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Preparation of Samarium(II) Triflate and It Mediated Grignard-type Reaction. In Situ Formation and Reaction of New Organosamarium Reagents

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Samarium(II) triflate was readily prepared by the reaction of samarium(III) triflate with *sec*-butyllithium at room temperature in THF. Its reducing ability was examined by pinacol coupling of carbonyl compounds. $Sm(OTf)_2$ mediated Grignard-type reaction in THF-HMPA effectively; alkylation and allylation of ketones or aldehydes by simple alkyl, allyl, and benzyl halides proceeded *via* organosamarium intermediates.

Recently, Curran et al. have proved that organosamarium species is an intermediate in samarium(II) diiodide mediated Barbier-type reaction which was originally reported by H. B. Kagan et al. 1-3) Like organolanthanoid halides prepared from lanthanide-lithium exchange,4) organosamarium reagents prepared from simple alkyl halides and samarium(II) diiodide also reveal unique reactivity towards ketones and aldehydes, e.g., exclusive 1, 2-addition to a carbonyl group.

Organolanthanoid triflates prepared from organolithium and lanthanoid(III) triflates (trifluoromethanesulfonate) are one of the attractive and beneficial reagents for selective organic reactions. Thus, they have been added to amides to produce unsymmetrical ketones without contamination of tertiary alcohols 5) and react in highly diastereoselective fashion with chiral ketones and aldehydes.6) However, synthetic utilities are limited because of availability of organolithium compounds. It was thought that if organolanthanoid triflates could be prepared from reduction of organic halides with low valent (divalent) samarium triflate, scope of the synthetic utilities would be more expanded. We have been investigated the new divalent samarium species for selective organic synthesis, and found that Lewis acidic samarium(III) triflate [$Sm(OTf)_3$] can be readily reduced into samarium(II) triflate [$Sm(OTf)_2$] by *sec*-BuLi in THF.7) In this report, we would like to report a Grignard-type reaction promoted by $Sm(OTf)_2$, and unique reactivity of the organosamarium.8)

When we treated 2.0 mmol of $Sm(OTf)_3$ with one equivalent of *sec*-BuLi in THF (20 cm^3) at ambient temperature, the purple solution of divalent samarium triflate was readily obtained. Iodimetric titration of samarium revealed that the concentration of divalent samarium was within a range of 0.086-0.091 mol dm^{-3}.9) We first tested the reducing ability of $Sm(OTf)_2$ by a reductive pinacol coupling of carbonyl compounds.10) Table 1 illustrates the typical results of the reaction. The results demonstrates that $Sm(OTf)_2$ effectively underwent the pinacol coupling under mild conditions. With aldehydes and aromatic ketones, yields of the corresponding pinacols were high without contamination of by-products. With aliphatic ketones such as cyclohexanone and 2-octanone, the reactions were slow and yields of the pinacols were not satisfactory. Addition of hexamethylphosphorictriamide (HMPA) accelerated the reaction rate and improved yields of products (Table 1 runs 4-5).

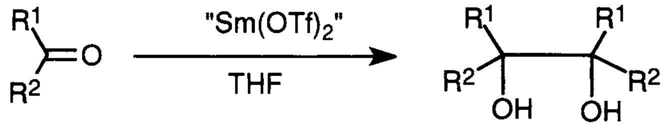

Table 1. Pinacol Coupling Reaction of Carbonyl Compounds Promoted by $Sm(OTf)_2$ [a)]

Run	Carbonyl Compds	Reaction Time/h	Conv./%	Yield/%[b)]
1	Acetophenone	1.25	95	94
2	Propiophenone	1.25	98	96
3	Cyclohexanone	10	58	55
4[c)]	Cyclohexanone	0.5	80	78
5[c)]	2-Octanone	2	60	56
6	Benzaldehyde	1	98	97
7	1-Phenylpropanal	5	98	79

a) Ketone (1.0 mmol), $Sm(OTf)_3$ (2.0 mmol), *sec*-BuLi (2.0 mmol), THF (20 cm^3); room temperature. b) Determined by GLC. c) HMPA (1.0 cm^3) was added.

We next investigated a Grignard-type reaction. To the deep purple solution of $Sm(OTf)_2$ was added alkyl iodide (0.25-0.5 equiv. to samarium) followed by ketones or aldehydes (1 equiv. to alkyl iodide) in the presence of hexamethylphosphoric triamide (HMPA) at room temperature. Grignard-type reaction proceeded smoothly to produce the corresponding adducts (secondary or tertiary alcohols) in moderate to good yields. The results are shown in Table 2. Quenching with D_2O instead of addition of a ketone or an aldehyde provided a deuteriated alkane demonstrating that the reduction of alkyl iodide with $Sm(OTf)_2$ should give the organosamarium intermediate. All cases of Table 2 suggests that organosamarium species should be involved in the reaction. Quite interestingly, even methyl and ethyl iodides gave the corresponding stable organosamarium reagents (runs 1-2), while samarium(II) diiodide mediated Grignard-type reaction can not be conducted with methyl and ethyl iodides because of unstability of the alkylsamarium intermediates.

