Preparation of Organoytterbium Reagent from Ytterbium Trichloride and Organomagnesium

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The preparation of organolanthanoid species from diorganomagnesium and lanthanoid salt is discussed. Treatment of cerium trichloride or ytterbium trichloride with diorganomagnesium gave the corresponding organolanthanoid species much more efficiently than treatment of the salt with organomagnesium halide.

Organocerium[1] and -ytterbium[2–4] reagents prepared from metal(III) salt and an organolithium or -magnesium compound have been utilized as a highly nucleophilic species for the addition to carbonyl compounds only after Imamoto's frontier work[5] had been reported. Although the structures of these organolanthanoids species have not been clear, their characteristic feature,[6] that possesses the high nucleophilicity to react with an easily enolizable ketone such as *β*–tetralone, offers useful synthetic methods. While the preparation of organocerium reagents was well optimized and documented by Imamoto,[5] the preparation of organoytterbium reagents from ytterbium chloride and organomagnesium reagents still contains some difficulties; the aging period of the mixing these precursors is a subtle step[2] to obtain reactive species. An appropriate aging period should be considered depending on the types of the Grignard reagent; the transmetallation could not be finished with a too short aging time, and the prolonged aging period would also lead to the deactivation of the reagent.[2] Molander tried to overcome this problem by the use of triflate instead of the chloride.[3] We found, however, that the use of diorganomagnesium, prepared by the addition of a stoichiometric amount of 1,4-dioxane to the corresponding Grignard reagent[7] facilitated the preparation of organolanthanoid species. Here we wish to report the efficient preparation of organolanthanoid reagent by the treatment of $CeCl_3$ or $YbCl_3$ with diorganomagnesium. It seems to offer an information concerned about the transmetallation mechanism.

The formation of butylytterbium species from butylmagnesium reagent and ytterbium trichloride may be monitored by the yield of butylated product of *β*-tetralone, that was easily enolized by butylmagnesium halide or dibutylmagnesium faster than the butylation reaction to carbonyl group.[1,5] Only organolanthanoid species could add to *β*-tetralone to afford the alcohol. In Figure 1, the results of the addition of organoytterbium reagent that was prepared by a treatment of $YbCl_3$ with butylmagnesium bromide or dibutylmagnesium at –78 °C under various aging periods were shown. The detailed procedure is as follows: Commercially available $YbCl_3{\cdot}6H_2O$ (n-Bu_2Mg procedure: 1.5 mmol; n-BuMgBr procedure: 3.0 mmol) was dried in vacuo at 140 °C for 2 h.[8] The obtained dried salt was charged with 5 ml of anhydrous THF, and the mixture was sonicated for 0.5 h using ultrasonic cleaner. The obtained suspension was cooled at –78 °C, and organomagnesium reagent (n-Bu_2Mg: 1.0 mmol, 0.5 M in ether; n-BuMgBr: 2.0 mmol, 1.2 M in ether) was added. After the mixture was stirred for the various aging period indicated in Figure 1 at the same temperature, *β*-tetralone (1.0 mmol) in THF (1.0 mmol) was added. The mixture was stirred for 5 min at –78 °C, and quenched with 1M HCl aq. The aging period of n-Bu_2Mg–$YbCl_3$ which gave the best yield of adduct was 2.5 min, while that of n-BuMgBr–$YbCl_3$ was 20 min. In other words, the formation of reagent completed within 2.5 min in the case of n-Bu_2Mg–$YbCl_3$, while the combination of n-BuMgBr–$YbCl_3$ required 20–30 min to obtain the reactive ytterbium species.

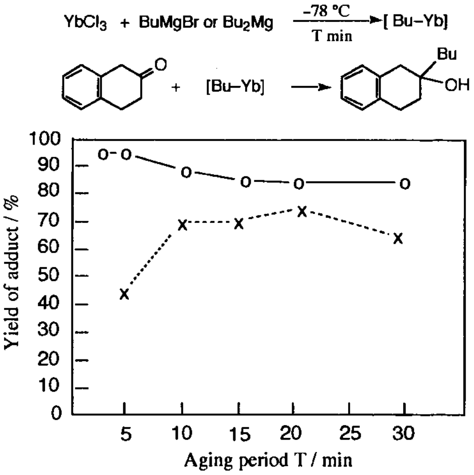


Figure 1. Reaction of *β*-tetralone with the organoytterbium reagent prepared from butylmagnesium reagent (-o-: n-Bu_2Mg + $YbCl_3$, -x-: n-BuMgBr + $YbCl_3$).

