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A new preparation of samarium dibromide and its use in stoichiometric and catalytic pinacol coupling reactions

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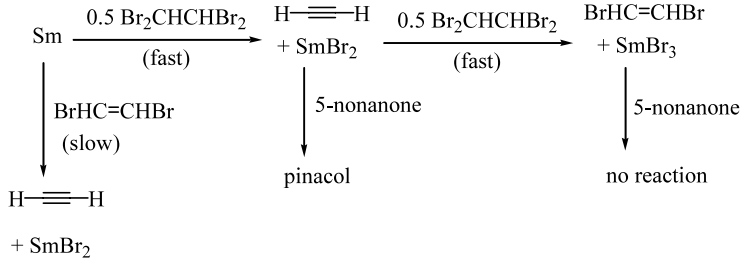
Abstract—A new convenient preparation of samarium dibromide in THF is reported. Pinacol coupling reactions using $SmBr_2$ in catalytic amounts together with mischmetall as a coreductant have been performed with a variety of carbonyl compounds.

1. Introduction

Intermolecular and intramolecular pinacol coupling reactions give an efficient way of forming carbon–carbon bonds.[1] Lanthanide metals have been used, sometimes in the presence of additives such as TMSCl or HMPA, to achieve in most cases coupling of aromatic ketones,[2] while divalent samarium compounds allow pinacolic coupling of aromatic as well as aliphatic ketones and aldehydes.[3–7] Although samarium diiodide has been widely employed in pinacolization, samarium dibromide seems to be a more powerful reagent.[8] Besides, we have recently reported that mischmetall (a cheap alloy of the light lanthanides used in large amounts for industrial applications) can act as a coreductant for catalytic reactions of some organic substrates with samarium diiodide.[9] This led us to examine the possibility of performing catalytic pinacol coupling reactions with samarium dibromide and mischmetall as a coreductant. A catalytic pinacolization has been previously reported with samarium diiodide, TMSCl as an additive and magnesium as a coreductant.[10] We have also described a catalytic pinacolization with samarium diiodide and mischmetall but this system is efficient only for aromatic ketones.[11]

2. Results and discussion

Before studying catalytic pinacolic coupling, we first tried to find an easy and reliable method of preparation of samarium dibromide. This compound can be prepared in several steps starting from samarium oxide or directly from samarium metal and 1,2-dibromoethane in THF.[12] However, the latter reaction usually needs a long induction time and small amounts of diiodoethane must be added to ensure reproducible results. To overcome this drawback, we attempted to use 1,1,2,2-tetrabromoethane instead of 1,2-dibromoethane. Mixing of samarium with one equivalent of $C_2H_2Br_4$ in THF resulted in a fast exothermic reaction, evolution of a



Scheme 1.

Keywords: pinacolic coupling; catalysis; 1,1,2,2-tetrabromoethane; mischmetall; samarium dibromide.
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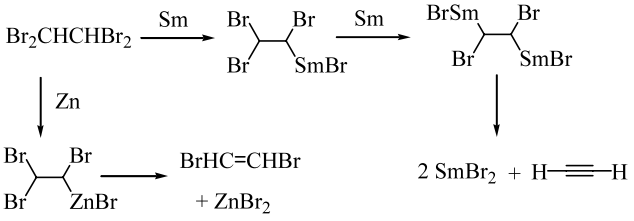
gas, and disappearance of samarium metal. A cream-coloured solid was formed which failed for the coupling of 5-nonanone into diol. It was identified as being samarium tribromide.[13] With half an equivalent of 1,1,2,2-tetrabromoethane a gas was also produced and a dark blue solid, which was slightly soluble in THF, was obtained. Its reaction with 5-nonanone furnished the expected diol in 87% isolated yield. These properties are quite in agreement with those of $SmBr_2$. The gas was identified as being acetylene by trapping with aqueous $Cu(NH_3)_2Cl$ (brick red cuprous acetylide was formed). In addition, we observed that Sm reacts slowly (within 3 days) at 20°C in THF with a mixture of 1,2-dibromoethene ($Z/E=20/80$) in THF affording samarium dibromide with evolution of acetylene.[14] Scheme 1 sums up the results.

The reaction of Sm with 1,1,2,2-tetrabromoethane clearly differs from that of Zn, which furnishes $ZnBr_2$ and a mixture of (*Z*)- and (*E*)-1,2-dibromoethene.[15] It can be assumed that Sm reacts with tetrabromoethane to give acetylene directly. Tentatively, the pathway depicted in Scheme 2 can be proposed.

