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Reduction with Samarium(0). Debromination of *vic*-Dibromides to Alkenes

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Three electrons from Sm(0) to Sm(III) can be available during the title reduction which was achieved in 90-95% yield with *vic*-dibromides such as *trans*-10,11-dibromodibenzosuberone, *meso*- and *dl*-1,2-dibromo-1,2-diphenylethane, ethyl 2,3-dibromo-3-phenylpropionate, 2,3-dibromo-3-phenylpropionic acid, and cholesterol dibromide. These reductions were accelerated with a catalytic amount of acid.

The chemistry of samarium(II) iodide (SmI_2) is one of the current interests in organic synthesis. SmI_2 has developed as a mild, neutral, and ether-soluble one-electron reductant and many examples have been reported to reduce various functional groups with SmI_2.1) However, there are some problems when it is used as a reductant. Though SmI_2 is expensive, only one electron is available and a stoichiometric amount is needed for the reduction. The storage of SmI_2 is difficult because it is very sensitive to air oxidation. The solution of SmI_2 is prepared almost exclusively by Kagan's method using samarium(0) (Sm) and 1,2-diiodoethane.2) This reaction, however, wastes two electrons from Sm to give SmI_2. Sm has a reducing power ($Sm^{3+}/Sm = -2.41$ V) similar to that of magnesium ($Mg^{2+}/Mg = -2.37$ V). These properties prompted us to use the stable Sm directly as a reductant instead of SmI_2. There are some reports on the direct use of Sm in organic synthesis.3) In these reports, solid Sm was activated by methyl or allyl iodide addition and heated before use. Very recently, Kamochi *et al.* reported the reduction of some functional groups using Sm in MeOH:HCl (1:2).4)

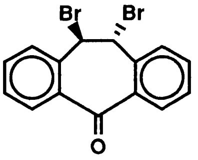
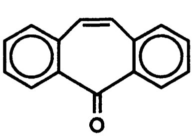
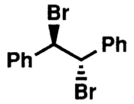
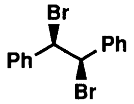
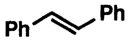
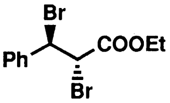
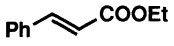
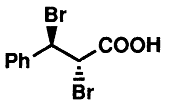
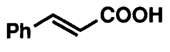
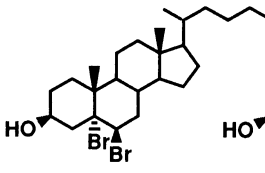
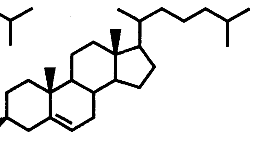
The debromination of *vic*-dibromides to alkenes is important in organic synthesis as a deprotection and some gentle methods (neutral, low reaction temperature, *etc.*) have been developed for this step.5) To the best of our knowledge, there is no example where a samarium compound is used as a reagent for the debromination. We report here the reductive debromination of *vic*-dibromides (benzylic *vic*-dibromides and cholesterol dibromide) to alkenes with Sm under mild conditions.

We first examined the debromination with SmI_2 as a preliminary experiment. SmI_2 (0.1 M solution in THF, 2 mmol) was added to *vic*-dibromide (1 mmol) and the reaction mixture was stirred at room temperature under an argon atmosphere. After the characteristic blue colour of SmI_2 had disappeared, the reaction mixture was worked up by the usual manner and the crude product was purified by a short silica-gel column chromatography. All *vic*-dibromides in Table 1 gave the corresponding alkenes within 5-20 min in high yields.

As the next trial, we examined the debromination with only Sm. Generally, all procedures were achieved under an argon atmosphere because this reaction is very sensitive to air as with SmI_2. The mixture of *vic*-dibromide (1 mmol) and Sm (0.72 mmol, 40 mesh) in THF (20 ml) was stirred at room temperature. The induction period was observed and then the colour of the solution turned to slightly turbid green brown. After

Sm had been consumed, the reaction mixture was diluted with water and then extracted with ether. The crude product was purified by a short silica-gel column chromatography. Talbe 1 shows that *vic*-dibromides gave the corresponding alkenes in as high yields as those with SmI_2. It shows that Sm can be used instead of SmI_2 as a reductant during this reaction though longer reaction time is needed.