In Figure 2, the stoichiometric relationship of the reaction between butylytterbium species and ketones is shown. A butylytterbium reagent prepared from $YbCl_3$ (1.5 mmol) and n-Bu_2Mg (1.0 mmol) was treated with an excess amount of *β*-tetralone (3.0 mmol); the amount of the formed adduct was 0.98 mmol. The same reagent was also treated with 2-heptanone (3.0 mmol) to afford 1.66 mmol of 5-methyldecan-5-ol. The result shows that only one of the pair of butyl groups in diorganomagnesium can be used as a nucleophile for an easily

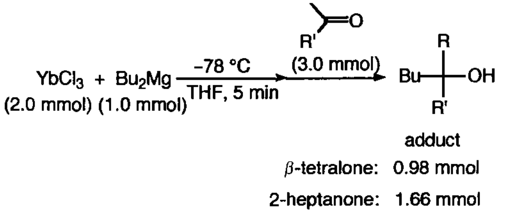


Figure 2. Stoichiometric relationship of the reaction between n-Bu_2Mg–$YbCl_3$ and ketones.

enolizable ketone, β-tetralone, showing the characteristic reactivity of organoytterbium reagent. The reaction with 2-heptanone shows that both butyl groups on diorganomagnesium keep the character as nucleophile.

In Figure 3, a similar experiment using *n*-BuMgBr and $YbCl_3$ is shown. In the reaction with β-tetralone, half of the amounts of butyl groups were transferred nucleophilicly to the carbonyl group.

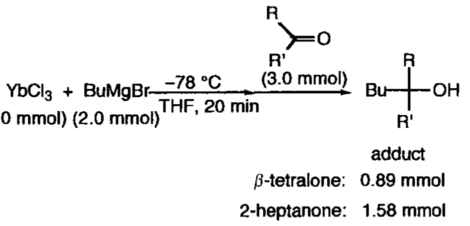
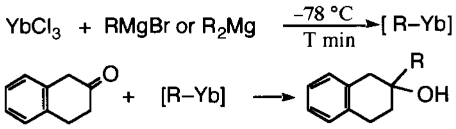


Figure 3. Stoichiometric relationship of the reaction between *n*-BuMgBr–$YbCl_3$ and ketones.

Table 1. The Addition of Organomagnesium–$YbCl_3$ or $CeCl_3$ to β-Tetralone.[a]



entry	MCl_3	R-Mg	T min	Yield / %
1	–	*n*-BuMgBr[b]	–	9
2	–	*n*-Bu_2Mg[c]	–	7
3	$CeCl_3$	*n*-BuMgBr[b]	5	66
4	$CeCl_3$	*n*-Bu_2Mg[c]	5	81
5	$YbCl_3$	*n*-BuMgBr[b]	5	44
6	$YbCl_3$	*n*-Bu_2Mg[c]	5	98
7	$YbCl_3$	PhMgBr[b]	5	9
8	$YbCl_3$	Ph_2Mg[c]	5	74
9	$YbCl_3$	PhMgBr[b]	15	28
10	$YbCl_3$	Ph_2Mg[c]	15	89
11	$YbCl_3$	CH_2=CHMgBr[d]	5	89
12	$YbCl_3$	$(CH_2=CH)_2Mg$[c]	5	94

[a] $YbCl_3$ (3.0 mmol), RMgBr (2.0 mmol), β-tetralone (1.0 mmol), and THF (6 mL) were used; $YbCl_3$ (2.0 mmol), R_2Mg (1.0 mmol), β-tetralone (1.0 mmol), and THF (6 mL) were used. [b] Prepared in ether. [c] Prepared by the addition of a stoichiometric amount of 1,4-dioxane to the corresponding organomagnesium halide. [d] Prepared in THF.

The combination of dibutylmagnesium and ytterbium trichloride can also be applied to the following system as shown in Table 1: *n*-Bu_2Mg–$CeCl_3$, Ph_2Mg–$YbCl_3$, and $(CH_2=CH)_2Mg$–$YbCl_3$. In all cases, the organolanthanoid reagents were obtained efficiently.

We suppose the transmetallation of alkyl group on butylmagnesium bromide to ytterbium metal may occur as dibutylmagnesium through Schlenk equilibrium (Figure 4).

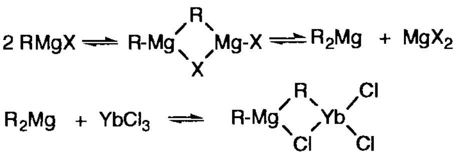


Figure 4. Schematic transmetallation pathway.

The transmetallation between diorganomagnesium and lanthanoid trichloride via the Schlenk equilibrium might be a crucial pathway in some transition metal salts and Griganrd reagents.[9] The studies for the transmetallation are now underway.

Dedicated to Professor Hideki Sakurai on the occasion of his 70th birthday.

References and Notes

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