

Samarium Dibromide, an Efficient Reagent for the Pinacol Coupling Reactions.

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Abstract : The preparation of SmBr_2 from Sm_2O_3 is described. This samarium (II) compound is a powerful one electron reductant able to very efficiently mediate pinacolic couplings. Cross couplings are effective in some cases, for example a chiral diol can be obtained from benzophenone and camphor. Intramolecular pinacolization of a diketone has also been performed.

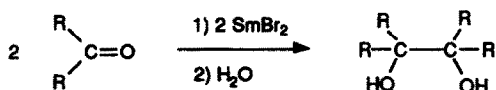
The reductive coupling of carbonyl compounds to give pinacols is an important method for the formation of vicinally functionalized C-C bonds¹. Many reductants, especially low-valent transition metal derivatives have been used for the pinacolization of ketones and aldehydes; for example, titanium reagents are efficient in many cases². Recently chemoselective pinacolization of functionalized carbonyl compounds has been established with the advent of lanthanoid systems: Imamoto et al. employed cerium based coupling reagents³, Fujiwara et al. demonstrated that aromatic aldehydes and ketones can be coupled to pinacols by ytterbium metal⁴, we have used samarium diiodide for the coupling of aromatic or aliphatic aldehydes⁵. Stereocontrolled formation of cyclic vicinal cis diols from dialdehydes or keto aldehydes in the presence of samarium diiodide have been recently described^{6,7,8}. However, samarium diiodide is a poor reagent for the coupling of aliphatic ketones. We wish to describe here a new synthesis of samarium dibromide and to report the results obtained in pinacolization of ketones and aldehydes with this samarium (II) compound.

In 1979, Rossmanith has reported the reduction of SmCl_3 into SmCl_2 in THF by lithium in the presence of naphthalene⁹. We found that the use of lithium dispersion instead of lithium chips allows to perform this transformation without added naphthalene¹⁰. We discovered that similarly samarium tribromide (prepared from Sm_2O_3), can be readily reduced at room temperature, under argon, into samarium dibromide using lithium dispersion in THF¹¹. A deep violet suspension of SmBr_2 mixed with soluble LiBr is obtained. Samarium dibromide is only slightly soluble in THF and can be separated from the soluble lithium salt by decantation, followed by washing with THF. Complexometric titration of samarium and argentimetric titration of bromide¹² indicate a Br/Sm ratio of two. After removal of THF under reduced pressure (1 torr), elemental analysis agrees with a formula $\text{SmBr}_2 / 1.5 \text{ THF}$. As samarium diiodide, samarium dibromide is air sensitive, turning red-brown

upon air exposure. The synthesis of samarium dibromide has been reported sixty years ago¹³. This compound was tediously prepared at 740°C by reduction of anhydrous SmBr₃ with H₂. It cannot be obtained (similarly to the preparation of SmI₂) from reaction of samarium with 1,2-dibromoethane. The easy preparation of SmBr₂, we describe here allows to explore the reactivity of this Sm(II) compound.

The reaction of samarium dibromide towards carbonyl compounds has been investigated (Table 1). This divalent samarium compound very efficiently mediates the pinacol formation in high yield, with aliphatic as well as with aromatic carbonyl compounds. The reaction is sensitive to the structure of the substrate; for example, in contrast to cyclohexanone, camphor is not coupled but is reduced into alcohol. Formation of pinacols probably proceeds *via* radical-radical coupling as it affords a mixture of *meso* and *dl* diols.

Table 1 : Pinacolization of Ketones or Aldehydes.



Carbonyl compound a)	Time (min)	Diol : gc yield %	Diol : isolated yield %
dodecanal	5	95	90
2-octanone	5	95	70
cyclohexanone	5	95	55
benzaldehyde	2	95	70
acetophenone	2	95	75
camphor	5	0 b)	-
benzophenone	120	0 c)	-
menthone	30	35 d)	30

a) Solvent : THF ; room temperature ; SmBr₂ / ketone = 1.1
for experimental details see note 14.

b) A 50/50 mixture of borneol and isborneol is obtained .

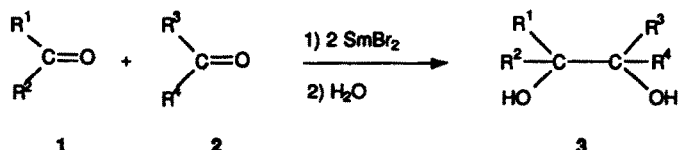
c) Formation of benzhydrol occurs.

d) A competitive reduction furnishes menthol (65 %).