Table 1. Reductive debromination of *vic*-dibromides to alkenes

Entry	Dibromide	Alkene	SmI_2 Time /min	SmI_2 Yield /%	Sm(0) Time /h	Sm(0) Yield /%	Sm(0)/HCl Time /min	Sm(0)/HCl Yield /%
1			5	94	5	90	10	96
2			5[a)]	95	5[a)]	93	10[a)]	95
3			10[a)]	95	40[a)]	95	360[a)]	93
4			10	92	6	93	20	98
5			10[b)]	89	10	93	120[b)]	89
6			20	97	8	95	180	95

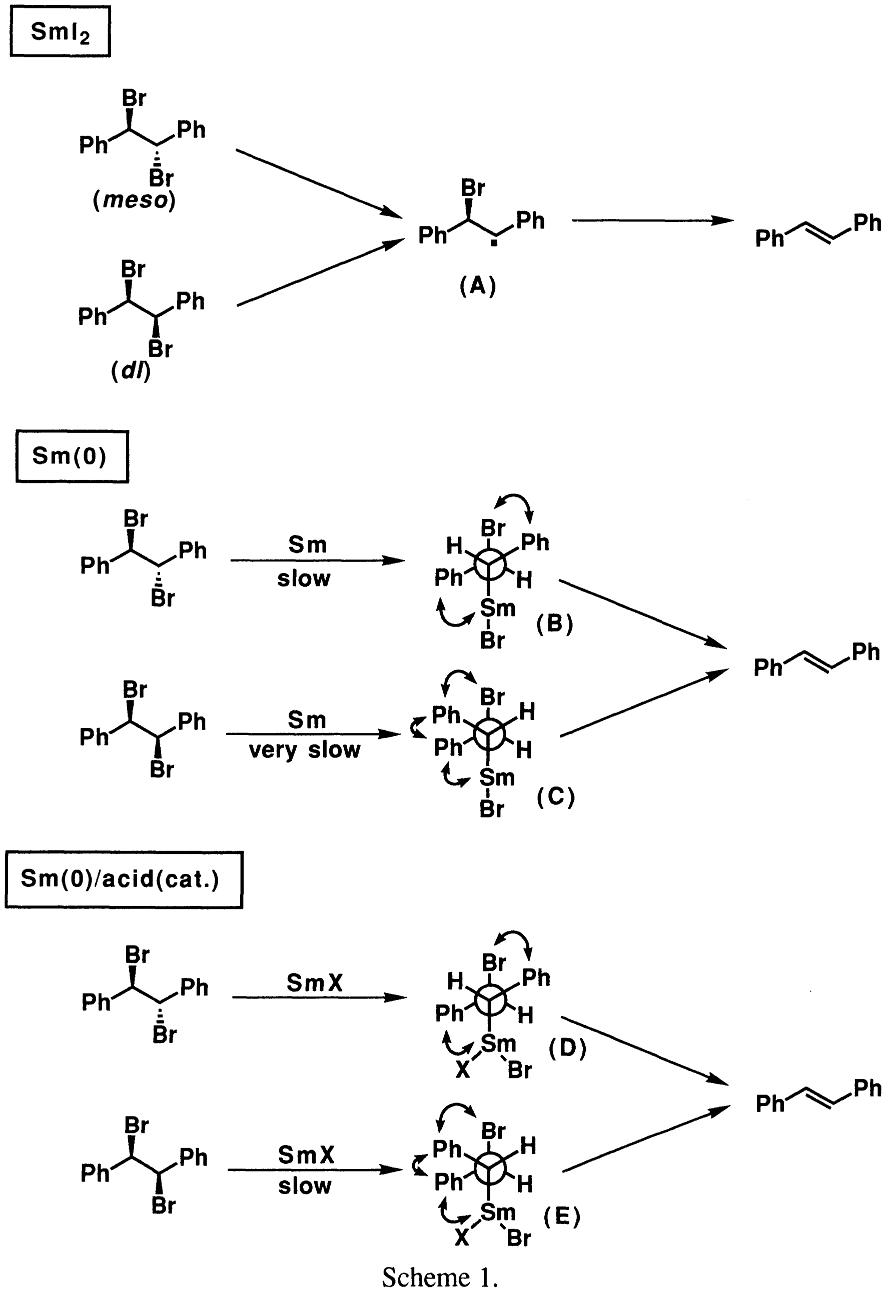
a) Trace amount of *cis*-stilbene was observed by n.m.r. in the reaction mixture.
b) Trace amount of 3-phenylpropionic acid was observed by n.m.r. in the reaction mixture.

