

Account

Application of Sm⁰/Auxiliary and Sm⁰/MCl_n System in Organic Synthesis

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Application of Sm⁰/auxiliary and Sm⁰/MCl_n system in organic synthesis was reviewed.

Keywords Sm⁰/auxiliary system, Sm⁰/MCl_n system, synthetic applications

Since pioneering studies by Kagan and co-workers demonstrated the particular effectiveness of samarium(II) iodide as a powerful one-electron transfer reductant,¹ it is well known that SmI₂ has been extensively applied to organic synthesis in the last decade. Because of its mild and neutral reaction conditions as well as excellent selectivity, the novel reactions and various chemical transformations induced by SmI₂ are daily on the increase.²

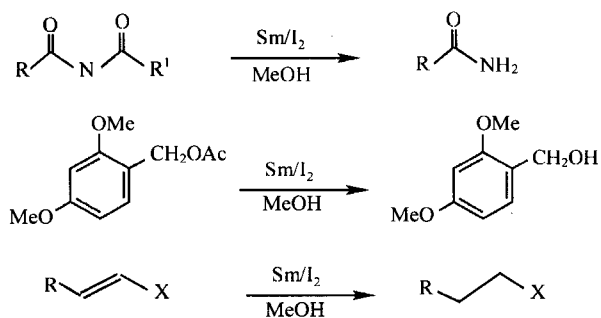
Though SmI₂ is a useful reagent, some problems are encountered when it is used as a reductant. For example, it is expensive, needs delicate treatment, careful storage because it is very sensitive to air oxidation and has been invariably used in stoichiometric amounts. On the other hand, metallic samarium, comparison with SmI₂, is stable in air. In addition, it has strong reducing power (Sm³⁺/Sm = -2.41 V) which is similar to that of magnesium (Mg²⁺/Mg = -2.37 V) and superior to that of zinc (Zn²⁺/Zn = -0.71 V). These properties prompted us to use the more convenient and cheaper samarium metal directly as a reductant instead of samarium(II) iodide. In this paper we will review our efforts in this area.

Application of Sm⁰/auxiliary system in organic synthesis

Though samarium metal itself has strong reducing power, in most cases, certain additives are still needed when it is used as a reductant because the surface of samarium metal is inactive. Thus Sm⁰/auxiliary systems are proposed. The explored systems include: Sm⁰/I₂, Sm⁰/TMSCl, Sm⁰/THF-NH₄Cl (aq.), Sm⁰/Cp₂TiCl₂, Sm(Hg), Sm⁰/cat. KI *etc.*

Sm⁰/cat. I₂ system

Most recently, Yanada *et al.* reported that in the presence of a catalytic amount of iodine samarium metal could induce deprotection reactions of esters and amides.³ In addition, Sm⁰/cat. I₂ system could also reduce selectively the carbon-carbon double bond of α,β-unsaturated carbonyl compounds.⁴

