SHORT PAPER

A novel method for pinacolic coupling of aromatic aldehydes and ketones with a Sm–ZnCl$_2$ system[†]

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Sm–ZnCl$_2$-system-mediated reductive coupling of aromatic aldehydes and ketones in THF–H$_2$O at room temperature affords the corresponding pinacols in moderate to good yields.

A very useful method for constructing carbon–carbon bond is the reductive coupling of carbonyl compounds to give pinacols and olefins.[1] The corresponding pincols can be used as intermediates for the preparation of ketones and olefins.[2] Generally, the reaction is performed by treatment of carbonyl containing compounds with an appropriate metal reagent to give the corresponding coupled product. A number of different types of metal reagents have been used to carry out the pinacol reaction. For instance, reaction with A1,[3] Ce–I$_2$,[4] Fe (CO)$_5$/pyridine,[5] Mg/MgI$_2$,[6] NbCl$_3$,[7] SmI$_2$,[8] TiCl$_4$/Zn,[9] Me$_3$SiSiMe$_3$,[10] VCl$_3$/Zn,[11] Yb,[12] and Cp$_2$Zr (Me) Cl/Me$_3$ SnLi[13]. The disadvantages of such procedures are that they have to be carried out at low temperature and under an inert gas atmosphere, since the active regents are sensitive to oxygen and the reaction with the reagents at high temperature gives an olefin. Herein, we report that a Sm–ZnCl$_2$ system promotes pinacolic coupling of aromatic aldehydes and ketones in a THF–H$_2$O mixed solvent.
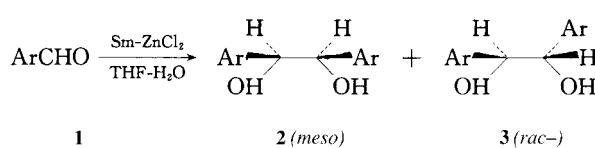
Scheme 1

Table 1 shows that the aromatic aldehydes are reduced by Sm–ZnCl$_2$ in the THF–H$_2$O to give the corresponding pinacols in moderate to good yields (entry 1–9). In our experiments, the optimum conditions were found when a mixture of *p*-chlorobenzaldehyde, samarium powder and zinc dichloride in 10% aqueous THF was stirred for 2h at room temperature; the pinacol was obtained in 83%. When the coupling reaction of *p*-chlorobenzaldehyde with Sm–ZnCl$_2$ was carried out at room temperature for 2h in THF containing 50, 20, 10 and 0% water respectively, the ratios of *rac/meso*[14] were 38 : 62, 30 : 70, 21 : 79, 33 : 67 respectively. However, the reason of the effect of water on the ratio of *rac/meso* is not clear yet. It is worthy of note that steric hindrance around the carbonyl group does affect the yield (**9**).

The coupling reaction of aromatic ketone (**4**) with Sm–ZnCl$_2$ was more selective and the corresponding pinacols were obtained in good yields (Table 2). In this case, the reaction can be completed within a shorter time.
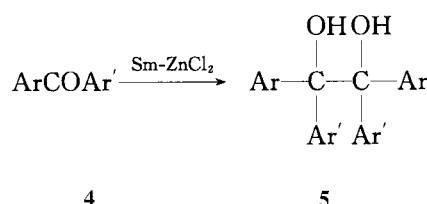
Scheme 2

The Sm–ZnCl$_2$ reagent is also effective for the coupling of acetophenone derivatives (**6**) and their coupling reaction products (**7**) were obtained in good yield (Table 3).

