charge (not over the center of the central six-membered ring). Also, the optimal position of the positive charge is symmetrical (that means the structures 12, 13, and 14 have C_s symmetry with a plane of symmetry defined by $\oplus$-C_9-C_{10}; this differs from **7a**, **8a**, and **9a**).

Comparison of θ and γ angles found for 12–14 with the data for the isolated anions of 2 (Table I) shows only minor differences. The only significant change is observed for the γ angle in 14. In this case the well-known effect of bending a proximal hydrogen atom away from a positive charge forces the H_{10} hydrogen atom to occupy a pseudoequational position and increases the γ angle from 3.6° (for the isolated 10-anion of 2) to 16.0° for 14. However, in the alternative structure 13, which is slightly more stable (by 0.65 kcal/mol), that angle is again very close to 0°. We therefore conclude that according to MNDO calculations, interaction of a purely coulombic nature with the cation does not cause significant changes in the structure of the anions considered herein. This means that calculated structures of the isolated anions of 9-R-9,10-dihydroanthracenes may well serve as models for not only gas-phase studies but also condensed phases (solution, various state of ion-pairing) provided that MNDO correctly reproduces structures of the isolated anions. This model of slightly puckered 9-R-9,10-DHA anions with the "anionic center" hybridization close to sp^2 agrees well with the recent alkylation and NMR studies.[1w]

Acknowledgment. We gratefully acknowledge the U.S. Department of Energy, Office of Basic Energy Sciences, for support of this work. We also appreciate the assistance of Dr. Ken Lipkowitz.

Chemistry of Organolanthanoids. Lanthanoid-Mediated C–C Bond Formation and Cleavage and C–C Double Bond Reduction

Zhaomin Hou, Yuzo Fujiwara,* Tetsuro Jintoku,† Norioki Mine, Kazuhiro Yokoo, and Hiroshi Taniguchi

Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan

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Reactions of the organolanthanoid σ-complexes RLnI with α,β-unsaturated carbonyl compounds and allylic alcohols under various conditions are described. An equivalent of RYbI reacts with α,β-unsaturated carbonyl compounds to give 1,2-addition products **1** regioselectively. On the other hand, the reaction of an excess of RYbI with chalcone gives C–C bond cleavage products **2** and **4** and deoxygenation product **3** instead of **1**. In the reactions of PhYbI with benzalacetone or cinnamyl alcohol, compounds **5**, derived from addition of RYbI to the C–C double bonds of the substrates, are obtained as main products. An excess of PhEuI reacts with α,β-unsaturated carbonyl compounds to give **2**–**4**. C–C double bonds conjugated with phenyl group are hydrogenated by PhYbI/MeOH. Reduction of *trans*-stilbene with Yb/MeOD gives the deuteriated product **6a**.

Although numerous compounds of lanthanoid metals (Ln) have been prepared and characterized,[1] much less is known about their applications in organic reactions. Recently, considerable efforts have been made on the utilization of these elements, especially their salts, in organic reactions, and some interesting synthetic procedures have been developed.[2,3] However, relatively few reports may be found on organolanthanoids in organic reactions.[4]

The first divalent organolanthanoid σ-complexes of type RLnI were prepared from lanthanoid metals and organic iodides (RI) in tetrahydrofuran(THF) by Evans et al.[5] We are interested in the reactions of lanthanoids for the aim of exploring new synthetic reactions and investigated some reactions of organolanthanoids RLnI with ketones, aldehydes, esters, nitriles, and acid chlorides.[6] We have showed that although the complexes RLnI are similar to the Grignard reagent (RMgX) in formula, they have rather different reactivities: the reaction of RLnI (Ln = Yb, Eu) with esters giving ketones as main products rather than tertiary alcohols[6a] and the reaction with aldehydes resulting in formation of Tishchenko condensation products (Ln = Sm, Pr, Nd, Dy).[6f] In this paper we report on the reactions of RLnI with α,β-unsaturated carbonyl compounds and allyl alcohols in which formation and/or cleavage of C–C bonds takes place depending upon reaction conditions. The PhYbI/MeOH-mediated hydrogenation of C–C double bonds conjugated with a phenyl group is also described.

