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Reduction and Coupling Reactions of Carbonyl Compounds Using Samarium Metal in Aqueous Media

Sanjay Talukdar and Jim-Min Fang*

Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, Republic of China

jmfang@mail.ch.ntu.edu.tw

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Direct use of metallic Sm as a reducing agent in organic transformations has drawn chemists' attention.[1] Such reactions are generally performed in THF. For example, alkyl iodides are reduced to alkanes by Sm in THF.[2a] Barbier reaction of 2-(3-iodopropyl)cycloheptanone with Sm in THF occurs intramolecularly to give a bicyclic alcohol.[2b] Iodomethylations of carbonyl compounds are achieved by treatment with Sm and CH_2I_2 in THF.[2c]

Since water is an environmentally benign medium, we wish to explore further the reactions of carbonyl compounds with Sm in aqueous media.[3] Sm is quite stable in water even though it has a high reduction potential ($Sm^{3+}/Sm = -2.41$ V).[4]

There are several methods[2,5] for activation of Sm metal such as amalgamation using I_2, HCl, and alkyl halides. Cyclopropanations of esters, α-halo ketones, and allylic alcohols are realized by using Sm(Hg)/ICH_2Cl or Sm/$HgCl_2$/ICH_2Cl in THF.[2d,e] Sm with a catalytic amount of I_2 in THF is used in the reductive coupling reactions of *N*-alkylideneanilines, giving vicinal diamines.[2f] Deoxygenative coupling reactions of benzamides, giving 1,2-diaminostilbenes, are carried out by using Sm with a catalytic amount of SmI_2 in THF.[2g] A minute amount of water is found to accelerate the pinacolic coupling reactions of aromatic carbonyl compounds mediated by Sm/Me_3SiCl in THF.[5a] Reductions of nitrobenzene,[5b] 1,2-dibromoalkanes,[5c,d] benzoic acid derivatives,[5e] and pyridines[5f] have been realized by using Sm/I_2 or Sm/HCl_{aq} in MeOH. Pinacolic coupling reactions of aromatic ketones have been achieved by using Sm with alkyl halides in MeOH.[5g] The expected Barbier-type addition products are not found.[5g]

Our study was initiated by examining the reactivity of 4-bromobenzaldehyde (**1b**) with Sm in aqueous media (Table 1). The Sm ingot was abraded (by a file) to give shining powders for the present study. Treatment of **1b** with Sm (1.2 molar proportions) in H_2O/THF (5:1) for 72 h afforded very low yields of pinacol **2b** (3%) and alcohol **3b** (2%) accompanied by a 95% recovery of **1b**. The residual Sm had tarnished by the end of the reaction. The reaction was not significantly improved by sonication or by using an excessive amount of Sm (entries 2 and 3, Table 1).

We thus searched for appropriate activators to enhance the reactivity of Sm in aqueous media.[2,5,6] Indeed, treatment of **1b** with Sm (3 molar proportions) in the presence of $HgCl_2$ (1.5 molar proportions) gave much higher yields of pinacol **2b** (48%) and alcohol **3b** (38%) in H_2O/THF media (entry 4, Table 1). Iodine was also an effective activator of Sm (entries 6−8).[2f] By using Sm (3 molar proportions) with I_2 (0.75 molar proportions), **1b** was completely converted in 16 h to give equal amounts of **2b** and **3b**. Preferable formation of pinacol **2b** over alcohol **3b** was realized by using Sm in saturated NH_4Cl/THF (5:1) or with $FeCl_3$ activation (entries 9 and 10, Table 1). The bromine atom of **1b** was retained in all of these reaction conditions.