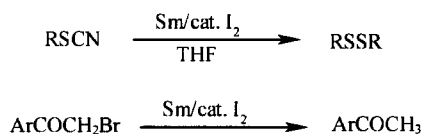


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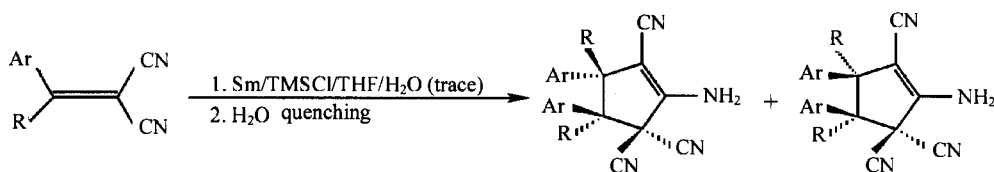
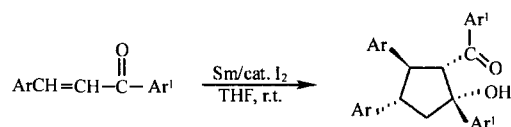
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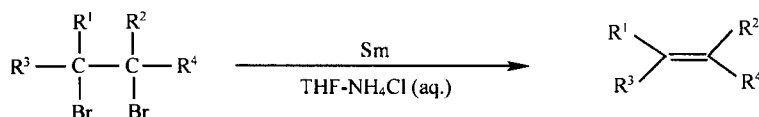
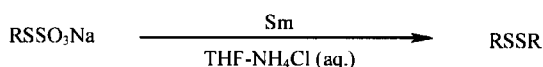
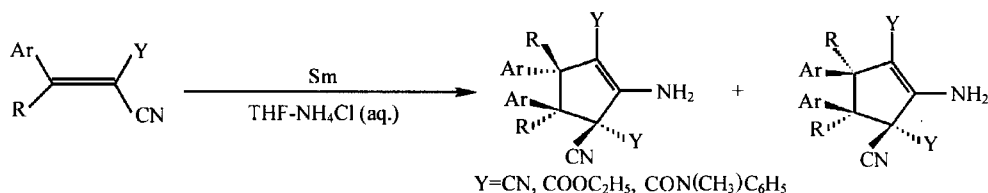
We found that, with Sm⁰/cat. I₂ system, azides, sodium alkyl thiosulfates and thiocyanates could be conveniently reduced to the corresponding amines and disulfides respectively.^{5,6} β-Ketosulfones, α-bromoketones and active haloalkanes could be smoothly reduced to the corresponding products in good to excellent yields by metallic samarium together with a catalytic amount of iodine.⁷



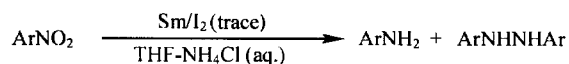
Cyclodimerization of α,β-unsaturated ketones in the absence of proton source was realized using Sm⁰/cat. I₂ system to give poly-substituted cyclopentaneols in good yields.⁸



As a new reductive system, Sm⁰/TMSCl/H₂O (trace) system could also be used in the cleavage of the Se—Se bond in diselenides. Selenide anions were easily formed *in situ* from the cleavage of the Se—Se bond by Sm⁰/TMSCl/H₂O (trace) system. These “living” species could undergo nucleophilic addition or nucleophilic substitution with a variety of reagents.^{13,14}



In the presence of a catalytic amount of iodine, aromatic nitro compounds could be reduced to the corresponding primary amines and hydrazines in good yields with Sm⁰/THF-NH₄Cl system in aqueous media.⁹



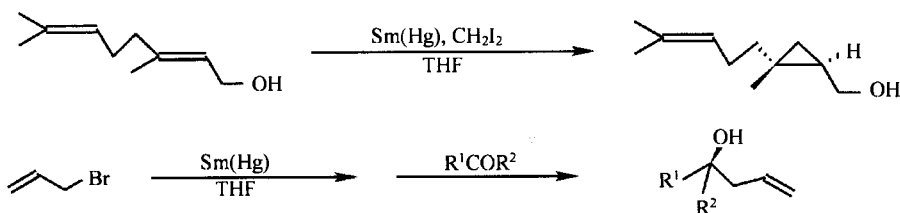
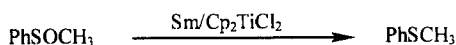
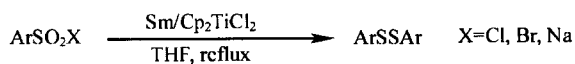
Sm⁰/TMSCl and Sm⁰/THF-NH₄Cl system

Very recently, Sm/Me₃SiCl/NaI and Sm/Me₃SiBr system have been used for intermolecular carbon-carbon bond formation reactions of carbonyl compounds.¹⁰ Our group have studied the reductive coupling of carbonyl compounds to afford pincols with the Sm⁰/TMSCl system.¹¹ By action of Sm⁰/TMSCl in the presence of a trace amount of water in THF at room temperature, 1,1-dicyanoalkenes led to the functionalized cyclopentenes through reductive dimerization followed by intermolecular cyclization with an one-pot manner. Interestingly, a trace amount of water not only could accelerate the reaction, but also increase the yields of products.¹²

