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Generation and Reaction of Samarium(II) Iodide Equivalent from Samarium and Chlorotrimethylsilane/Sodium Iodide System in Acetonitrile

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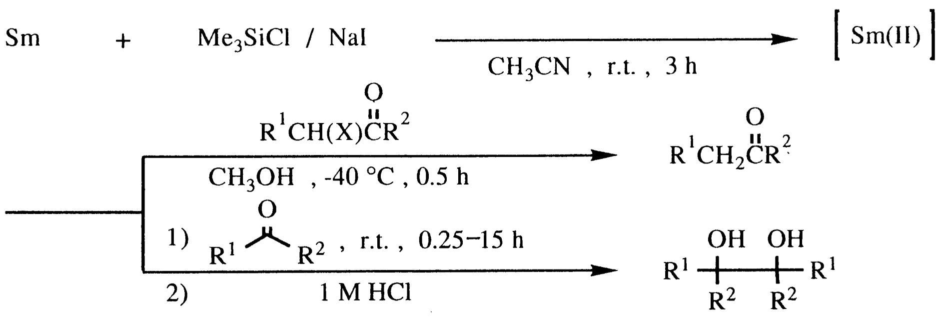
Samarium(II) iodide equivalent was generated from metallic samarium and Me_3SiCl/NaI reagent in acetonitrile under ambient conditions. Dehalogenation of α-halocarbonyl compounds and reductive coupling of ketones were successfully carried out by the use of the samarium(II) species, thus generated, in acetonitrile.

In recent years, much attention has been paid to the utilization of samarium(II) iodide for its great potential in synthetic transformations.1) Although samarium(II) iodide is usually prepared from metallic samarium and 1,2-diiodoethane,2) diiodomethane,3) or molecular iodide4) in THF, an alternative route to samarium(II) species is desired to extend the scope in organic synthesis.

Previously, we reported that treatment of tin with $Me_3SiCl/NaI/H_2O$ in acetonitrile followed by allylic alcohols results in allylic tin species of which subsequent reaction with aldehydes produces regioselectively linear homoallylic alcohols (α-adducts), which are difficult to obtain in higher selectivity by conventional methods.5)

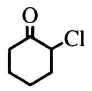
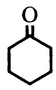
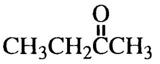
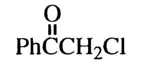
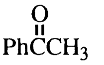
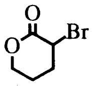
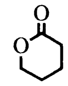
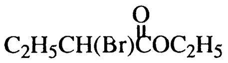
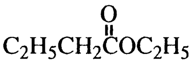
We now find that treatment of samarium metal with Me_3SiCl/NaI reagent in acetonitrile under ambient conditions provides a unique route to samarium(II) iodide equivalent. This paper describes a new preparation method and reaction of samarium(II) iodide equivalent thus generated.



Samarium(II) iodide equivalent was easily generated as follows: To a solution of sodium iodide (0.9 g, 6 mmol) in dry acetonitrile (20 mL) was added chlorotrimethylsilane (0.76 mL, 6 mmol), followed by samarium grain (2 mgatom) under nitrogen atmosphere at room temperature. The mixture was stirred for 3 h at room temperature. Samarium was gradually dissolved in acetonitrile, and the color of the solution changed to deep green, which was quite similar to the THF solution of samarium(II) iodide obtained by Kagan's method.[2)]

In order to evaluate the synthetic potential of the samarium(II) species thus prepared, dehalogenation of α-halocarbonyl compounds was first examined.[6)] Table 1 shows dechlorination of 2-chlorocyclohexanone (**1**) to cyclohexanone (**2**) by $Me_3SiCl/NaI/Sm$ system under several reaction conditions.

Table 1. Dehalogenation of α–Halocarbonyl Compounds with Sm(II) Species Generated from Me_3SiCl / NaI / Sm System [a)]

Run	Substrate	Me_3SiCl / NaI / Sm (mmol)	Solv.	Conv. / %	Product / % [b)]	
1	 **1**	6 / 6 / 0	CH_3CN	38	 **2**	18
2	**1**	4 / 4 / 2	CH_3CN	78	**2**	88
3	**1**	6 / 6 / 2	CH_3CN	89	**2**	99
4	**1**	6 / 6 / 2	THF	93	**2**	88
5	**1**	6 / 6 / 2	DME	93	**2**	55
6	 $CH_3CH(Cl)\overset{\overset{O}{\parallel}}{C}CH_3$	6 / 6 / 2	CH_3CN	76	 $CH_3CH_2\overset{\overset{O}{\parallel}}{C}CH_3$	82
7	 $Ph\overset{\overset{O}{\parallel}}{C}CH_2Cl$	6 / 6 / 2	CH_3CN	84	 $Ph\overset{\overset{O}{\parallel}}{C}CH_3$	95
8		6 / 6 / 2	CH_3CN	85		93
9	 $C_2H_5CH(Br)\overset{\overset{O}{\parallel}}{C}OC_2H_5$	6 / 6 / 2	CH_3CN	80	 $C_2H_5CH_2\overset{\overset{O}{\parallel}}{C}OC_2H_5$	91

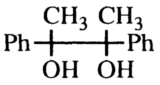
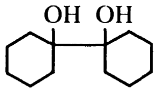
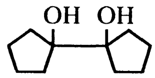
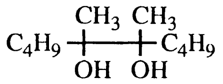
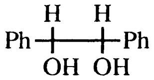
a) α–Halocarbonyl compound (1 mmol) was allowed to react with samarium(II) species generated from Me_3SiCl /NaI /Sm in solvent (20 mL) involving CH_3OH (1 mL) at -40 °C for 0.5 h.

b) GC yields based on substrates consumed.