After a comprehensive survey on the optimization of reaction conditions, we found that the reaction in aqueous HCl solution (2 M)[5d−f] produced an 88% yield of pinacol **2b** in a chemoselective manner (entry 12, Table 1). Thus, Sm (3 molar proportions) was added in several portions to a suspension of **1b** (1 mmol) in 2 M HCl/THF (5:1) over a period of 1 h at room temperature. Upon addition of Sm powders, a transient purple color and hydrogen evolution were observed. The reaction mixture was continuously stirred without rigorous exclusion of oxygen. It required 32 h for the consumption of 4-bromobenzaldehyde as shown by TLC analyses. The media became transparent at the end of the reaction, and no residue of Sm particles remained. The reaction did not proceed to completion if the amount of Sm was less than 1.2 molar proportions. A considerable portion of starting material **1b** was recovered if the reaction was conducted by addition of aqueous HCl solution to the suspension of **1b** and Sm in THF (entry 13, Table 1). The reaction in aqueous HBr was less chemoselective (entry 14, Table

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* To whom correspondence should be addressed. Fax: (886-2)-2363-6359.

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Table 1. Reactions of 4-Bromobenzaldehyde (1b, 1 mmol) with Samarium in Various Conditions[a]

entry	Sm (mmol)	reaction medium, additive (mmol)	reaction time (h)	pinacol **2b**[b] (yield, %) (*dl*/*meso*)	alcohol **3b**[b] (yield, %)	recovery of **1b**[b] (%)
1	1.2	H_2O/THF[c]	72	3 (54:46)	2	95
2[d]	1.2	H_2O/THF[c]	32	6 (50:50)	<2	92
3	3.0	H_2O/THF[c]	48	3 (55:45)	2	95
4	1.2	H_2O/THF,[c] $HgCl_2$ (0.6)	48	8 (61:39)	4	88
5	3.0	H_2O/THF,[c] $HgCl_2$ (1.5)	36	48 (38:62)	38	14
6	1.2	H_2O/THF,[c] I_2 (0.6)	32	22 (50:50)	19	59
7	3.0	H_2O/THF,[c] I_2 (0.75)	16	50 (40:60)	50	0
8	3.0	H_2O/THF,[c] I_2 (1.5)	36	42 (45:55)	41	17
9	3.0	H_2O/THF,[c] $FeCl_3$ (1.5)	36	71 (48:52)	12	0
10	3.0	satd. NH_4Cl/THF[c]	36	66 (50:50)	20	14
11	1.2	2 M HCl/THF[c]	32	53 (33:66)	4	42
12	3.0	2 M HCl/THF[c]	32	88 (36:64)[e]	5	0
13[f]	3.0	2 M HCl/THF[c]	32	40 (49:51)	4	56
14	3.0	2 M HBr/THF[c]	32	77 (47:53)[e]	14	0
15[g]	3.0	2 M HI/THF[c]	32	<2		0

[a] The reaction was conducted at room temperature by addition of Sm in several portions over a period of 1 h to the suspension of **1b** in the indicated medium. [b] Except for entries 12 and 14, the data for **1b**, **2b**, and **3b** were calculated on the basis of ^1H NMR spectral analysis of the crude product mixture. [c] The ratio of water (or aqueous solution) to THF is 5:1 (v/v). [d] Irradiation in an ultrasonic bath (35 kHz). [e] The isolated yields are reported. [f] The HCl solution was added in several portions to the suspension of Sm and 4-bromobenzaldehyde in THF. [g] The reaction gave many unidentified products.

Table 2. Reactions of Aromatic Carbonyls (1 mmol) with Samarium (3 mmol) in 2 M HCl/THF (5:1) at 20 °C (1−3 days)