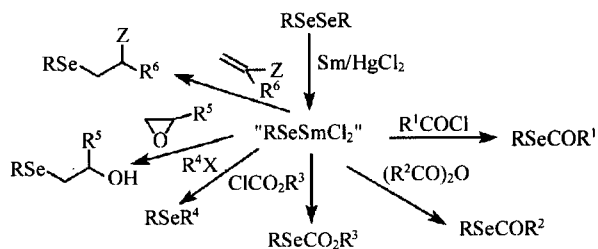
Interestingly, it was found that Sm⁰/THF-NH₄Cl (aq.) system is nearly as effective as Sm⁰/TMSCl/H₂O (trace) system for the reductive dimerization cyclization of *gem*-diactivated alkenes. This system could also be applied to reductive debrominating of *vic*-dibromides and reduction of sodium alkyl thiosulfates at room temperature.¹⁵

$\text{Sm}^0/\text{Cp}_2\text{TiCl}_2$ system

We found that auxiliary Cp_2TiCl_2 could activate metallic samarium. By the treatment of $\text{Sm}^0/\text{Cp}_2\text{TiCl}_2$ system, nitroarenes and azides could be reduced to the corresponding amines;^{16,17} arylsulfonyl derivatives, sulfoxides, α -bromoketones and active haloalkanes could be readily converted to the corresponding disulfides, sulfides, ketones and reductive coupling products.^{18,19}

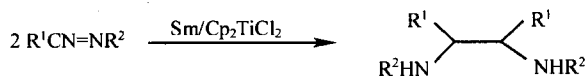


The application of the $\text{Sm}(\text{Hg})$ system to the pinacol coupling reaction of carbonyl compounds has been investigated.²⁴ Also by this system, reductive cleavage of the Se—Se bond in diselenides was realized. This reaction gave “living” selenide anion species *in situ*, which reacted with acyl chlorides, acid anhydrides, methyl chloroformate, organic halides, epoxides, α , β -unsaturated esters and α , β -unsaturated nitriles to afford selenoesters, selenoformates and unsymmetrical selenides.²⁵

 $\text{Sm}^0/\text{cat. KI}$ system

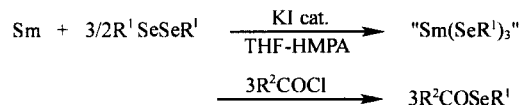
Our group recently found that with the aid of a

Dimerization of aldimines to vicinal diamines mediated with $\text{Sm}^0/\text{Cp}_2\text{TiCl}_2$ system is also successful.²⁰

 $\text{Sm}(\text{Hg})$ system

As early as 1987, Molander reported highly stereocontrolled cyclopropanation reaction of allylic alcohols using samarium/mercury amalgam (produced from $\text{Sm}^0/\text{HgCl}_2$ system) in conjunction with diiodomethane.^{21,22} Wu studied $\text{Sm}(\text{Hg})$ -mediated Barbier-type reactions of allyl bromide and ketones with specially high regio- and chemoselectivity.²³

catalytic amount of potassium iodide samarium metal mediated reductive cleavage of diselenides to generate samarium(III) selenolates, which further reacted with acid chlorides to give selenoesters in moderate yields.²⁶



So far the mechanism of the reactions promoted by $\text{Sm}^0/\text{auxiliary}$ system is not clarified yet. Some maybe due to the activation of the surface of metallic samarium by the additives; some maybe due to the formation of dimetallic complexes or co-reductants system.

