

Mischmetall: An Efficient and Low Cost Coreductant for Catalytic Reactions of Samarium Diiodide

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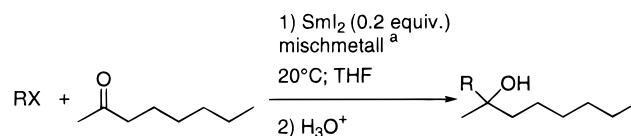
Introduced for the first time to synthetic organic chemistry in 1977,¹ samarium diiodide has emerged as one of the most useful reagents. Except in reactions where it is the precursor of a Sm(III) catalyst,² it is used in stoichiometric amounts. Its preparation requires samarium powder or ingots,^{1,3} neither of which are very expensive.⁴ However, the cost of samarium diiodide could be considered as a major drawback, potentially limiting the development of its chemistry.

Very recently, interesting attempts have been reported to run reactions with catalytic quantities of SmI₂ and an in situ regeneration system for the Sm(II) species. Magnesium has been employed with SmI₂ for the pinacolic coupling of aromatic aldehydes and ketones⁵ and for the coupling of imines.⁶ Corey has described the use of a zinc amalgam with SmI₂ for the deoxygenation of styrene oxide, the cyclization of 1-iodo-6-phenyl-5-hexyne, and the annulation of ketones and acrylate esters to give γ -lactones. However, in the latter example, the cleavage of the Sm(III)–O alkoxide bond must be performed with trimethylsilyl triflate, an expensive reagent.⁷ Moreover, magnesium and zinc are reactive toward many organic substrates and, therefore, not suitable for use in many reactions mediated by SmI₂.

Ideally, a system for in situ regeneration of SmI₂ should be (1) cheaper than samarium metal, (2) able to quickly reduce samarium(III) species into samarium(II) ones, which implies the ability to cleave Sm(III)–O bonds, (3) unreactive toward organic substrates, and (4) simple and usable in a variety of the organic reactions mediated by SmI₂.

Due to their thermochemical properties (redox properties and strength of the Ln–O bonds) and the low reactivity of lanthanide metals (if they are not activated with iodine or mercury salts),⁸ cerium, lanthanum, neo-

Table 1. Catalytic Barbier-Type Reactions



run	RX	reaction conditions ^a	isolated yields of products (%)
1	allyl iodide	1.5 h then 0.5 h	90
2	allyl bromide	3.5 h then 0.5 h	91
3	benzyl bromide	3.0 h then 0.5 h	91
4	ethyl iodide	3.5 h then 1 h	52
5	ethyl iodide	6.5 h then 1 h	67
6	ethyl iodide	2.5 h then 1 h	67 ^b

^a See ref 10. ^b With 0.001 equiv of NiI₂.

dymium, or praseodymium fit all of the above requirements, except for the first one.

Fortunately, the alloy of the light lanthanides (La 33%, Ce 50%, Nd 12%, Pr 4%, Sm and others lanthanides 1%) known as *mischmetall* (or cerium mixed metal) is available at a low price.⁹

We report here some results on the use of mischmetall in samarium diiodide-catalyzed Barbier-type reactions, reduction of organic halides, pinacolic coupling of acetophenone, and the coupling of an acid chloride.

The results concerning Barbier-type reactions are gathered in Table 1.¹⁰

Samarium diiodide is used in catalytic quantities (0.2 equiv, 10 mol %). In the absence of SmI₂, no reaction occurs, except in the case of allyl iodide where 20% of the tertiary alcohol and 10% of the pinacols from 2-octanone are obtained. The slow addition of a THF/ketone/organic halide mixture to the THF/SmI₂/mischmetall suspension leads to the persistence of the deep blue SmI₂ color. A quick addition leads to the disappearance of the color though it is, however, restored within 1–3 h depending on the halide; in these cases, small amounts (~5%) of byproducts (2-octanol and pinacol coupling products of 2-octanone) are detected. Yields of tertiary alcohols are close to those obtained under stoichiometric conditions.^{1,11} Addition of HMPA (4 equiv with respect

(9) Mischmetall as small ingots (about 5 g) is purchased from Fluka (about \$6 per 500 g). It is an industrial material used, for example, as an additive for iron-smelting. It is also the main component of flints. Mischmetall ingots are easily scraped in air with a rasp; the powder is kept under argon (average MW of mischmetall is 140).

(10) **Procedure for Samarium Diiodide-Catalyzed Reactions: Barbier-Type Reactions.** In a Schlenk tube under argon, 5 mmol (0.7 g, 1.4 equiv.) of mischmetall powder were suspended in THF (7 mL), with 0.7 mmol (0.2 equiv.) of SmI₂. A solution of 2-octanone (3.5 mmol) and organic halide (4.2 mmol, 1.2 equiv.) in THF (7 mL) was slowly added to the THF/SmI₂/mischmetall suspension at such a rate that the deep blue color of SmI₂ was maintained (see Table 1). The mixture was then stirred for an additional period of 0.5 or 1.0 h (see Table 1) and then quenched with HCl (1 M) and stirred for 15 min to obtain a clear solution that was extracted with ether. The combined extracts were washed with sodium thiosulfate and brine. The organic layer was dried over MgSO₄, and the solvents were removed under reduced pressure. The crude material was purified by flash chromatography on silica gel. Similar procedures were used for other SmI₂-catalytic reactions: reduction of organic halides, pinacol coupling of acetophenone, and coupling of 1-methyl-1-cyclohexanecarboxylic acid chloride. The *dl/meso* ratio of pinacol coupling products was determined from previously published NMR data.¹⁴

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(3) In contrast, the preparation of SmBr₂ can be performed either from samarium metal or from samarium oxide: Lebrun, A.; Rantze, E.; Namy, J. L.; Kagan, H. B. *New J. Chem.* **1995**, *19*, 699–705.