entry	substrate	pinacol[a] (yield, %) (*dl*/*meso*)	alcohol[a] (yield, %)
1	PhCHO (**1a**)	**2a** (80) (48:52)	**3a** (18)
2	4-BrC_6H_4CHO (**1b**)	**2b** (88) (36:64)	**3b** (5)
3	4-PhC_6H_4CHO (**1c**)	**2c** (75) (92:8)	**3c** (5)
4	3-$CF_3C_6H_4CHO$ (**1d**)	**2d** (92) (58:42)	
5	4-NCC_6H_4CHO (**1e**)	**2e** (79) (52:48)	**3e** (14)
6	4-$MeO_2CC_6H_4CHO$ (**1f**)	**2f** (46) (57:43)[b]	**3f** (2)
7	2-$O_2NC_6H_4CHO$ (**1g**)	no reaction[c]	
8	3-$O_2NC_6H_4CHO$ (**1h**)	no reaction[c]	
9	4-MeC_6H_4CHO (**1i**)	**2i** (83) (51:49)	**3i** (10)
10	4-$MeOC_6H_4CHO$ (**1j**)	**2j** (84) (12:88)	**3j** (2)
11	2-HOC_6H_4CHO (**1k**)	**2k** (60) (56:44)	**3k** (16)
12	PhCOMe (**1l**)	**2l** (92) (49:51)	**3l** (2)
13	PhCOEt (**1m**)	**2m** (85) (62:38)	**3m** (2)
14	4-$MeOC_6H_4COMe$ (**1n**)	**2n** (85) (64:36)	
15	2-MeC_6H_4COMe (**1o**)	**2o** (90) (49:51)	**3o** (2)
16	2-acetylnaphthalene (**1p**)	**2p** (94) (62:38)	
17	PhCOPh (**1q**)	**2q** (94)	

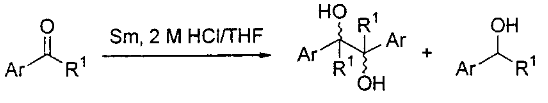
[a] The isolated yields are reported. The ratio of *dl* and *meso* isomers was determined by the ^1H NMR analysis of the crude product mixture. [b] The starting material **1f** was recovered (~50%). [c] The starting materials **1g** and **1h** were recovered (>95%).

Table 3. Reactions of Aliphatic Carbonyls (1 mmol) with Samarium (3 mmol) in 2 M HCl/THF (5:1) at 20 °C (18−28 h)

entry	substrate	alcohol[a] (yield, %) (cis/trans)
1	$CH_3(CH_2)_7CHO$ (**4a**)	**5a** (94)
2	$PhCH_2CHO$ (**4b**)	**5b** (87)
3	$Ph(CH_2)_2CHO$ (**4c**)	**5c** (95)
4	$PhCH(CH_3)CHO$ (**4d**)	**5d** (100)
5	$PhCH_2COMe$ (**4e**)	**5e** (95)
6	2-adamantanone (**4f**)	**5f** (94)
7	$MeCOCH_2COOBu^t$ (**4g**)	**5g** (97)
8	2-methylcyclohexanone (**4h**)	**5h** (89) (50:50)
9	2-*tert*-butylcyclohexanone (**4i**)	**5i** (85) (60:40)
10	2-methoxycyclohexanone (**4j**)	**5j** (87) (80:20)
11	4-*tert*-butylcyclohexanone (**4k**)	**5k** (90) (15:85)

[a] The isolated yields are reported. The ratio of cis and trans isomers was determined by the ^1H NMR analysis of the crude product mixture. No pinacols were detected in the crude product mixtures according to the ^1H and ^{13}C NMR analyses.

1), whereas many unidentified products complicated the reaction in aqueous HI (entry 15, Table 1).



(1)

1a–q **2a–q** (major) **3a–q** (minor)

Ar = Ph, YC_6H_4, naphthyl

R^1 = H, Me, Et, Ph

The protocol using Sm (3 molar proportions) in 2 M HCl/THF (5:1) was applied to the pinacolic coupling reactions of other benzaldehydes and aromatic ketones (eq 1 and Table 2). In most cases, high yields of pinacols were obtained as mixtures of *dl* and *meso* isomers under such reaction conditions.[7,8] The pinacolic coupling reaction of benzophenone was also successfully carried out by using Sm in aqueous media to give a 94% yield of benzopinacol (entry 17, Table 2). Unimolecular reduction, giving alcoholic products, was either a minor pathway or did not occur. Benzaldehydes bearing trifluoromethyl, cyano, or hydroxyl groups proceeded similarly to give pinacols **2d**, **2e**, and **2k** as the major products, respectively (entries 4, 5, and 11, Table 2). The reaction of **1f** bearing a methoxycarbonyl group was incomplete after 36 h (entry 6, Table 2), and nitrobenzaldehydes **1g** and