Reaction of mischmetall with an excess of 1,1,2,2-tetrabromoethane in THF was also investigated. As with samarium an exothermic reaction occurred, but acetylene was given off slowly and 1,2-dibromoethenes were detected. A yellow solid, identified as a mixture of lanthanide tribromides,[13] was obtained after disappearance of the metal.



Scheme 2.

Samarium dibromide prepared from Sm and 0.5 equiv. tetrabromoethane in THF was next tested for the pinacolization of some representative carbonyl compounds, results are gathered in Table 1.

As expected, all reactions afford diols in good to excellent isolated yields, thus demonstrating the value of the preparation.[16]

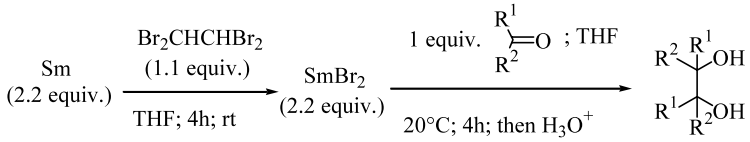
For economic reasons, it is highly desirable to develop methods that use the mixture of lanthanide metals. We considered then the possibility of performing catalytic pinacolizations using $SmBr_2$ in catalytic amounts and mischmetall as a coreductant.

In SmI_2 catalytic Barbier-type reaction, we had previously observed that a simple experimental procedure, which starts from a mixture of samarium metal and mischmetall treated by 1,2-diiodoethane gave excellent results.[9] Here we have used this methodology, changing the diiodide for the tetrabromide.

The results are collected in Table 2.

This procedure involving a mixture of Sm and mischmetall has allowed us to isolate diols in moderate to good yields. In some cases a slow addition of the carbonyl compound was necessary in order to allow regeneration of Sm(II) species thus preventing formation of by-products. With cyclohexanone and cyclopentanone a fast addition gave a complex mixture of products, which were formed in aldol-type reactions while with octanal a mixture of trioxanes arising from trimerization of the aldehyde was obtained (identified by GC–MS). This feature was not unexpected since it is known that these reactions are efficiently catalysed by lanthanide(III) species.[17] The quantities of each reagent (mischmetall, samarium, tetrabromoethane) have been optimized according to the procedure (fast or slow addition of the carbonyl compounds).[18,19] We observed in some cases that an excess of tetrabromoethane, with respect to samarium, has a beneficial effect on the

Table 1. Stoichiometric pinacolization with $SmBr_2$



Entry	Carbonyl compound	Yields (%)[a]
1	5-Nonanone	87
2	Cyclopentanone	74
3	Acetophenone	94[b]
4	Octanal	62[c]
5	1,3-Dibenzoyl-propane[d]	78[e]

[a] Isolated yields.
[b] *dl*/*meso* = 80/20.
[c] *dl*/*meso* = 50/50.
[d] $SmBr_2$/carbonyl compound = 0.5.
[e] *cis*-1,2-Diphenyl-cyclopentan-1,2-diol.

$$2\ LnBr_3 + 3\ Sm \longrightarrow 3\ SmBr_2 + Ln$$

Ln = mischmetall

Scheme 3.

Table 2. Catalytic pinacolizations with $SmBr_2$ and mischmetall

mischmetall: **x** mmol + Sm: **y** mmol → pinacol
1) $Br_2CHCHBr_2$: **z** mmol; THF; 20°C; 2h
2) carbonyl compound: **4** mmol; THF 20°C; **conditions**; then H_3O^+

Entry	Carbonyl compounds	*x*/*y*/*z*	Conditions[a]	Yields (%)[b]
1	Cyclobutanone	5/1.4/0.7	Slow	66
2	Cyclopentanone	5/1.4/0.7	Slow	42
3	Cyclohexanone	5/1.4/0.7	Slow	55
4	Cyclooctanone	5/1.4/0.7	Slow	69
5	Benzaldehyde	5/1.4/0.7	Slow	62[c]
6	Phenylacetone	5/1.4/0.7	Slow	32[d]
7	4-Phenylbutane-2-one	5/1.4/0.7	Fast	60[d]
8	Octanal	5/1.4/0.7	Slow	61[d]
9	Pivalaldehyde	5/1.4/0.7	Slow	63[e]
10	Acetophenone	5/0.7/1.4	Fast	72[f]
11	1,3-Dibenzoylpropane[g]	5/0.7/1.4	Fast	70[h]
12	2-Octanone	5/0.7/1.4	Slow	72[d]
13	3-Octanone	5/0.7/1.4	Fast	54[d]
14	5-Nonanone	5/0.7/1.4	Fast	68