Table I. Reactions of RYbI with α,β-Unsaturated Carbonyl Compounds[a]

run	RYbI	carbonyl compd	1,2-addition product (yield, %[b])
1	PhYbI	chalcone[c]	**1a** (62)
2	PhYbI	acrolein	**1b** (66)
3	PhYbI	methyl vinyl ketone	**1c** (37)
4	PhYbI	benzalacetone	**1d** (43)
5	MeYbI	2-cyclohexen-1-one	**1e** (39)

[a] Yb/RI/carbonyl compound = 0.5:0.75:0.5 (mmol); room temperature; 18 h. [b] GC yields based on the substrate. [c] Yb/PhI/chalcone = 1.25:1.0:1.0; −30 °C, 1 h, and then room temperature, 18 h.

Preliminary accounts of a portion of this work have appeared.[7]

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† On leave of absence from Idemitsu Petrochemical Co. Ltd., Tokuyama, Japan.

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Table II. Reactions of PhYbI with Chalcone at Various Substrate Ratios[a]

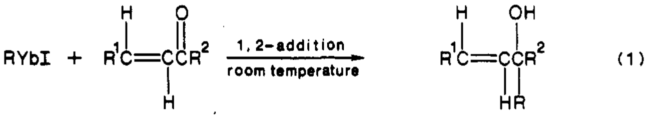
		product yield, %[b]		
run	PhYbI:chalcone	**2a**	**3a**	**1a**
1	1.0:1.0	*d*	*d*	62
2	1.5:1.0	12[c]	5	40
3	2.0:1.0	22[c]	36	*d*
4	3.0:1.0	31[c]	30	*d*

[a] −30 °C, 1 h, and then room temperature, 18 h. [b] GC yields based on chalcone. [c] Diphenylmethanol (**4a**) was also formed in almost equimolar amounts with respect to **2a**. [d] Trace.

Results and Discussion

1,2-Addition to α,β-Unsaturated Carbonyl Compounds. Addition of an equivalent amount of α,β-unsaturated carbonyl compounds to the organolanthanoid σ-complexes RYbI, prepared in situ from Yb metal and RI, gave 1,2-addition products exclusively (eq 1 and Table I), and little 1,4-addition product could be detected.

$$\mathrm{Yb} + \mathrm{RI} \xrightarrow[-30\,^{\circ}\mathrm{C}]{\mathrm{THF}} \mathrm{RYbI}$$

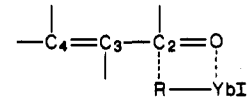


(1)

1a, R = R^1 = R^2 = Ph
b, R = Ph, R^1 = H, R^2 = H
c, R = Ph, R^1 = H, R^2 = Me
d, R = R^1 = Ph, R^2 = Me
e, R = Me, R^1, R^2 = (CH$_2$)$_3$

These results are in sharp contrast to those in the case of the Grignard reagent which usually gives mixtures of 1,2- and 1,4-addition products.[8] Similar regioselectivity was reported recently by Beletskaya[9] and Imamoto.[3h]

This unique regioselectivity could be explained by the hard and soft acids and bases (HSAB) theory. According to the HSAB theory, the lanthanoid complexes (RLnI) are harder than the Grignard reagents and in the conjugated enone system C$_2$ (carbonyl carbon) is harder than C$_4$ (in A).[10] Thus the attack of RYbI is enhanced at the harder site, i.e., C$_2$, to give 1,2-addition products selectively.