Attempts to *cross-couple* ketones (Table 2) has led to almost statistical mixtures of diols (entries 1, 2, 3) with aliphatic or cyclic ketones. It is interesting to note that the diolate of cyclohexanone which is produced in quantitative yield in less than 5 min can then react with 2-octanone in the presence of SmBr₂ to give the diol 3, (Table 2, entry 3). This observation indicates that under these conditions, this reductive coupling is reversible. In the case of benzophenone (entries 7, 8) diphenyl diols have been selectively obtained. Such a pinacol coupling reaction is uneffective with SmI₂ (and with alkali metals), it can be mediated by ytterbium metal and has been

previously described by Fujiwara ⁴. It is noteworthy that camphor and benzophenone alone in presence of SmBr₂ do not lead to pinacols, whereas they combine with each other. This reaction could involve a bielectronic transfer from two SmBr₂ to the diaryl ketone and then an attack by the resultant dianion on the aliphatic ketone ¹⁵. The diol resulting from the cross coupling of camphor with benzophenone has not been prepared before, it could be useful as a chiral ligand. The diolate is unstable in the reaction medium, hydrolysis must be carried out 5 min after addition of camphor, it otherwise decomposes to the samarium alkoxides of benzhydrol and borneol.

Table 2 : Cross Couplings of Ketones and Aldehydes.



Entry	1 a)	2	3 : gc yield % (isolated yield %)
1	2-octanone b)	cyclohexanone	50
2	cyclohexanone c)	benzaldehyde	45
3	cyclohexanone d)	octanone	45
4	camphor d)	cyclohexanone	0 e)
5	camphor d)	acetone	0 e)
6	menthone d)	acetone	55 (41)
7	benzophenone f)	2-octanone	65
8	benzophenone f)	camphor	65 (40) g)
9	benzophenone f)	menthone	70 (40) h)

a) Solvent : THF ; room temperature ; SmBr₂/1/2 : 2.2/1/1. b) 1+2 are added in 10 min to SmBr₂. c) 1 is added first then 2 in 0.5 min d) 1 is added first then 2 in 120 min e) pinacolization of 2 occurs. f) 1 is added first then 2 after 15 min ; reaction time : 5 min. g) A single stereoisomer resulting from the endo attack on camphor is obtained ; mp : 77°C ; [α]_D = -40.5 (c=1 ; methanol). h) mp : 122°C ; [α]_D = 95.4 (c=1 ; methanol).

The intramolecular coupling of 1,4-diphenyl-1,4-butanedione leads, (on the basis ¹H NMR. data 16,17), to the trans 1,2-diphenyl-1,2-butanediol in almost quantitative yield. This trans diol has been previously obtained in the pinacolization of this diketone by Mg/MgI₂.

Further studies dealing with intramolecular pinacolizations of diketones and dialdehydes by SmBr₂ are in progress. The scope of reactivity of SmBr₂ is currently under investigation.

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References and notes.

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11. To 34.8 g of Sm_2O_3 (0.1 mol) suspended in 100 mL of water are added within 2 min, 100 mL of HBr (8.65 N). The temperature must be kept below 45°C. The yellow solution is stirred for two hours then it is concentrated under vacuum. Water (200 mL) is added and the solution is concentrated again. The same operation is repeated with 200 mL of ethanol. The solid is washed with 200 mL of hexane and dried. 99.2 g of $\text{SmBr}_3 \cdot 6 \text{H}_2\text{O}$ (yield : 99.5 %) are obtained.
In a Schlenck tube, 49.4 mL of methyl orthoformate (0.45 mol) are added to 30 g of $\text{SmBr}_3 \cdot 6 \text{H}_2\text{O}$ (6×10^{-2} mol) and stirred for one hour. The methyl formate and methanol are distilled (about 15 mL). THF purified on benzophenone sodium ketyl (150 mL) is added and distilled off. This operation is repeated twice. After cooling, 300 mL of THF are added, then 0.42 g of lithium dispersion (6×10^{-2} mol.). The mixture is stirred for 20 hours at room temperature. A deep violet suspension of SmBr_2 is obtained, the yield is quantitative.
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14. In a Schlenck tube, 1.82 mmol of ketone are added to 2 mmol of SmBr_2 suspended in 10 mL of THF, the mixture is stirred for 5 min., then hydrolyzed. After removal of the solvent the crude material is diluted with 20 mL of ethyl acetate and chromatographed on silica gel (eluent : ethyl acetate, 150 mL). The diol is recrystallized in hexane.
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