene: mp 33-35 ℃

(lit.,[11] 38-39 ℃); MS (m/z); 226 (M^+). 4,4'-Dichloroazoxybenzene: mp 155 ℃ (lit.,[9] 156-157 ℃); MS (m/z); 266 (M^+). 4,4'-Dichloroazobenzene: mp 182-184 ℃ (lit.,[9] 186-187 ℃); MS (m/z); 250 (M^+). 4,4'-Dimethoxyazobenzene: mp 158-160 ℃ (lit.,[14] 160 ℃); MS (m/z); 242 (M^+). 4,4'-Dimethoxyazoxybenzene: mp 116-119 ℃ (lit.,[14] 119-120 ℃); MS (m/z); 258 (M^+).

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Comparative Oxidation of Carbon Monoxide over Supported Catalysts

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Carbon monoxide becomes one of the hazardous pollutants in air, which is produced during high temperature combustion in industrial boilers and motor vehicles.

The most popular method for CO removal or lowering its concentration is the catalytic oxidation to CO_2. The activity of transition metal oxides and noble metals for CO oxidation has been described in numerous literatures.[1~3] Typical catalysts used for this purpose contain noble metals such as Pd, Pt, or Rh dispersed on various oxides. Although transition metals alone show insufficient activity for low temperature CO oxidation, catalysts with mixed bimetallic composition (transition metal + noble metal) have higher activity than noble metals alone. There are several factors affecting the catalytic activity such as composition of metals, types of supports, pretreatment of catalysts and methods for metal loading.

In this work the influence of metal loadings as well as the metallic compositions on the activity of the catalysts has been investigated.

Experimental

γ-Al_2O_3 (Janssen, 50-200 μ, 210 m^2/g) and HZSM-5 (PQ Co., 430 m^2/g) were purchased commercially.

Typical procedures for the preparation of metal-containing catalysts are as follows.

Impregnation. In order to prepare γ-Al_2O_3 supported catalysts containing 4.0 wt% Cu, simply expressed as 4.0% Cu/γ-Al_2O_3 hereinafter, 1.52 g of $Cu(NO_3)_2 \cdot 3H_2O$ was dissolved in 100 mL distilled water, to which 9.6 g of γ-Al_2O_3 was added. The mixture was stirred at 60-70 ℃ for 8-10 h until the water is completely evaporated. The resulting product was dried at 100 ℃ overnight.

Ion-exchange + impregnation. In order to prepare ZSM-5 supported catalysts containing 2.0 wt% Cu, simply being termed hereinafter as 2.0% Cu/ZSM-5i, 0.76 g of $Cu(NO_3)_2 \cdot 3H_2O$ was dissolved in 250 mL H_2O into which 9.8 g of ZSM-5 was dispersed. The resulting suspension was stirred for 50 h at 30-40 ℃. After 50 h, temperature was increased to 50-60 ℃ and complete removal of water was attempted. Finally the residue was dried at 100 ℃ overnight.

For the preparation of bimetal-containing zeolite catalysts such as Pt-Cu/ZSM-5i and Pt-Co/ZSM-5i, Pt was introduced into HZSM-5 first by ion-exchange, which was calcined in air at 520 ℃ for 3 h. Pt-ZSM-5 was then impregnated with aqueous solution of copper and cobalt nitrate, respectively. The zeolite-supported catalysts were dried at 100 ℃ over-