Application of Sm^0/MCl_n system in organic synthesis

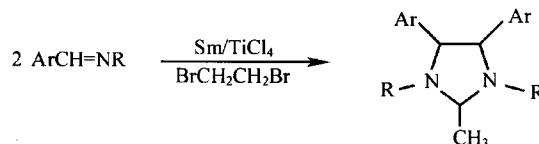
Since the general approach for the preparation of highly reactive metal powders was reported in 1972,²⁷ active metals have attracted considerable attention in organic synthesis.²⁸ Due to the high reactivity of active metals, reactions are typically carried out more efficient-

ly under milder conditions, and with a wider array of substrates than that with other current methods. Many low valent metals, which are mostly active metals, can be produced *in situ* by mixing samarium powder and a variety of metallic chlorides (MCl_n). Thus, the Sm⁰/MCl_n system is formed. Such systems include: Sm⁰/TiCl₄, Sm⁰/NiCl₂, Sm⁰/CoCl₂, Sm⁰/CrCl₃, Sm⁰/BiCl₃, Sm⁰/SbCl₃, Sm⁰/CdCl₂, and Sm⁰/ZnCl₂, *etc.*

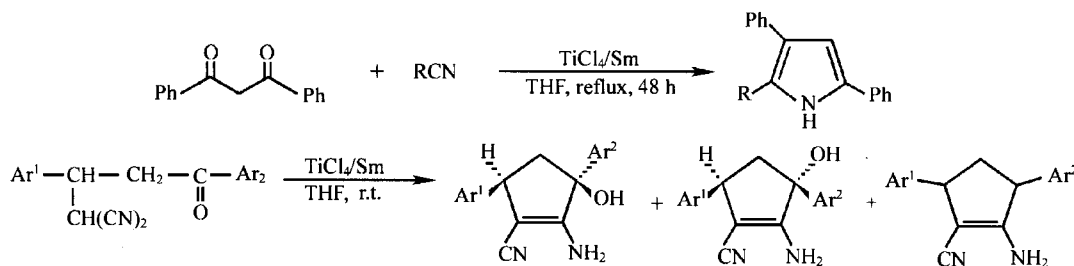
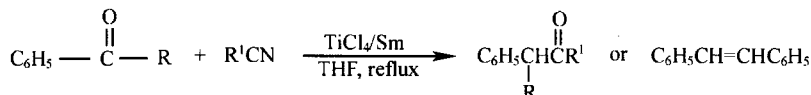
Application of Sm⁰/MCl_n system under anhydrous conditions

Low valent titaniums are widely used as reagents in organic synthesis.²⁹ We explored the Sm⁰/TiCl₄ system and applied it to synthesize a series of compounds. With Sm⁰/TiCl₄ system, we found sulfoxides could be reduced to sulfide.³⁰ Arylsulfonyl and sodium arylsulfonates as well as sodium alkyl thiosulfates and thiocyanates could

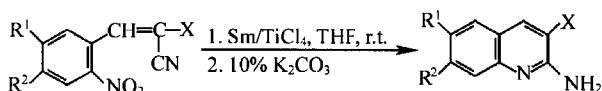
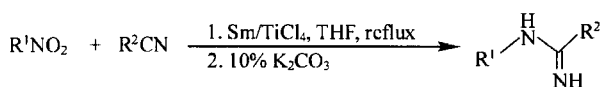
be reduced to corresponding disulfides.³¹⁻³³ In addition, α-ketosulfones could also be reductively desulfonated.³⁴ *N*-Alkyl imines led to the formation of imidazolines with Sm⁰/TiCl₄ system.¹¹



The intermolecular and intramolecular reductive coupling reactions of ketones with nitriles have been successfully promoted by a low-valent titanium species prepared by Sm⁰/TiCl₄ system. Substituted ketones, monocyclic α-amino alcohols and monocyclic amines with a number of substitution patterns have been prepared in good yields at room or reflux temperature under neutral conditions.³⁵