Molander et al. have demonstrated that methylytterbium reagent prepared from methyllithium and $Yb(OTf)_3$ reacts with 2-methylcyclohexanone in a high diastereoselective fashion, i.e., high level of equatorial attack to 2-methylcyclohexanone.[6)] The "methylsamarium reagent" prepared from methyl iodide and $Sm(OTf)_2$ also showed high diastereoselectivity in the addition reaction to 2-methylcyclohexanone; the ratio of axial alcohol to equatorial alcohol being 96:4 (run 7). Samarium(II) diiodide mediated reaction of methyl iodide with 2-methylcyclohexanone provided the adduct in a lower selectivity (axial alcohol:equatorial alcohol=80:20) with a low yield (10-20%). The 1-phenylethyl samarium reagent prepared from $Sm(OTf)_2$ also achieved a higher diastereoselectivity (>98% de, Table 2, run 8) than that prepared from samarium(II) diodide (82% de).[2)] Diastereoselective alkylation was also observed in the reaction with 4-*tert*-butylcyclohexanone (60% de, Table 2, run 11). On the other hand, it has been reported that samarium(II) diiodide mediated alkylation of 4-*tert*-butylcyclohexanone gave the axial alcohol in only 27% de.[2)]

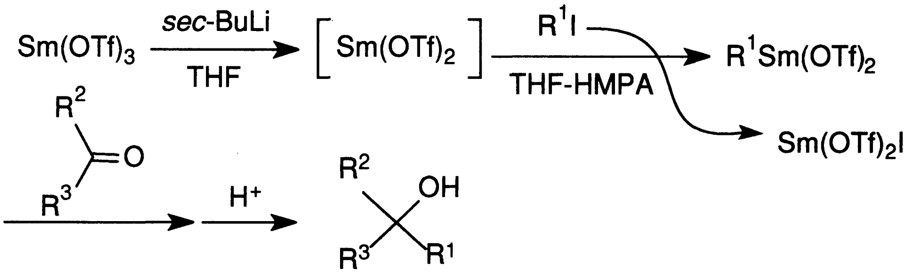

Table 2. Grignard-type Reaction Mediated by $Sm(OTf)_2$ [a]

Run	R in RI	Carbonyl Compound	Yield(%) of Adduct [b]
1	CH_3	Acetophenone	56
2	C_2H_5	Acetophenone	60
3	n-C_3H_7	Acetophenone	55
4	n-C_4H_9	Acetophenone	58
5	CH_3	Cyclohexanone	70
6	CH_2=$CHCH_2$	Cyclohexanone	65
7	CH_3	2-Methylcyclohexanone	72[c]
8	$PhCH_2CH_2$	2-Methylcyclohexanone	80[d]
9	CH_2=$CHCH_2$	2-Methylcyclohexanone	60
10	CH_3	4-*tert*-Butylcyclohexanone	75[e]
11	$PhCH_2CH_2$	4-*tert*-Butylcyclohexanone	90[f]
12	CH_3	Diisopropylketone	51
13	CH_3[g]	β-Tetralone	30
14	n-$C_{12}H_{25}$	Acetone	86[h]
15	$PhCH_2CH_2$	Acetone	67[h]
16	$PhCH_2CH_2$	Benzaldehyde	53[h]
17	CH_2=$CHCH_2$	Acetophenone	67
18	CH_2=$CHCH_2$	Propiophenone	72[h]
19	$PhCH_2$[i]	Acetone	30[j]

a) RI (0.5 mmol), ketone (0.5 mmol), $Sm(OTf)_3$ (2.0 mmol), *sec*-BuLi (2.0 mmol), THF (20 cm^3), HMPA (1.0 cm^3); for the reaction procedure and reaction conditions, see the text. b) Determined by GLC. c) Axial alcohol:equatorial alcohol=96:4. d) Axial alcohol:equatorial alcohol=>99:<1. e) Axial alcohol:equatorial alcohol=75:25. f) Axial alcohol:equatorial alcohol=80:20. g) 1.0 mmol of CH_3I was used. h) Isolated yield. i) Benzyl bromide (0.5 mmol) was employed. j) Bibenzyl was a by-product (5-10%).

It should be noted that allyl iodide provided the "allylsamarium reagent" on treatment with this low valent samarium triflate under the conditions. Trapping with ketones gave the corresponding homoallylic alcohols in good yields (runs 6, 9, 17, 18). Considering that samarium(II) diiodide undergoes Wurtz-type coupling of allyl halides in the absence of ketones or aldehydes, the success of generating allylsamrium species is surprising.[11] We also found that the "benzylsamarium reagent" could be prepared from benzyl bromide, which added to an appropriate ketone such as acetone under the same conditions (run 19).

The organosamarium species prepared by $Sm(OTf)_2$ displays unique stability and reactivity compared to the organosamarium species generated by a samarium(II) diiodide mediated procedure. We believe $Sm(OTf)_2$ is promising in selective organic synthesis.

The following experimental procedure for Grignard-type reaction is representative. To a stirred solution of $Sm(OTf)_3$ (1.20 g, 2.0 mmol) in THF (20 cm^3) at -20 °C was added cyclohexane solution of *sec*-BuLi (1.0 mol dm^{-3}, 2.0 mmol). The mixture was warmed to room temperature at which time a purple solution of the divalent samarium triflate was obtained. HMPA (1.0 cm^3) was added to the solution and stirred for 1 h at room temperature, then methyl iodide (0.071 g, 0.5 mmol) was added. After 1 h, acetophenone (0.06 g, 0.5 mmol) was added to the resulting solution and stirred for 0.5 h. The solution was hydrolyzed with a diluted HCl. The organic phase was separated, and aqueous phase was extracted with diethyl ether. The combined organic extracts were washed with brine and dried ($MgSO_4$). Capillary GLC analysis revealed the presence of 2-phenyl-2-propanol of which quantity was determined by using an internal standard (0.28 mmol, 56%).

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