Table 2. Reductive debromination of 10,11-dibromodibenzosuberone to dibenzosuberenone with Sm and a catalytic amount of various acids

Acid (0.2 mmol)	-	35% HCl	*p*-TsOH·H_2O	AcOH	98% H_2SO_4	$Sm(OTf)_3$
Reaction time	5 h	10 min	30 min	1 h	1 h	3 h
Yield /%	90	96	96	94	94	94

The debromination with Sm was accelerated with a catalytic amount of acid. Table 2 shows this result using 10, 11-dibromodibenzosuberone (1 mmol) as a substrate. The debromination proceeded within 10 min with Sm (0.8 mmol) and 35% HCl (0.2 mmol). This reaction needed 5 h without acid (with only Sm). Slight hydrogen evolution was observed at the first stage and Sm was almost consumed during the reduction. It is known that several rare-earth monohalides are prepared by disproportionation between rare-earth metals and their trihalides (or dihalides).6) These suggest that the true reducing species is low valent SmX (X=Cl, OTs, OAc, *etc.*).4,6) Table 1 summarizes the results of debromination of *vic*-dibromides with Sm/HCl (cat.). It shows that all reactions with Sm are accelerated with acid and give the corresponding alkenes in high yields.

Though the detailed machanism of above debromination has not been clarified yet, we propose a plausible mechanism in Scheme 1 from the different reactivity of reagents during the debromination of *meso*- and *dl*-1,2-



Scheme 1.

dibromo-1,2-diphenylethane. In the case of SmI_2, the debromination of both dibromides to *trans*-stilbene proceeded within the similar short time. It shows that the reaction intermediates from both dibromides are the same radical⁷⁾ or anion species (**A**). In the case of Sm, metal insertion might occur at first stage to give the intermediate (**B**) or (**C**), and then SmBr is removed from (**B**) or (**C**) to give the second intermediate like (**A**) from which *trans*-stilbene is produced. Because of the steric interaction in the intermediate (**C**), debromination of *dl*-1,2-dibromo-1,2-diphenylethane needed longer reaction time than that of *meso*-1,2-dibromo-1,2-diphenylethane. After the induction period during which SmBr accumulates, the reaction may occur mainly with SmBr as mentioned later because the reaction of *vic*-dibromide with Sm needs longer time. In the case of Sm/HCl (cat.), active SmX may be produced at first stage and then SmX insertion gave the intermediate (**D**) or (**E**). SmBrX is removed from (**D**) or (**E**) to give the second intermediate like (**A**) and *trans*-stilbene is produced. Because of the less hinderance in the intermediate (**D**), the *meso*-1,2-dibromo-1,2-diphenylethane gave *trans*-stilbene faster than *dl*-1,2-dibromo-1,2-diphenylethane. SmBrX generated during the reaction reacts with *vic*-dibromide like SmI_2 or reacts with Sm to regenerate SmX.

Though Sm is less active and Sm/HCl (cat.) is slightly less active than SmI_2 and the simplicity of procedures is similar in both methods, the following disadvantages of SmI_2-reduction can be improved by using Sm or Sm/HCl (cat.): 1) the cost for the reagent, 2) difficulty of storage (SmI_2 must be kept under an inert atmosphere with a small amount of Sm and it is better to use within a few days to ensure reproducible results).²⁾ The debromination of *vic*-dibromides to alkenes is important in organic synthesis as a deprotection and various new methods are developed.⁵⁾ The debrominations with SmI_2 and especially with Sm or Sm/acid (cat.) are attractive additions to existing methodology because these reactions occur at room temperature under a neutral condition with Sm or under a weak acidic condition with Sm/acid (cat.).

In conclusion, it is proved that three electrons from Sm(0) to Sm(III) can be directly available during the reductive debromination of *vic*-dibromides (benzylic *vic*-dibromides and cholesterol dibromide) to alkenes. This method may provide a new way for using samarium in organic synthesis.

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7) The polymer derived from THF was found in some cases. It was generated probably via radical reaction.

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