[a] Slow: carbonyl compound was slowly added within 14 h with a syringe pump, the mixture was then stirred for an additional period of 2 h. Fast: carbonyl compound was quickly added, the mixture was then stirred for 16 h.
[b] Isolated yields.
[c] *dl*/*meso* = 57/43.
[d] *dl*/*meso* = 50/50.
[e] *dl*/*meso* = 100/0.
[f] *dl*/*meso* = 80/20.
[g] Carbonyl compound: 2 mmol.
[h] *cis*-1,2-Diphenylcyclopentan-1,2-diol.

yields in pinacol (entries 10–14), probably in making easier regeneration of samarium dibromide (more bromide ions are available).

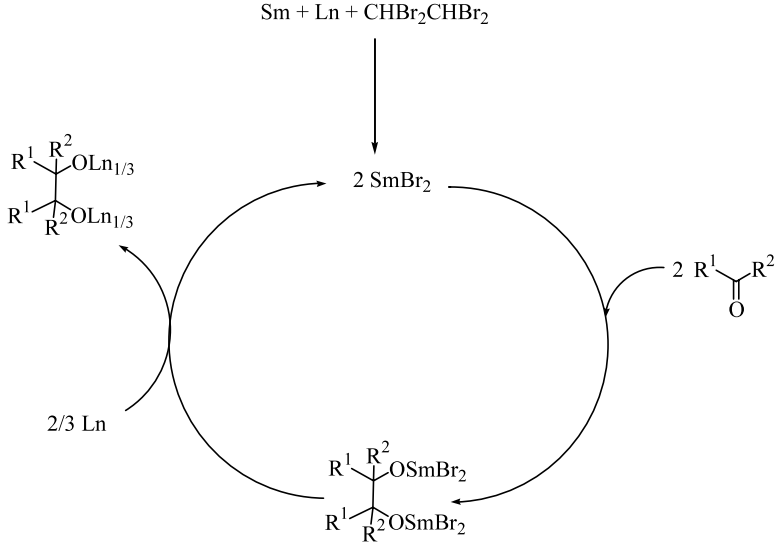
In the absence of samarium, the diols were not obtained, either the carbonyl compound was recovered or a complex mixture of products was formed. Without tetrabromoethane, no reaction took place.

The procedure (mixing of the metals prior to addition of tetrabromoethane) was a success because either samarium metal is much more reactive with tetrabromoethane than mischmetall or it is able to reduce $LnBr_3$ into Ln giving $SmBr_2$ (Scheme 3).

Lack of solubility of $SmBr_2$ and $LnBr_3$ in THF does not permit a check of this latter assumption. However, it was possible to observe that mixing of LnI_3 (Ln = mischmetall) with samarium metal in THF results in the formation of SmI_2, the deep blue-green color of which is easy to detect. This fact gives support to the above hypothesis.

The following catalytic scheme can be proposed. In contrast to the previously reported SmI_2-catalytic pinacolization,[10] there is no need to use TMSCl together with a coreductant since cerium, lanthanum and neodymium (the main components of mischmetall) are able to cleave the Sm–O bond and to reduce Sm(III) species into Sm(II) ones (Scheme 4).

In conclusion, we have found a rapid and convenient method of preparation of $SmBr_2$. A new reaction of samarium metal with 1,1,2,2-tetrabromoethane has been explored. In contrast to zinc, samarium metal gives acetylene directly. The efficiency of $SmBr_2$ in pinacolic coupling of a variety of carbonyl compounds has been demonstrated. It can be employed as well in stoichiometric as in catalytic amounts. In the latter case, mischmetall is a suitable coreductant which avoids the use of TMSCl.



Scheme 4.