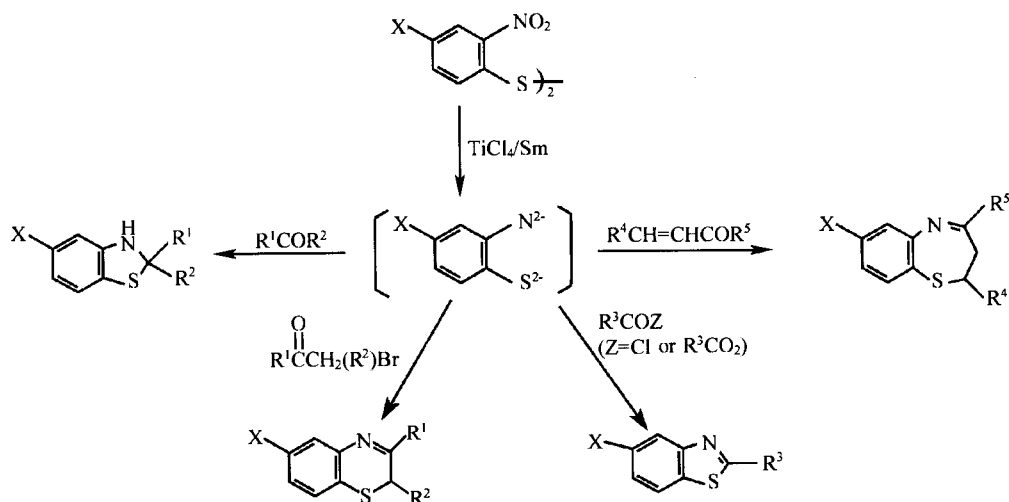
Sm⁰/TiCl₄ system could also be used to promote intermolecular or intramolecular reductive coupling of nitro group with cyano group to produce amidines and 2-aminoquinoline derivatives respectively.³⁶



Very recently, Sm⁰/TiCl₄-mediated simultaneous reduction of nitro group and S—S bond in nitrodisulfides have been used to generate a series of heterocyclic compounds.^{37,38} The reaction was suggested to proceed *via* a

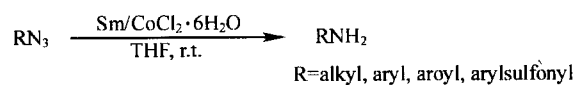
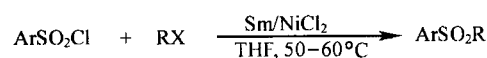
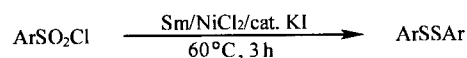
“living” double-anion intermediate, which was trapped by aldehydes, ketones, acid chlorides, acid anhydrides, α,β-unsaturated ketones and ω-bromoketones respectively to afford the desired heterocyclic compounds in good yields under mild and neutral conditions.

Sm⁰/NiCl₂ system can not only promote the formation of a S—S bond, but also induce cleavage of a S—S bond. With Sm⁰/NiCl₂/cat. KI system, arylsulfonyl chlorides could be readily converted into disulfides.³⁹ On the other hand, Sm⁰/NiCl₂ or Sm⁰/NiCl₂·6H₂O system was successfully applied to the one-pot synthesis of thioesters from disulfides and acid chlorides or acid anhydrides.⁴⁰ In addition, sulfones were easily prepared *via* coupling reaction of sulfonyl chlorides with active alkyl halides promoted by Sm⁰/NiCl₂ system.⁴¹ Similar-