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(7) The real nature of reducing species in the Sm/HCl/H_2O/THF system was unclear. An initial reaction of Sm with aqueous HCl might generate $SmCl_3$, which might undergo disproportionation with excess of Sm to low-valent samarium species (SmCl, $SmCl_2$ or the corresponding hydroxides) as the reducing agent. See: (a) Moeller, T. In *Comprehensive Inorganic Chemistry*; Bailar, J. C., Emeleus, H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon Press: Oxford, Vol. 7, 1973; p 3599 and 3615. (b) Enemaerke, R. J.; Daasbjerg, K.; Skrydstrup, T. *Chem Commun.* **1999**, 343. (c) Fuchs, J. R.; Mitchall, M. L.; Shabangi, M.; Flowers, R. A., II. *Tetrahedron Lett.* **1997**, *38*, 8157. $SmCl_3$-catalyzed electrolyses of aromatic aldehydes and ketones in DMF or NMP also give pinacols. See: (d) Leonard, E.; Dunbach, E.; Pericho, J. *Chem. Commun.* **1989**, 276.

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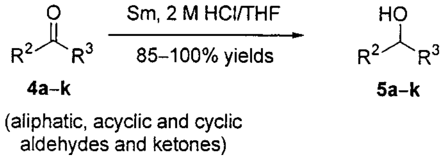
Table 4. Comparison of the Reactions of Carbonyl Compounds Using Sm Metal in Various Conditions: (i) Sm/2 M HCl/THF, (ii) Sm(Hg)/THF, (iii) Sm/Me_3SiCl/H_2O (trace), (iv) Sm/I_2/MeOH, (v) Sm/I_2/Ti(O*i*-Pr)$_4$/MeOH, (vi) Sm/Allyl Bromide/MeOH, (vii) Sm/THF/HMPA

substrates	reaction conditions	no. of examples	products (yield, %) pinacols	products (yield, %) alcohols	ref
benzaldehydes	i	7	75−92	0−18	this study
	ii	7	65−82		10a
	iii	5	78−83		5a
	iv	2	71 and 91	22 and 0	5c
	v	8	90−98	0−8	5c
$PhCH(OMe)_2$	i	1	98		this study
2-HOC_6H_4CHO	i	1	60	16	this study
	v	1	10	88	5c
acetophenones	i	3	85−92		this study
	ii	2	71−74		10a
	iii	1	80		5a
	iv	1	71	24	5c
	v	1	5	7	5c
	vi	5	50−69	0−11	5g
PhCOPh	i	1	94		this study
	v	1		18	5c
	vi	1	59		5g
	vii	1	62	31	10b
aliphatic aldehydes	i	4		87−100	this study
	iii	1	no reaction		5a
	iv	2		94−95	5c
aliphatic ketones	i	6		87−97	this study
	iii	1	no reaction		5a

1h were inert under such reaction conditions (entries 7 and 8, Table 2).

Unlike aromatic carbonyl compounds, the reactions of aliphatic aldehydes and ketones (**4a**−**k**) using Sm (3 molar proportions) in 2 M HCl/THF (5:1) gave exclusively the corresponding alcohols **5a**−**k** in very high yields (Table 3).[9] No reductive coupling products were formed



(2)

as shown by the ^1H NMR analyses. The reduction of *tert*-butyl acetoacetate gave a 97% yield of *tert*-butyl 3-hydroxybutanoate without hydrolysis or reduction of the ester group (entry 7, Table 3). The reduction of 2-methylcyclohexanone gave 2-methylcyclohexanol as a mixture of cis and trans isomers in equal amounts (entry 8, Table 3). In the reductions of 2-*tert*-butylcyclohexanone and 2-methoxycyclohexanone, the ratios of cis alcohol products **5i** and **5j** increased to 60% and 80%, respectively (entries 9 and 10, Table 3). The increase of stereoselectivity could be attributable to the steric effect of the neighboring *t*-Bu group and the chelation effect of methoxy group. However, the reduction of 4-*tert*-butylcyclohexanone afforded predominantly the thermodynamically stable trans isomer with the hydroxyl group on the equatorial position (entry 11, Table 3).