Acknowledgements

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16. In a Schlenk tube under argon, 4.4 mmol of Sm (0.66 g) powder were suspended in THF (10 mL), with 2.2 mmol of $Br_2CHCHBr_2$ at room temperature within 4 h. Ketone or aldehyde (2 mmol) in THF (30 mL) was then added to the THF/$SmBr_2$ suspension. The mixture was stirred for a period of 24 h, then diluted with ether, quenched with HCl (1 M) and stirred for 15 min to obtain a clear solution, which was extracted with ether. The combined extracts were washed with brine, sodium thiosulfate and brine. The organic layer was dried over $MgSO_4$, and the solvents were removed under reduced pressure. The crude material was purified by flash chromatography on silica gel.
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18. **Fast addition**: In a Schlenk tube under argon, 5 mmol (0.7 g) of mischmetall powder were suspended in THF (2 mL), with 0.7 mmol of Sm (0.105 g) and 1.4 mmol of $Br_2CHCHBr_2$ at room temperature within 2 h. Ketone or aldehyde (4 mmol) in THF (12 mL) was then added to the THF/$SmBr_2$/mischmetall suspension. The mixture was stirred for a period of 16 h. Workup was performed as described above.
Slow addition: In a Schlenk tube under argon, 5 mmol (0.7 g) of mischmetall powder were suspended in THF (2 mL), with 1.4 mmol of Sm (0.21 g) and 0.7 mmol of $Br_2CHCHBr_2$ at room temperature within 2 h. THF (5 mL) was then added. Ketone or aldehyde (4 mmol) in THF (7 mL) was slowly added within 14 h to the THF/$SmBr_2$/mischmetall suspension. The mixture was then stirred for an additional period of 2 h. Workup was performed as described above.
19. Selected spectral data: ***cis*-1,2-Diphenylcyclopentane-1,2-diol**. Purification: column chromatography on silica gel (EtOAc–pentane, 20:80) afforded pure alcohol (0.383 g; 70% yield): $R_f = 0.4$; *dl*/*meso*: 0/100 ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.05 (m, 10H, 2 Ph), 3.00 (s, 2H, 2 OH), 2.58 (m, 2H), 2.45–2.00 (m, 4H); ^{13}C NMR (63 MHz, $CDCl_3$): δ 142.4, 127.2, 126.9, 126.2, 85.7 (C-1, C-2), 36.9, 20.0; GC/MS: m/z (%) = 55 (19), 77 (27), 104 (50), 105 (100), 120 (19), 133 (13), 218 (6), 236 (2), 254 (4); HRMS (m/z): calcd for $C_{17}H_{18}O_2$ (M^+), 254.1307; found, 254.1310; FTIR (CaF_2/CCl_4): ν_{max} = 3614, 3567, 3093, 3064, 3041, 3029, 2953, 2879, 1497, 1369, 1195, 1124, 1065, 1035. **Bicyclobutyl-1,1′-diol**. Purification: column chromatography on silica gel (EtOAc–pentane, 40:60) afforded pure alcohol (0.188 g; 66% yield): $R_f = 0.27$; ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.14 (s, 2H, 2 OH), 2.00 (m, 6H), 1.63 (m, 2H); ^{13}C NMR (63 MHz, $CDCl_3$): δ 78.4, 30.5, 12.8; HRMS (m/z): calcd for $C_8H_{12}O$ ($M^+ - H_2O$), 124.0888; found, 124.0885. Anal. calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92; O, 22.50. found: C, 67.31; H, 9.91; FTIR (CaF_2/CCl_4): ν_{max} = 3625, 3573, 2989, 2948, 2870, 2841, 1458, 1417, 1355, 1301, 1251, 1151, 1125, 1041. **2,2,5,5-Tetramethyl-hexane-3,4-diol**. Purification: column chromatography on silica gel (EtOAc–pentane, 10:90) afforded pure alcohol (0.219 g; 63% yield): $R_f = 0.34$; *dl*/*meso*: 100/0 ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.33 (d, $J = 6.7$ Hz, 2H, 3-H_2, 4-H_2), 2.34 (d, $J = 6.7$ Hz, 2H, 2 OH), 0.90 (s, 18H, 9 CH_3); ^{13}C NMR (63 MHz, $CDCl_3$): δ 74.8 (C-3, C-4), 35.2 (C-2, C-5), 25.8 (CH_3); HRMS (m/z): calcd for $C_{10}H_{22}O_2$ (M^+), 174.1620; found, 174.1620; FTIR (CaF_2/CCl_4): ν_{max} = 3642, 3543, 2961, 2909, 2870, 1477, 1465, 1394, 1365, 1240, 1181, 1088, 1060, 1009.