Dechlorination was found to be satisfactorily achieved by the use of three equivalents of Me_3SiCl/NaI with respect to samarium in acetonitrile, involving methanol as the proton source,[7)] under very mild conditions (-40 °C) (Run 3). Among the solvents employed, acetonitrile is the best solvent (Runs 3-5). It is interesting to note that the dehalogenation readily proceeded in acetonitrile, because THF was the essential solvent to carry out such a reaction so far.[8)] Thus, dehalogenation of a wide range of α-halocarbonyl compounds were examined (Table 1, Runs 3 and 6-9). Aliphatic, alicyclic, and aromatic α-haloketones were dehalogenated to the corresponding ketones in good yields (Runs 3, 6,and 7). α-Bromolactone and ester were also reduced in good yields (Runs 8 and 9). It is now apparent that the $Me_3SiCl/NaI/Sm$ system is a new route to generate samarium(II) iodide equivalent in acetonitrile.

On the other hand, the reductive coupling of carbonyl compounds is known as another notable reaction accomplished by samarium(II) iodide.[12)] Thus, the coupling reaction of some carbonyl compounds was carried out by using $Me_3SiCl/NaI/Sm$ system in acetonitrile at room temperature (Table 2).

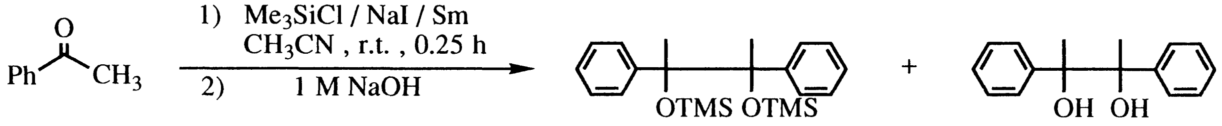
Table 2. Reductive Coupling of Carbonyl Compounds with Sm(II) Species Generated from Me_3SiCl / NaI / Sm System [a)]

Run	Substrate	Time / h	Solvent	Conv. / %	Product / %[b)]	
1	Acetophenone **3**	0.25	CH_3CN	86	 $\mathrm{Ph-\overset{CH_3}{\underset{OH}{C}}-\overset{CH_3}{\underset{OH}{C}}-Ph}$ **4**	84
2	**3**	0.25	THF	73	**4**	12
3	Cyclohexanone	15	CH_3CN	91		96
4	Cyclopentanone	15	CH_3CN	89		51
5	2-Hexanone	15	CH_3CN	70	 $\mathrm{C_4H_9-\overset{CH_3}{\underset{OH}{C}}-\overset{CH_3}{\underset{OH}{C}}-C_4H_9}$	54
6[c)]	Benzaldehyde	0.5	CH_3CN	75	 $\mathrm{Ph-\overset{H}{\underset{OH}{C}}-\overset{H}{\underset{OH}{C}}-Ph}$	89

a) Substrate (2 mmol) was allowed to react with Me_3SiCl / NaI / Sm (6 / 6 / 2 mmol) in solvent (20 mL) at room temperature.
b) GC yields based on substrates consumed. c) HMPA (1 mL) was added.

When acetophenone (**3**) was allowed to react with samarium(II) species generated from $Me_3SiCl/NaI/Sm$ system in acetonirtile, followed by protonation with 1 M HCl, reductive coupling product, 2,3-diphenylbutane-2,3-diol (**4**), which consisted of about a 1:1 ratio of *threo* and *erythro* isomers, was obtained in 84% yield (Run 1). Unlike the dehalogenation, the coupling reaction did not take place selectively in THF; **4** was formed in unsatisfactory yield (Run 2). Cyclohexanone gave pinacolic product, 1,1'-dicyclohexane-1,1'-diol, in fair yield, though the long reaction time was required (Run 3). Cyclopentanone and 2-hexanone gave the corresponding pinacolic products in slightly lower yields (Runs 4 and 5). Although benzaldehyde produced no coupling product under these conditions, hydrobenzoin was obtained in 89% yield when HMPA was added to the system (Run 6).

It is attractive to note that when **3** was allowed to react with $Me_3SiCl/NaI/Sm$ in acetonirtile, followed by quenching with base, **3** gave the corresponding pinacolic compound, **5** (63%) bearing trimethylsiloxy group, together with a small amount of **4** (12%).



3 **5** (63%) **4** (12%)

Further new synthetic application of the samarium(II) species generated from $Me_3SiCl/NaI/Sm$ system in acetonirtile is in progress.

References

1) For review, see: G. A. Molander, *Chem. Rev.*, **92**, 29 (1992); J. A. Soderquist, *Aldrich. Acta.*, **24**, 15 (1991); J. Inanaga, *Yuki Gosei Kagaku Kyoukaishi*, **47**, 200 (1989); H. B. Kagan, *New J. Chem.*, **14**, 453 (1990); T. Imamoto, *Yuki Gosei Kagaku Kyoukaishi*, **46**, 540 (1988); H. B. Kagan and J. L. Namy, *Tetrahedron*, **24**, 6573 (1986); Y. Fujiwara, *Kagakuzokan*, **109**, 241 (1986).
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7) Methanol was added to protonate the resulting samarium enolate.
8) Recently, some reactions, such as the coupling between acid chloride and ketone,9) reductive cross-coupling of 1,3-dioxolane with carbonyl compound,10) and intramolecular cyclization,11) are reported to be mediated by samarium(II) iodide in acetonitrile rather than THF.
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