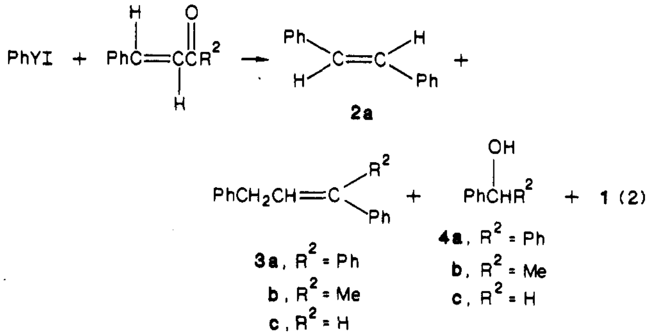
A

Table III. Reactions of PhYbI with Chalcone at Various Temperatures[a]

		product yield, %[b]		
run	reaction conditions	**2a**	**3a**	**1a**
1	−30 °C, 18 h	*e*	*e*	41
2	−30 °C, 1 h; then r.t.,[c] 3 h	21[d]	16	24
3	−30 °C, 1 h; then r.t.,[c] 18 h	31[d]	30	*e*
4	−30 °C, 1 h; then 60 °C, 3 h	21[d]	9	*e*

[a] Yb/PhI/chalcone = 3.5:3.0:1.0. [b] GC yields based on chalcone. [c] r.t. = room temperature. [d] Diphenylmethanol (**4a**) was also formed in almost equimolar amounts with respect to **2a**. [e] Trace.

Effect of the Molar Ratio on the Reaction of PhYbI with Chalcone. As described above, the reaction of an equimolar amount of PhYbI with chalcone gives 1,2-addition product **1a** selectively (run 1, Table I), but interestingly enough, as the ratio of PhYbI to chalcone increases, *trans*-stilbene (**2a**), the C–C bond cleavage product, or triphenylpropene **3a**, the deoxygenation product,[9] becomes the main product instead of **1a** (eq 2 and runs 2–4, Table II). If the reaction is carried out only at −30 °C without heating up to room temperature, **1a** is still formed exclusively, although excess of PhYbI is present (run 1, Table III). The reaction at 60 °C resulted in decrease in yield (run 4, Table III) which might be due to the decomposition of the complex PhYbI at this temperature. In any reactions where *trans*-stilbene (**2a**) was obtained, almost equimolar amount of diphenylmethanol (**4a**) was also formed. It was thought that **2a** was formed via cleavage of the acyl–vinyl carbon bond of chalcone and addition of a Ph group of PhYbI. To test this, the reaction of chalcone with *p*-methylphenylytterbium iodide (*p*-MeC$_6$H$_4$YbI) was carried out. From this reaction, the methyl-substituted stilbene (**2b**, *p*-MeC$_6$H$_4$CH=CHPh, 19%) was obtained with **3d** (15%) and **4d** (14%) (eq 3), and the unsubstituted stilbene **2a** was not detected, indicating that one Ph group of **2a** was derived from the complex PhYbI and not from chalcone in the reaction of PhYbI with chalcone. This is the first example of the formation of stilbene via the C–C bond cleavage of chalcone activated by organolanthanoids, and there is no precedented example even in the d-block transition-metal chemistry.[11]

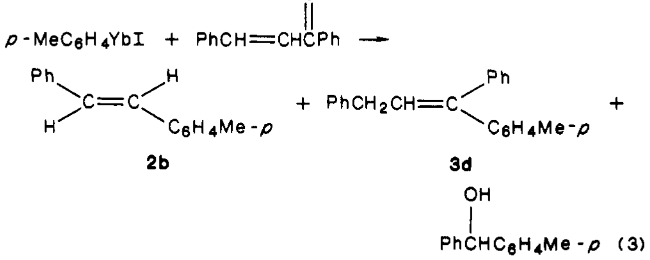


(2)

2a

3a, R^2 = Ph
b, R^2 = Me
c, R^2 = H

4a, R^2 = Ph
b, R^2 = Me
c, R^2 = H



(3)