Table 1 Reductive coupling reaction of aromatic aldehydes using a Sm–ZnCl$_2$ system

Entry	Substrate	Yield (%)[a]	*meso : rac*[b]
1	C$_6$H$_5$CHO	78	25 : 75
2	*p*-ClC$_6$H$_4$CHO	83	21 : 79
3	*p*-CH$_3$C$_6$H$_4$CHO	82	36 : 64
4	*p*-CH$_3$OC$_6$H$_4$CHO	92	28 : 72
5	*o*-BrC$_6$H$_4$CHO	83	27 : 73
6	*m*-BrC$_6$H$_4$CHO	80	25 : 75
7	*p*-BrC$_6$H$_4$CHO	87	30 : 70
8	3,4-(OCH$_2$O)C$_6$H$_3$CHO	85	25 : 75
9	[Cl-substituted aryl]CHO	75	33 : 67
10	C$_6$H$_5$CH$_2$CHO	Reduction	
11	[cyclohexanone structure]=O	Reduction	

[a]Isolated yields of pinacol. [b]Ratios determined by ^{1}H NMR.

Table 2 Reductive coupling reaction of diaromatic ketone (**4**) using Sm–ZnCl$_2$ in 10% aqueous THF

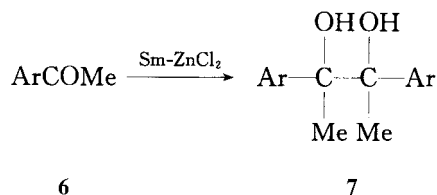| **4**		Reaction	Yield of
Ar	Ar′	time (h)	**5** (%)[a]
C$_6$H$_5$	C$_6$H$_5$	0.5	72
p-CH$_3$C$_6$H$_4$	*p*-CH$_3$C$_6$H$_4$	0.5	73
p-CH$_3$OC$_6$H$_4$	C$_6$H$_5$	0.5	77[b]

[a]Isolated yield of pinacol. [b]The ratio of *rac-/meso* was not determined.

Table 3 Reductive coupling reaction of acetophenone derivative using Sm–ZnCl$_2$ in THF–H$_2$O

6	Reaction time (h)	Yield of **7** (%)[a]	*meso : rac*[b]
C$_6$H$_5$	2	72	40 : 60
p-BrC$_6$H$_4$	2	78	35 : 65

[a]Isolated yield of pinacol. [b]Ratio was determined by ^{1}H NMR.

It is proposed that the reaction may proceed *via* a single electron transfer, with the active zinc (the black suspension) supplying the electrons to organic substrates. Another possible pathway may involve the surface of samarium. No reaction was observed with either samarium or zinc dichloride alone. The amount of samarium powder is important. When benzaldehyde was stirred with 1 equiv. or samarium powder in 10% aqueous THF for 2h at room temperature, 35% of the corresponding pinacol was isolated. When 3 equiv. of samarium powder was used, the isolated yield of pinacol was increased to 78%.

$$\text{ArCOMe} \xrightarrow{\text{Sm-ZnCl}_2} \overset{\displaystyle \text{OH OH}}{\underset{\displaystyle \text{Me Me}}{\text{Ar}-\text{C}-\text{C}-\text{Ar}}}$$

6   7

Scheme 3

In conclusion, it is clear that the coupling method with Sm–ZnCl$_2$ is effective, simple and has many advantages in comparison to usual methods.

Experimental

^{1}H NMR spectra were recorded on a Bruker AC 80 (80MHz) instrument. All NMR samples were measured in CDCl$_3$ using TMS as internal standard. IR spectra were obtained on a Perkin-Elmer 683 spectrophotometer as KBr plates. Elemental analyses were carried out on Carlo Erba 1106 analyser. Metallic samarium, zinc dichloride, aromatic aldehydes and ketones, and tetrahydrofuran were purchased from commercial sources and used without purification.

General procedure with Sm–ZnCl$_2$ system: A mixture of aromatic aldehyde (1 mmol), samarium powder (3 mmol), zinc dichloride (1 mmol), THF 9 ml and H$_2$O 1 ml was stirred at room temperature for 2h. Dilute hydrochloric acid (1N, 10 ml) and diethyl ether (20 ml) were added. The organic layer was separated and the aqueous layer was extracted with diethyl ether (20 ml). The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$ and the solvent was removed under reduced pressure. The residue was then purified by preparative TLC on silica gel with petroleum ether/diethyl ether (7 : 3) as eluent. The structure of the products were determined by ^{1}H NMR, IR and elemental analyses.

