separation on silica afforded pure product. Yield 0.32 g (20%); ¹H NMR (CDCl₃) δ 7.99 (bs, 1H, N-H), 7.18-7.15 (m, 1H, thiophene-H), 6.96-6.91 (m, 1H, thiophene-H), 6.85-6.83 (m, 1H, thiophene-H), 6.74-6.72 (m, 1H, pyrrole-H), 6.16-6.15 (m, 1H, pyrrole-H), 6.05 (m, 1H, pyrrole-H), 4.17 (s, 2H, meso-H).

Dipyrromethane (4). To a mixture of thiophene-methanol (0.26 g, 3.4 mmol) and pyrrole (0.46 g) was added BF₃·OEt₂ (0.48g, 3.4 mmol) under nitrogen atmosphere. The mixture was stirred for 60 min at 10 °C then diluted with methylene chloride (100 mL). The dark brown mixture was washed with aqueous sodium hydroxide (0.1 N, 100 mL), water and dried (anhydrous Na₂SO₄). Evaporation of the solvent to dryness and column chromatographic separation on silica afforded pure product. Yield 0.073 g (15%); ¹H NMR (CDCl₃) δ 7.70 (bs, 2H, N-H), 6.60-6.58 (m, 2H, pyrrole-H), 6.02 (m, 2H, pyrrole-H), 3.92 (s, 2H, meso-H).

2,6-pyrrocarbonylpyrridine (7). To a solution of pyrrole (1.32 mL, 19.6 mmol) in 15 mL THF was added a solution of ethyl magnesium bromide (3.0 M in diethyl ether solution, ~8.5 mL) until gas evolution was ceased. The mixture was stirred for 30 min at room temperature then a solution of pyridine dicarbonyl dichloride (1.0 g, 4.9 mmol) in 20 mL THF was added dropwise. The solution was stirred an additional 1 h and then diluted with 50 mL THF. The mixture was washed with 100 mL 25% NaOH, H₂O and dried (Na₂SO₄). The solvent was evaporated to dryness and the resulting brown solid was chromatographied on silica (ethyl

acetate/hexane=5/5). Yield 0.11g (8%); ¹H NMR (CDCl₃) δ 10.65 (bs, 2H, N-H), 8.36 (d, 2H, J=8.0 Hz, Ar-3,5-H), 8.12 (t, 1H, J=8.0 Hz, Ar-4-H), 7.49-7.46 (m, 2H, pyrrole-H), 7.13-7.12 (m, 2H, pyrrole-H), 6.42-6.37 (m, 2H, pyrrole-H).

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Activated Zirconium Metal Powder Prepared by Reduction of Zirconium(IV) chloride with Lithium Promoted Coupling of Aldehydes, Ketones and Organic Halides

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Within the area of metal catalyzed or promoted organic reactions, an increasing interest is centered to the use of highly reactive metal powders which are prepared simply by the treatment of metal halides with a group I or group II elements.[1]

Although activated metal powders (Ni,[2] Zn,[1a,3] W,[4] U,[5] Th,[6] Ce,[7] Tl,[8] Cu,[9] Ti,[10] Mn[11]) prepared by this method have been employed for the reductive coupling of ketones,[10] benzoyl chloride,[12] aldehydes[13] and organic halides,[2,3,5,8,9,11] no successful examples for the use of zirconium metal to reductive coupling of carbonyls and organic halides have been reported so far. In a previous communication, we reported that activated nickel catalyzed hydrosilylation of olefin with chlorosilane[14,15] and activated metal reduced nitroarenes.[16] In this paper we describe in detail the preparation of activated zirconium slurries by the reduction of zirconium tetrachloride with lithium and the reaction of the resulting metal

slurries with a aldehydes, ketones and alkyl halides.

The results of coupling reaction using activated zirconium metal powders are summarized in the Table 1. High yields and mild reaction conditions are the obvious advantage of this method. Interestingly, commercially available zirconium powder was inert for the coupling reaction (run 2). Aryl and benzyl halides coupled to give the corresponding coupling products in high yields with stirring at room temperature (run 6-9). These results show that yields are comparable to or greater than those from the cases using ordinary metals.[17] Coupling reaction of benzal chloride with activated zirconium proceeded smoothly at room temperature to give only *trans*-stilbene in 85% yield (run 10). Benzaldehyde also coupled to give only *trans*-stilbene (run 1) and *p*-anisaldehyde coupled to give only *trans*-1,2-bis(4-methoxyphenyl)ethylene (run 3). Acetophenone coupled to give a mixture of *cis* and *trans*-2,3-diphenyl-2-butene along

Notes

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Table 1. Coupling of Aldehydes, Ketones and Organic Halides with Activated Zirconium[a]