2b **3d** **4d**

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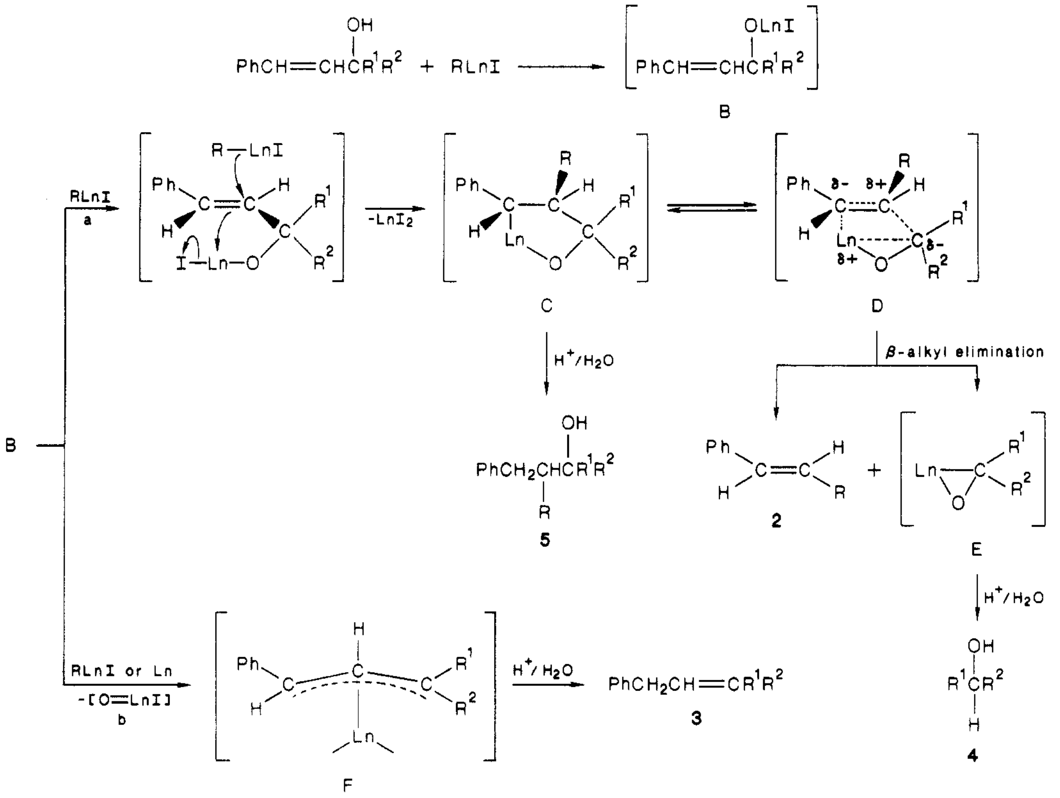
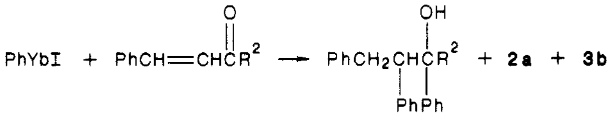
Scheme I. Possible Reaction Mechanism



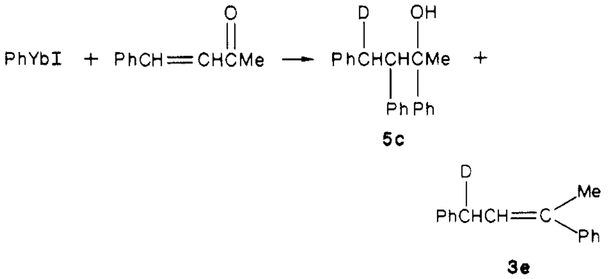
Reaction of Excess PhYbI with Benzalacetone and Cinnamaldehyde. Besides **2a** (1%) and **3b** (28%), the reaction of excess PhYbI with benzalacetone gave an unexpected compound **5a** as a main product (43%) derived from the addition of PhYbI to the C–C double bond of the substrate (eq 4). In the case of cinnamaldehyde, the addition product **5b** (12%) was also obtained with **3c** (16%), and **2a** could not be detected.



$$\mathrm{PhYbI + PhCH{=}CHC(O)R^2 \longrightarrow PhCH_2CH(Ph)CH(OH)(Ph)R^2 + \mathbf{2a} + \mathbf{3b,c}} \quad (4)$$