1,2-Diphenyl-1,2-ethanediol (rac- and meso)[15]: ^{1}H NMR (δ_H) 2.49 (s, 2H, OH, this signal disappeared by adding D$_2$O), 4.69 (s, *rac*-) and 4.75 (s.*meso*), 7.05–7.46 (m, 10H); IR v$_{max}$/cm^{-1} 3100–3500, 3080, 3040, 2920, 1600, 1500, 1450, 1390, 1280, 1020, 1000, 920, 840, 750, 680.

1,2-Di(4-chlorophenyl)-1,2-ethanediol (rac- and meso)[16]: ^{1}H NMR (δ_H) 2.85 (s, 2H, OH, this signal disappeared by adding D$_2$O), 4.45 (s, *rac*) and 4.60 (s, *meso*), 6.75–7.35 (m, 8H); v$_{max}$/cm^{-1} 3200–3580, 3080, 3040, 2995, 2960, 2920, 2860, 1600, 1580, 1480, 1440, 1200, 1120, 1020, 900, 740, 650.

1,2-Di(4-methylphenyl)-1,2-ethanediol (rac- and meso)[15]: ^{1}H NMR (δ_H) 2.14 (6H, s, 2Me), 3.13 (s. 2H, OH, this signal disappeared by adding D$_2$O), 4.48 (s, *rac*) and 4.58 (s, *meso*), 6.75–7.32 (m, 8H); IR v$_{max}$/cm^{-1} 3100–3600, 3080, 3040, 2940, 1600, 1580, 1540, 1490, 1440, 1380, 1270, 1200, 1110, 1020, 850, 820, 770, 720, 640.

1,2-Di(4-methoxyphenyl)-1,2-ethanediol (rac- and meso)[17]: ^{1}H NMR (δ_H) 2.90 (s, 2H, OH, this signal disappeared by adding D$_2$O), 3.78 (s, 6H), 4.55 (s, *rac*) and 4.70 (s, *meso*), 6.60–7.30 (m, 8H); IR v$_{max}$/cm^{-1} 3100–3600, 3080, 3040, 2940, 1600, 1540, 1490, 1440, 1380, 1270, 1200, 1110, 1020, 850, 820, 770, 720, 640.

1,2-Di(2-bromophenyl)-1,2-ethanediol (rac- and meso)[18]: ^{1}H NMR (δ_H) 2.90 (s, 2H, OH, this signal disappeared by adding D$_2$O), 4.55 (s, *rac*) and 4.65 (s, *meso*), 6.60–7.58 (m, 8H); IR v$_{max}$/cm^{-1} 3100–3600, 3080, 3040, 2990, 2960, 2920, 2860, 1600, 1580, 1485, 1440, 1205, 1120, 1020, 900, 740, 645.

1,2-Di(3-bromophenyl)-1,2-ethanediol (rac- and meso)[18]: ^{1}H NMR (δ_H) 2.90 (s, 2H, OH, this signal disappeared by adding D$_2$O), 4.55 (s, *rac*) and 4.65 (s, *meso*), 6.60–7.50 (m, 8H); IR v$_{max}$/cm^{-1} 3100–3600,

3080, 3040, 2990, 2960, 2920, 2860, 1600, 1580, 1480, 1440, 1200, 1120, 1020, 900, 740, 645.

1,2-Di(4-bromophenyl)-1,2-ethandeiol (rac- and meso)[16]: ^{1}H NMR (δ_H) 2.45 (s, 2H, OH, this signal disappeared by adding D$_2$O), 4.52 (s, *rac*) and 4.70 (s, *meso*), 6.70–7.70 (m, 8H); IR v$_{max}$/cm^{-1} 3100–3600, 3080, 3050, 3020, 2960, 2890, 1580, 1500, 1450, 1200, 1065, 1020, 900, 760, 690, 620.