Run	Metal Activation	Substrates	Reaction Condition	Results and Yields (%, isolated)
1	ZrCl₄/Li, DME, stir, 1h	C₆H₅CHO	DME, reflux, 5h	trans-C₆H₅CH=CHC₆H₅ (86)
2	Zr[b]	C₆H₅CHO	DME, reflux, 5h	No reaction
3	ZrCl₄/Li, DME, stir, 1h	p-CH₃OC₆H₄CHO	DME, reflux, 5h	trans-1,2-Bis(4-methoxyphenyl)ethylene (78)
4	ZrCl₄/Li, DME, stir, 1h	C₆H₅COCH₃	DME, reflux, 6h	C₆H₅CH₃C=CC₆H₅CH₃ (cis, 11, trans 81)[c] CH₃CH(C₆H₅)CH(C₆H₅)CH₃ (8)[c]
5	ZrCl₄/Li, DME, stir, 1h	Cyclohexanone	DME, reflux, 10h	Bicyclohexylidene (43)[c]
6	ZrCl₄/Li, DME, stir, 1h	C₆H₅Br	DME, stir, 3h	Biphenyl (90)
7	ZrCl₄/Li, DME, stir, 1h	C₆H₅Cl	DME, stir, 3h	Biphenyl (86)
8	ZrCl₄/Li, DME, stir, 1h	C₆H₅CH₂Br	DME, stir, 3h	C₆H₅CH₂CH₂C₆H₅ (88)
9	ZrCl₄/Li, DME, stir, 1h	C₆H₅CH₂Cl	DME, stir, 3h	C₆H₅CH₂CH₂C₆H₅ (93)
10	ZrCl₄/Li, DME, stir, 1h	C₆H₅CHCl₂	DME, stir, 3h	trans-C₆H₅CH=CHC₆H₅ (85)
11	ZrCl₄/Li, DME, stir, 1h	C₆H₅COCl	DME, stir, 3h	C₆H₅COCOC₆H₅ (50)[c]
12	ZrCl₄/Li, DME, stir, 1h	C₆H₅COCOC₆H₅	DME, stir, 3h	No reaction
13	ZrCl₄/Li, DME, stir, 1h	n-CH₃(CH₂)₆CH₂Br	DME, stir, 3h	n-CH₃(CH₂)₁₄CH₃ (88)[c,d]

[a] After stirring a mixture of ZrCl₄ (4 mmol), Li (16 mmol) and 5 mL of dimethoxyethane (DME) under nitrogen atmosphere for 1 h, organic substrates (4 mmol) were injected and refluxed (see experimental for details). [b] Commercially purchased zirconium powder (Aldrich Chemicals) was used. [c] GC yields. [d] n-Octane was also formed in 12% yield by GC.

with 2,3-diphenylbutane (run 4). However, cyclohexanone gave coupling product in only 43% after refluxed for 10 h (run 5). Benzoyl chloride also coupled to give benzil in 60% under stirring for 3 h and yield was not improved with longer reaction time or reflux (run 11). However, benzil was not reduced by activated zirconium powder (run 12). n-Octyl bromide afforded the corresponding coupled product along with n-octane (run 13). Attempts to crossed coupling reaction of benzyl chloride and benzoyl chloride resulted in the homo coupling products as a major product. Analysis by GC showed that benzyl phenyl ketone was formed only 3% yield. It should be noted that THF was not so good solvent as DME due to decomposition during reduction. To gain some insight into the mechanism, a mixture of benzyl chloride and trimethyl chlorosilane was added to activated zirconium solution and stirred at room temperature for 3 h. Bibenzyl was only isolated and no trapping product such as benzyltrimethylsilane was formed. Therefore, Grignard type of intermediate (PhCH₂ZrCl) may not be involved for this unusual coupling reactions at this stage. This unexpected reactivity of activated zirconium metal powders in the coupling reaction to form the carbon-carbon bond formation may be due to the high surface area, some unique species, or a combination of both.[18]

In conclusion, we have demonstrated that activated zirconium metal can catalyze the coupling reaction of aldehydes, ketones and organic halides under mild reaction condition. We are presently exploring the abilities of this kind of activated metal slurries to a variety of functional group and these will be reported in due course.