5a, $R^2 = CH_3$
b, $R^2 = H$

It was also found that quenching the reaction of PhYbI with benzalacetone with D_2O gave the deuteriated products **5c** and **3e** in 40% and 27% yields, respectively (eq 5).



$$\mathrm{PhYbI + PhCH{=}CHC(O)Me \longrightarrow PhCH(D)CH(Ph)C(OH)(Ph)Me + PhCH(D)CH{=}C(Me)Ph} \quad (5)$$

5c **3e**

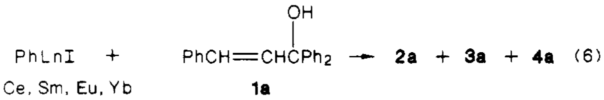
Reaction of Excess PhEuI with α,β-Unsaturated Carbonyl Compounds. In the reaction of an excess of PhEuI with α,β-unsaturated carbonyl compounds, products **2a** and **3** were also obtained. Unlike in the case of PhYbI, however, the addition products **5** were not detected (Table IV).

Table IV. Reactions of PhEuI with α,β-Unsaturated Carbonyl Compounds[a]

run	R	PhEuI: PhCH=CHC(O)R	product (yield, %[b])
1	Ph	1.0:0.5	**2a** (29), **3a** (7), **4a** (2)
2	Me	1.25:0.5	**2a** (35), **3b** (8), **4b** (trace)
3	H	1.0:0.5	**2a** (8),[c] **3c** (trace), **4c** (trace)

[a] −30 °C, 1 h, and then room temperature, 18 h. [b] GC yields based on PhCH=CHC(O)R. [c] 1,3-Diphenyl-1-propanone ($PhCH_2CH_2C(O)Ph$) was also formed in 12% yield.

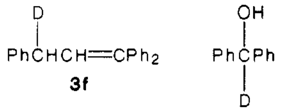
Reaction of Excess PhLnI with Allylic Alcohols. The results of the reactions of excess PhLnI with 1,1,3-triphenylprop-2-en-1-ol (**1a**) are summarized in eq 6 and Table V. As is shown in Table V, in this case compounds



$$\mathrm{PhLnI + PhCH{=}CHC(OH)Ph_2 \longrightarrow \mathbf{2a} + \mathbf{3a} + \mathbf{4a}} \quad (6)$$

Ln = Ce, Sm, Eu, Yb **1a**

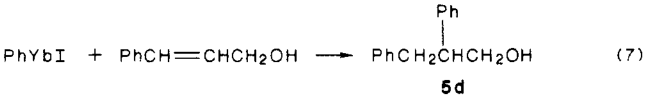
2a, **3a**, and **4a** were also obtained. Furthermore, in the case of PhYbI, D_2O quenching of the reaction mixture gave **2a** and the deuteriated products **3f** and **4e** in 20%, 47%, and 17% yields, respectively. On the other hand, the reaction



$$\mathrm{PhCH(D)CH{=}CPh_2 \qquad PhC(OH)(D)Ph}$$

3f **4e**

of PhYbI with cinnamyl alcohol gave the addition product, 2,3-diphenyl-1-propanol (**5d**) in 39% isolated yield and no C–C bond cleavage product **2a** could be detected (eq 7). In the case of the Grignard reagent (PhMgI), this type of addition did not occur.



$$\mathrm{PhYbI + PhCH{=}CHCH_2OH \longrightarrow PhCH_2CH(Ph)CH_2OH} \quad (7)$$

5d

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(11) To our knowledge, only one example of metal-mediated C–C bond cleavage has been reported on thermal decomposition of organoaluminum compounds: Phohl, W. *Ann. Chem.* **1960**, *629*, 207.

Table V. Reactions of PhLnI with Triphenylallyl Alcohol[a]

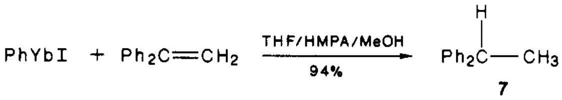
run	Ln	PhLnI:PhCH=CHC(OH)Ph$_2$	product yield, %[b]		
			2a	**3a**	**4a**
1	Ce	3.0:0.5[c]	5	16	*d*
2	Sm	3.0:0.5[c]	3	24	2
3	Eu	1.0:0.5	53	13	6
4	Yb	1.5:0.5[c]	22	48	19

[a] Room temperature, 18 h. [b] GC yields based on the alcohol. [c] The lower ratio gave lower yield of each product. [d] Trace.