We can make a comparison of our current study with the previous reports (Table 4).[5,10] In addition to the reactions of carbonyl compounds in Sm/2 M HCl/THF (condition (i)), six other conditions have been applied: (ii) Sm amalgam in THF,[10a] (iii) Sm/Me_3SiCl with a trace amount of H_2O in THF,[5a] (iv) Sm/I_2 in MeOH,[5c] (v) Sm/I_2/Ti(O*i*-Pr)$_4$ in MeOH,[5c] (vi) Sm/allyl bromide/MeOH,[5g] and (vii) Sm in THF/HMPA.[10b] Benzaldehyde underwent pinacolic coupling reactions exclusively or predominantly in the reaction conditions (i)−(v). We also found that the dimethyl acetal of benzaldehyde reacted with Sm (3 molar proportions) in 2 M HCl/THF (5:1) gave pinacol **2a** in 98% yield as a mixture of *dl* and *meso* isomers (44:56). The reaction of 2-hydroxybenzaldehyde still gave pinacol **2k** as the major product (60%) by using our method, whereas unimolecular reduction occurred preferably by using Sm/I_2/Ti(O*i*-Pr)$_4$/MeOH to give 88% of benzyl alcohol.[5c] The reaction condition (v) using Sm/I_2/Ti(O*i*-Pr)$_4$/MeOH is ineffective for pinacolic couplings of acetophenone or benzophenone.[5c] The pinacolic coupling reaction of benzophenone can be accomplished by using Sm activated by HCl, allyl bromide or HMPA.[5g,10b] Our method using Sm/2 M HCl/THF is very efficient for unimolecular reduction of both aliphatic aldehydes and ketones. Use of Sm/I_2/MeOH can only reduce aliphatic aldehydes,[5c] whereas aliphatic carbonyls are inert in Sm/Me_3SiCl/H_2O.

In summary, Sm with aqueous HCl is an environmentally benign reducing agent by comparison with other activation methods requiring toxic Hg or HMPA. Our current method also showed several distinct features comparable or superior to conditions (ii)−(vii). Using of Sm/2 M HCl/THF, aromatic carbonyls including 4-hydroxybenzaldehyde and benzophenone underwent pinacolic coupling reactions in an efficient manner (Table 2).[11] Treatment of benzaldehyde dimethyl acetal with Sm/2

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[9] (a) Huffman, J. W. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 8, Chapter 1.4. Aldehydes and aromatic ketones, but not aliphatic ketones, are reduced to alcohols by using Fe/HOAc or Zn in alkaline solution. Aliphatic ketones are reduced by Na in EtOH or Na(Hg) in water under careful operation. The amalgams of Zn, Mg, Ni, Cu, Sn or Pb in aqueous THF are not effective in reductions of cyclohexanones. (b) According to ref 8b, cyclohexanecarbaldehyde is reduced by Al/KF in aqueous medium to give 10% of cyclohexylmethanol. However, cyclohexanone and 2-hexanone cannot be reduced by using Al with various fluoride salts. (c) Bordoloi, M. *Tetrahedron Lett.* **1993**, *34*, 1681. Aliphatic ketones are reduced by Mg/$CaCl_2$ in water.