Experimental

Anhydrous metal halides and alkyl halides were purchased from Aldrich, Junsei, Yakuri, Gelest. Tetrahydrofuran (THF) and dimethoxyethane (DME) were refluxed over sodium metal and benzophenone until the deep blue color of benzophenone ketyl was observed, then distilled just prior to use. High quality hydrocarbon solvents such as

hexane or pentane were obtained by stirring the sulfuric acid for 3 days followed by distillation. Lithium powder (99%) was purchased from Aldrich Chemicals. ¹H NMR were obtained on a Bruker AC 80 spectrometer. Chemical shifts were reported in ppm downfield from TMS and coupling constant were obtained from first order analysis of the spectra. Infrared spectra were taken on a Jasco-A-1. Mass spectra (70 eV electron impact) were taken on a Finnigan 4510 instrument equipped with a Finnigan-incos data system. GLC was done with a Varian 3300 instrument equipped with a FID detector and stainless steel column packed with 10% OV-101, Chromosob W HP 80/100 (2 m × 1/8 in). Flash column chromatography was carried out on Merck silica gel 60 (70-230 mesh). Thin layer chromatography was performed on silica gel plate (E. Merck, 60, No. 5539).

General procedure for the preparation of activated zirconium metal powders. In a nitrogen atmospheric glove box, a 100 mL two-neck round bottom flask, equipped with a magnetic stirrer and a condenser topped with a nitrogen inlet, was charged with 0.93 g (4 mmol) of ZrCl₄ and 0.11 g (16 mmol) of Li powder. 5 mL of freshly distilled dimethoxyethane (DME) was syringed into the flask. After stirring these reagents under a atmosphere nitrogen at room temperature for 1 h, the finely divided metal appeared as black powders which settled in a dark solution. The activated zirconium in a dark solution was used in this investigation without any further treatment.

Typical Experiment: Coupling reaction of benzaldehyde was illustrated. To the above mentioned activated metal slurry was injected 0.64 g (4 mmol) of benzaldehyde. The mixture was refluxed under nitrogen for 5 hr. The resulting solution was then allowed to cool to room temperature and hexane was added. The mixture became clear along with the catalyst settled down at the bottom. The solution was filtered to remove the catalyst through a pad of silica gel column (1 cm dia × 5 cm packed) using hexane-methylene chloride (1 : 1, v/v) as an eluent. Removal of the solvent under reduced pressure gave 0.31 g

(86%) of *trans*-stilbene, mp 123.5-124 °C (lit.[19] 124 °C). *cis*-Stilbene (liquid) was not detected by GC. The yields are based on quantities obtained after this step. Some physical properties of the products are as follows.

trans-1,2-Bis(4-methoxyphenyl)ethylene: mp 209-211 °C. ^{1}H NMR (CDCl$_3$) δ 7.4 (d, *J*=8.8 Hz, 4H), 6.9 (d, *J*=8.8 Hz, 4H), 6.9 (s, 2H), 3.61 (s, 6H). GC/Mass; 240 (M⁺, 100), 225 (64), 182 (13), 165 (32), 153 (26), 120(11), 89(7). 1,6-Diphenyl-1,3,5-hexatriene: mp 192-195 °C (lit.[42]; 199-203 °C); ^{1}H NMR (CDCl$_3$) 7.41-7.24 (m, 10H), 6.80-6.56 (m, 6H). GC/Mass; 232 (M⁺, 100), 215 (17), 191 (7), 141 (43), 128 (36), 115 (32), 91 (55). *cis*-2,3-Diphenyl-2-butene GC/Mass; 208 (M⁺, 100), 193 (94), 178 (57), 165 (19), 115 (47), 91 (19), 77 (13). *t*-2,3-Diphenyl-2-butene: GC/Mass; 208 (M⁺, 100), 193 (95), 178 (58), 165 (15), 115 (49), 91 (23), 77 (19). 2,3-Diphenylbutane: GC/Mass; 210 (M⁺, 49), 119 (15), 105 (100), 91 (58), 77 (13). Bicyclohexylidene: GC/Mass; 164 (M⁺, 42), 149 (5), 135 (11), 121 (15), 107 (16), 93 (27), 124 (27), 82 (100), 67 (82), 55 (45), 41 (45).

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Photochemical Formation of Hydrazine in Aqueous Ammonia

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Although ammonia is one of the most important precursors producing nitrogen containing compounds, ammonia with foul oder, generated from decomposition of a large amount of garbage, causes a serious environmental pollution. Therefore, decomposition of ammonia has attracted considerable attention in respect to environmental pollution of the atmosphere. Large number of investigations on the decomposition of gaseous ammonia have been thus reported by means of radiolysis[1] and photolysis.[2-9] Very recently, we

have described the photochemical decomposition of aqueous ammonia in the absence and presence of oxygen.[10] It was found from the study that hydrazine was produced by the dimerization of NH$_2$ radicals. Hydrazine can be used as a reducing agent and as a raw material for chemical syntheses. Consequently, it is interesting to study quantitatively on the photochemical formation of hydrazine under various experimental conditions. In aqueous ammonia solution, NH$_{3(aq)}$, NH$_4^+{}_{(aq)}$, OH$^-{}_{(aq)}$ and H$_2$O species exist and