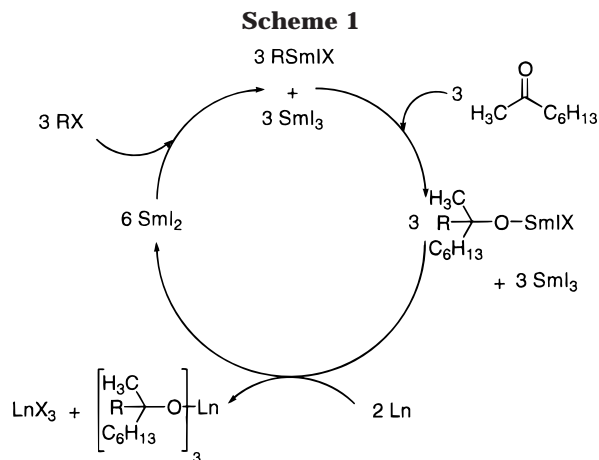
(4) Samarium chunks (99.9%) can be purchased from Acros (about \$6 per 50 g).

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to SmI_2) presumably impedes the reduction of Sm(III) species into Sm(II) ones; no turnover of SmI_2 can be effected and only about 10% of the tertiary alcohol is detected. In contrast, the beneficial effect on Barbier-type reactions of very small quantities of NiI_2 (0.001 equiv) is reinforced again (run 6).¹² We have also verified that cerium or lanthanum metal can be used instead of mischmetal; under the conditions of run 1 or 2, the tertiary alcohol is obtained in similar yields.

A possible reaction pathway involves a Barbier-type reaction mediated by SmI_2 , through an organosamarium compound that leads to a samarium(III) alkoxide and SmI_3 . These species are then reduced by Ln (La, Ce, Pr, or Nd) metals to give Ln(III) alkoxides and regeneration of samarium diiodide (Scheme 1).

This assumption is supported by the following observations. Treatment of a yellow suspension of $(t\text{-Bu})\text{OSmI}_2$ with mischmetal in THF leads to the fast formation (10 min) of the deep blue SmI_2 color. Samarium diiodide is regenerated from SmI_3 in a similar fashion.

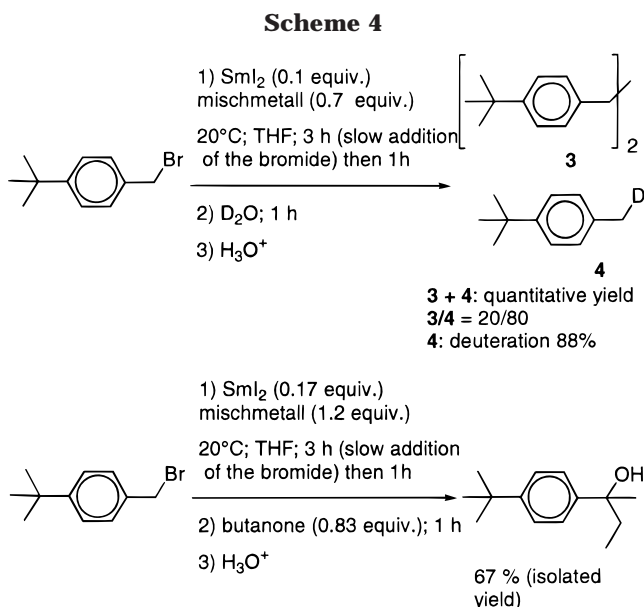
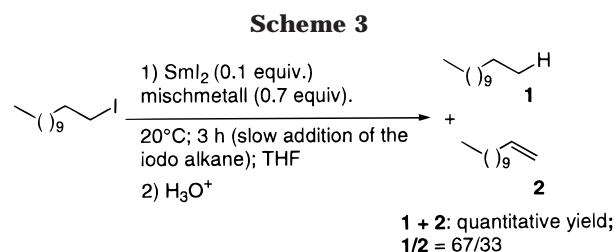
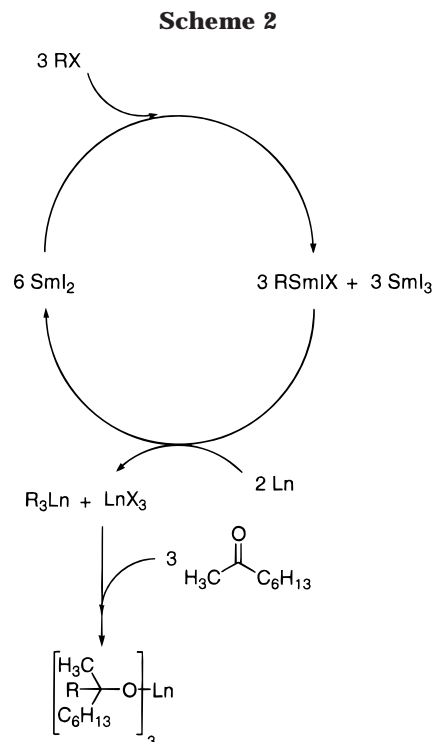
Alternatively, a transmetalation could take place after formation of an organosamarium compound, leading to another organometallic compound such as R_3Ln (Ln other than Sm) and regeneration of samarium diiodide. Addition of R_3Ln to the ketone could furnish Ln(III) alkoxides (Scheme 2).