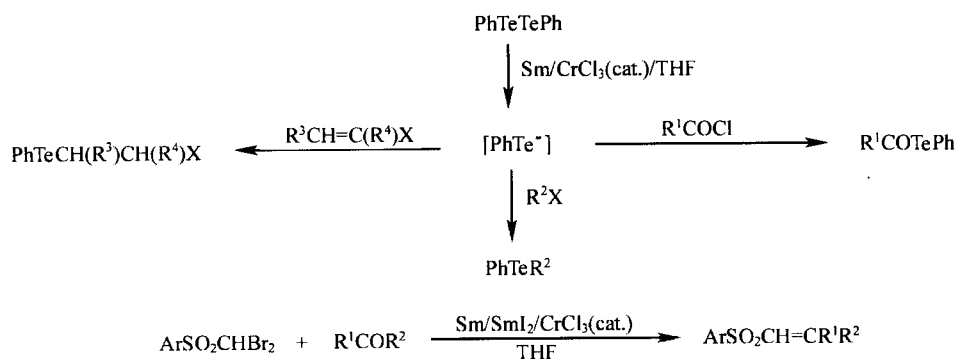


ly, $\text{Sm}^0/\text{CoCl}_2$ system could induce the cleavage of Se—Se bonds in diselenides to synthesize selenoesters in an one-pot manner.⁴² Besides, azides were chemoselectively converted to amines with $\text{Sm}^0/\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ system.⁴³

Low valent chromium(II)s are widely used one-electron transfer reductants in organic synthesis.⁴⁴ There are many methods for the preparation of low valent chromium(II) species, among which $\text{Sm}^0/\text{CrCl}_3$ system is very effective and convenient.⁴⁵ By the treatment of $\text{Sm}^0/\text{cat. CrCl}_3$ system, the reduction of diphenyl ditellurides led to telluride anions. This species reacted with acid chlorides, organic halides, α, β -unsaturated esters and α, β -unsaturated nitriles to afford telluroesters and unsymmetrical phenyltellurides in moderate to good



yields under mild and neutral conditions.⁴⁶ In the presence of a catalytic amount of CrCl_3 , metallic samarium in conjunction with samarium diiodide promoted a direct alkylidenating reaction of ketones with geminal dibromomethyl sulfones to give alkylidene sulfones in moderate to good yields.⁴⁷



Application of Sm^0/MCl_n system in an aqueous media

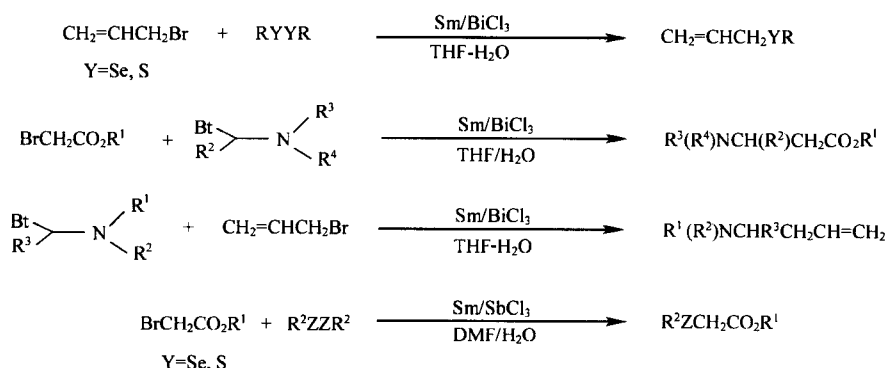
Metal-mediated organic reactions in aqueous media

have received considerable attention in the last decade.⁴⁸ Such aqueous reactions offer a number of advantages over conventional organometallic reactions in

organic solvent. They are practically convenient, environmentally friendly and do not require anhydrous organic solvents. Fortunately, many active metals produced from Sm⁰/MCl_n system could undergo reactions in a medium containing water, for example, Sm⁰/BiCl₃, Sm⁰/SbCl₃, Sm⁰/CdCl₂, Sm⁰/ZnCl₂ system *etc.*