[10] (a) Wang, L.; Zhang, Y. *Synth. Commun.* **1998**, *28*, 3991. (b) Hou, Z.; Takamine, K.; Aoki, O.; Shiraishi, H.; Fujiwara, Y.; Taniguchi, H. *J. Org. Chem.* **1988**, *53*, 6077. Treatment of benzaldehyde with Sm and a catalytic amount of C_2H_5I affords benzyl benzoate as a consequence of reduction and Tishchenko reaction. See: (c) Yokoo, K.; Mine, N.; Taniguchi, H.; Fujiwara, Y. *J. Organomet. Chem.* **1985**, *279*, C19.

M HCl/THF also yielded 1,2-diphenyl-1,2-ethanediol via a consecutive hydrolysis and pinacolic coupling reaction. On the other hand, unimolecular reductions of aliphatic aldehydes and ketones were accomplished in Sm/2 M HCl/THF (Table 3). 2-Methoxycyclohexanone was cleanly reduced in Sm/2 M HCl/THF to give 2-methoxycyclohexanol, although SmI_2 is known to cause a reductive cleavage of α-MeO group.[12] Reduction of *tert*-butyl acetoacetate in Sm/2 M HCl/THF afforded *tert*-butyl 3-hydroxybutanoate without attacking the ester group.

Experimental Section

Representative Procedure for the Reaction of Carbonyl Compounds with Samarium in Aqueous Media. To a suspension of 4-bromobenzaldehyde (**1b**, 185 mg, 1 mmol) in 2 M HCl/THF (5:1, 5 mL) was added Sm (450 mg, 3 mmol, freshly abraded from ingot) in several portions over a period of 1 h at room temperature. Upon addition of Sm powders, the medium turned purple but the color discharged instantly. Evolution of heat and hydrogen gas was obvious. The reaction mixture was continuously stirred without rigorous exclusion of oxygen. Complete consumption of 4-bromobenzaldehyde required 32 h, as shown by TLC analyses. The medium became transparent yellow solution, and no residue of Sm particles remained. The solution was neutralized and extracted with EtOAc/hexane (1:1). The organic phase was washed with brine, dried (Na_2SO_4) and concentrated in vacuo. The crude product mixture (176 mg) contained pinacol *dl*-**2b**, pinacol *meso*-**2b** and alcohol **3b** in a ratio of 34:60:6 according to the ^1H NMR analysis. Pure pinacols (164 mg, 88%) were obtained by crystallization from EtOAc/hexane (1:9).

The pinacols **2a**−**q** and alcohols **3a**−**q** and **5a**−**k** exhibited their IR, ^1H and ^{13}C NMR spectra consistent with those reported in the literature.

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[11] SmI_2 or Ce/I_2 in THF fail to conduct the pinacolic coupling reaction of benzophenone. See: (a) Kahn, B.; Rieke, R. D. *Chem. Rev.* **1988**, *88*, 733. (b) Furstner, A.; Csuk, R.; Rohrer, C.; Weidmann, H. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1729. (c) Imamoto, T.; Kusumoto, T.; Hatanaka, Y.; Yokoyama, M. *Tetrahedron Lett.* **1982**, *23*, 1353. Pinacolic coupling of benzophenone can be achieved by using $Yb/(C_6F_5)_2Hg$ in THF. See: (d) Deacon, G. B.; Tuong, T. D. *J. Organomet. Chem.* **1981**, *205*, C4.

[12] For C_α−O bond cleavage of α-alkoxy-, α-acetoxy-, and α-hydroxyketones by SmI_2, see: (a) Inanaga, J. *Heteroatom. Chem.* **1990**, *3*, 75. (b) Pratt, D. V.; Hopkins, P. B. *Tetrahedron Lett.* **1987**, *28*, 3065. (c) Molander, G. A.; Hahn, G. *J. Org. Chem.* **1986**, *51*, 1135. (d) White, J. D.; Somers, T. C. *J. Am. Chem. Soc.* **1987**, *109*, 4424. (e) Holton, R. A.; Williams, A. D. *J. Org. Chem.* **1988**, *53*, 5981.