1,2-Di(3,4-methylenedioxyphenyl)-1,2-ethanediol (rac- and meso)[4]: ^{1}H NMR (δ_H) 2.50 (s, 2H, OH, this signal disappeared by adding D$_2$O), 4.55 (s, *rac*) and 4.75 (s, *meso*), 6.30 (4H, s, OCH$_2$O), 6.95–7.75 (m, 6H, ArH); IR v$_{max}$/cm^{-1} 3100–3600, 3080, 2940, 1600, 1540, 1490, 1440, 1270, 1200, 1110, 1020, 860, 770.

1,2-Di(2,6-dichlorophenyl)-1,2-ethanediol (rac- and meso): ^{1}H NMR (δ_H) 2.74 (s, 2H, OH, this signal disappeared by adding D$_2$O), 4.49 (s, *rac*) and 4.70 (s, *meso*), 6.90–8.00 (m, 6H, ArH); IR v$_{max}$/cm^{-1} 3100–3600, 3080, 3040, 2990, 2960, 2860, 1600, 1580, 1480, 1440, 1220, 1120, 1020, 900, 760. Anal Calcd for C$_{14}$H$_{10}$O$_2$Cl$_4$, C 47.73, H 2.84; Found C 47.85, H 2.97.

Tetraphenyl-1,2-ethanediol[13]: ^{1}H NMR (δ_H) 2.74 (s, 2H, OH, this signal disappeared by adding D$_2$O), 7.10–7.64 (m, 20H, ArH); IR v$_{max}$/cm^{-1} 3500–3600, 3030, 1490, 1440, 1300, 1150, 1030, 750, 730, 690.

Tetra (4-methylphenyl)-1,2-ethanediol[13]: ^{1}H NMR (δ_H) 2.17 (s, 12H, 4Me), 3.20 (s, 2H, OH, this signal disappeared by adding D$_2$O), 7.01–7.70 (m, 16H, ArH); IR v$_{max}$/cm^{-1} 3500–3600, 3080, 3030, 1580, 1490, 1440, 1380, 1270, 1150, 1020, 750, 750, 720, 690.

1,2-Diphenyl-1,2-di(40methoxyphenyl)-1,2-ethanediol (rac and meso): ^{1}H NMR (δ_H) 3.15 (s, 12H, 4Me), 3.20 (s, 2H, OH, this signal disappeared by adding D$_2$O), 3.80 (m, 6H, 2CH$_3$O), 6.68–7.45 (m, 18H, ArH); IR v$_{max}$/cm^{-1} 3500–3600, 3080, 3040, 2940, 1600, 1450, 1490, 1440, 1380, 1270, 1200, 1110, 1020, 850, 820, 770, 720, 690. Anal Calcd for C$_{28}$H$_{26}$O$_4$, C 78.87, H 6.10; Found C 79.07, H 6.27.

2,3-Diphenyl-2,3-butanediol (rac and meso)[17]: ^{1}H NMR (δ_H) 1.48 (s, *rac*) and 1.58 (s, *meso*), 2.47 (s, 2H, OH, this signal disappeared by adding D$_2$O), 7.10–7.40 (m, 10H); IR v$_{max}$/cm^{-1} 3100–3600, 3080, 3040, 2990, 2940, 2890, 2860, 1600, 1500, 1480, 1420, 1380, 1200, 1100, 1020, 900, 850, 760.

2,3-Di(4-bromophenyl)-2,3-butanediol (rac and meso)[19]: ^{1}H NMR (δ_H) 1.48 (s, *rac*) and 1.58 (s, *meso*), (6H, 2Me), 2.47 (s, 2H, OH, this signal disappeared by adding D$_2$O), 6.70–7.70 (m, 8H); IR v$_{max}$/cm^{-1} 3100–3600, 3080, 3050, 2970, 2960, 2890, 1580, 1500, 1460, 1380, 1200, 1100, 1020, 900, 870, 690, 620.

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