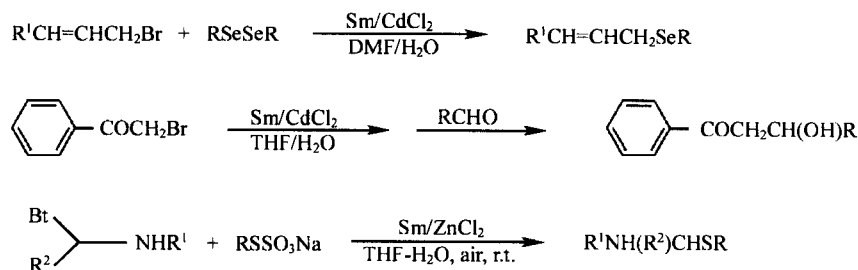
We found that in aqueous media allyl sulfides and allyl selenides were synthesized *via* the reaction of allyl bromide with disulfides and diselenides promoted by Sm⁰/BiCl₃ system in moderate to good yields.⁴⁹ In addition, Sm⁰/BiCl₃ system could mediate Reformatsky-type reaction of β-bromoesters with 1-(α-aminoalkyl) benzo-

triazole to yield β-aminoesters in aqueous media.⁵⁰ Also using benzotriazole methodology homoallylic amines were prepared *via* reaction of allyl bromide with 1-(α-aminoalkyl) benzotriazole promoted by Sm⁰/BiCl₃ system in THF-H₂O mixture.⁵¹ Similarly, allyl and benzyl selenides were synthesized by reactions of allyl and benzyl bromides with diselenides achieved by Sm/SbCl₃ system in aqueous media in moderate to good yields.⁵² And α-selenoesters and α-thiolester are synthesized *via* reactions of α-bromoesters with diselenides and disulfides promoted by Sm/SbCl₃ system in aqueous media.⁵³



Promoted by metallic cadmium which was produced by reduction of CdCl₂·H₂O with samarium *in situ*, allyl bromide and α-bromocarboxylates reacted with diorgano diselenides in aqueous solutions to give allylic-type selenides and α-selenocarboxylates in moderate to good yields.⁵⁴ In the presence of cadmium(II) chloride-metallic samarium, α-bromoacetophenone reacted with aldehydes

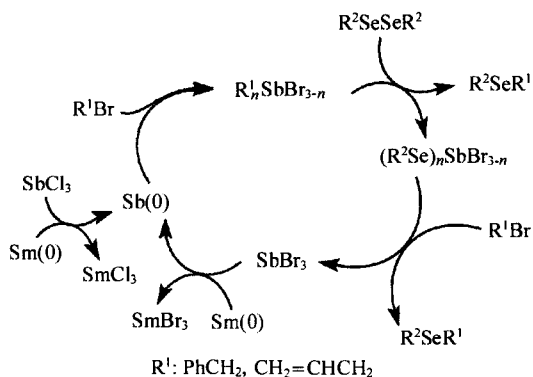
in THF-H₂O under mild conditions to give β-hydroxy ketones in good yields.⁵⁵ Unsymmetrical α-amino sulfides are synthesized in moderate to good yields *via* the reactions of 1-(α-aminoalkyl)benzotriazole with alkylthiosulfates promoted by the Sm⁰/ZnCl₂ system in THF-water.⁵⁶



Mechanism of reactions promoted by Sm⁰/MCl_n system

It is worthwhile to note that in most reactions promoted by Sm⁰/MCl_n system the chloride salts could be

used in a catalytic amount. A typically representative mechanism of Sm⁰/cat. SbCl₃ system mediated allylation of diselenides was proposed as follows:⁵³



Conclusion

In summary, as a new type of reductive system, $\text{Sm}^0/\text{auxiliary}$ and Sm^0/MCl_n system are very effective for a variety of chemical transformations. The remarkable advantages of these reactions lie in mild, neutral and/or environmentally friendly reaction conditions, simple operation, less amounts of metallic samarium (comparison with SmI_2) and good yields. It may open new ways for using metallic samarium instead of (or partly instead of) samarium(II) diiodide in organic synthesis.

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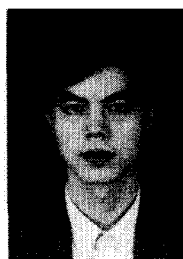
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