The samarium diiodide-catalyzed reaction of 1-iodododecane has also been studied (Scheme 3).

Slow addition (over 3 h) of the halide to the THF/ SmI_2 /mischmetal suspension allows the persistence of the deep blue color of SmI_2 . A mixture of dodecane and 1-dodecene is quantitatively obtained in a 2/1 ratio. Hydrolysis with D_2O does not lead to any deuterium incorporation, and without SmI_2 the halide is quantitatively recovered. The presence of 1-dodecene suggests the formation of either an organometallic species that undergoes a β -hydrogen elimination or a radical disproportionation reaction.

Samarium diiodide-catalyzed reactions of 4-(*t*-Bu)-benzyl bromide have also been performed (Scheme 4).

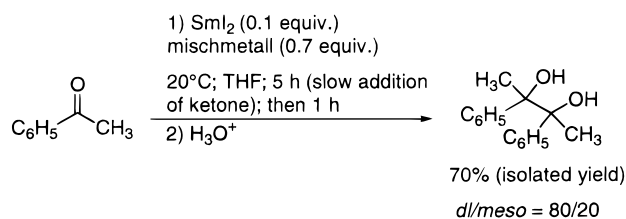
Quenching of the reaction mixture with D_2O gives 4-*tert*-butyltoluene with incorporation of deuterium and small amounts of 4,4'-di-*tert*-butyldibenzyle. Trapping with butanone furnishes the tertiary alcohol in good yield (10% of 4,4'-di-*tert*-butyldibenzyle and 18% of 4-*tert*-butyltoluene are also detected). These experiments



strongly support the formation of stable organometallic species. As it is known that 4-(*tert*-butyl)benzylsamarium diiodide obtained from the reaction of 4-(*tert*-butyl)benzyl bromide with SmI_2 is not stable in THF,¹³ the formation of an organometallic compound such as R_3Ln (Ln other

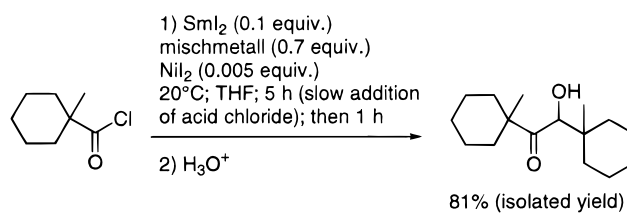
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Scheme 5

than Sm; R = 4-(*tert*-butyl)benzyl) is likely. This indicates that the reaction pathway proposed in Scheme 2 for the SmI₂-catalyzed Barbier reactions cannot be ruled out. Without SmI₂ only 4,4'-*tert*-butyldibenzyle is obtained. Surprisingly, an equimolar mixture of 2-octanone and 4-(*tert*-butyl)benzyl bromide is unreactive with mischmetall alone.

The pinacolic coupling of acetophenone can also be readily performed using SmI₂ as a catalyst and mischmetall as a coreductant (Scheme 5). In contrast to the previously reported procedure that uses magnesium as a coreductant, there is no need to add trimethylsilyl chloride to cleave the Sm(III)–O bonds.⁵ The pinacolic coupling products are obtained in good isolated yields, and small amounts (less than 5%) of 1-phenylethanol are also detected. The *dl/meso* ratio (80/20)^{10,14} is the same as that measured when the reaction is performed under stoichiometric conditions (79/21). This result is in good agreement with a pinacolization mediated by SmI₂ lead-

Scheme 6

ing to a samarium(III) pinacolate, the reduction of which by mischmetall regenerates SmI₂. Without samarium diiodide, no reaction occurs.

The coupling of acid chlorides to give α -ketols, mediated by Sm(II) species has been extensively studied.¹⁵ We found that it can be also performed with the (SmI₂-catalytic)/mischmetall system under the conditions indicated in Scheme 6. The use of a very small amount of NiI₂ avoids the formation of byproducts.¹² Mischmetall alone is unreactive (Scheme 6).

To conclude, we have found an efficient, simple, and low-cost system to perform catalytically the reactions of samarium diiodide. Many transformations mediated by this useful reagent could be conducted under these conditions. We are currently exploring the scope of potential applications for the (SmI₂-catalytic)/mischmetall system, especially in the case of polyfunctionalized substrates.

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