Reaction Mechanism. On the basis of the above results, we suggest the reaction mechanism shown in Scheme I. First, RLnI reacts with the allylic alcohol to give an Ln–alkoxide complex B[12] to which another molecule of RLnI attacks to give the metallacyclic intermediate C (path a).[13] C would exist in equilibrium with D whose bonds are more polarized than those of C.[14] Hydrolysis of C would give the addition product **5**. In the case of chalcone and triphenylallyl alcohol ($R^1 = R^2 =$ Ph in D), the equilibrium between C and D would move to the right by stabilization of phenyl resonance in D. D would undergo β-alkyl elimination to give **2**, the C–C bond-cleavage product, and the three-membered metallacycle E,[15] which would give alcohol **4** after hydrolysis. Less formation of **4** than **2** in the case of PhEuI might be due to the possible decomposition of **E** before hydrolysis, to give unidentified oligomers. With excess of RLnI or Ln metals, **B** also undergoes C–O bond cleavage and electron transfer from RLnI or Ln metals to give π-complex F, which would give **3** after hydrolysis (path b).

Reduction of C–C Double Bond by PhYbI. Since the addition product was obtained in the reaction of PhYbI with cinnamyl alcohol, we tried the reaction of PhYbI with *trans*-stilbene under the same conditions to test whether the addition reaction would occur in the case of simple olefins. However no such an addition product was obtained, but instead, bibenzyl (**6**), the reduction product, was formed in 18% yield. When some amounts of MeOH was added as a hydrogen source, the yield of **6** greatly increased up to 87% (eq 8). 1,1-Diphenylethylene can also be reduced to 1,1-diphenylethane (**7**) by PhYbI almost quantitatively (eq 9). Furthermore, Yb metal was also found to be able to reduce *trans*-stilbene to **6** in excellent yield, and when MeOD is used instead of MeOH, the deuteriated reduction product **6a** is formed (eq 10). Reduction of other unsaturated C–C bonds with Yb metal gives the corresponding saturated compounds in good to excellent yields.[16] Studies on reduction of other substrates with lanthanoid-based reducing agents are under progress.

$$\text{PhYbI} + \text{PhCH=CHPh} \xrightarrow[87\%]{\text{THF/MeOH}} \underset{\mathbf{6}}{\text{PhCH}_2\text{CH}_2\text{Ph}} \qquad (8)$$



$$\text{PhYbI} + \text{Ph}_2\text{C=CH}_2 \xrightarrow[94\%]{\text{THF/HMPA/MeOH}} \text{Ph}_2\text{C(H)}\text{—CH}_3 \qquad (9)$$

7

$$\text{Yb} + \text{PhCH=CHPh} \xrightarrow[95\%]{\text{THF/MeOD}} \text{PhCH(D)CH(D)Ph} \qquad (10)$$

6a

Conclusion. To our knowledge, addition of organometal complexes RMX (M = metal) to the C–C double bond of α,β-unsaturated carbonyl compounds and allylic alcohols is rare,[13,17] and the C–C bond cleavage of these compounds by RLnI complexes has not been reported. The data presented here demonstrate that the organolanthanoid σ-complexes RLnI have very unique reactivity which Grignard reagents or d-block transition metals do not have. They are not only able to form a C–C bond but also to cleave it, as well as to act as powerful reducing agents.

Experimental Section

General Methods. Infrared spectra were recorded on a Hitachi 270-30 IR spectrometer. ^{1}H NMR were recorded on a Hitachi R-600 spectrometer and are reported in ppm from internal tetramethylsilane on the δ scale with splitting pattern and relative integrated area. The letter designates the multiplicity of the signal: s, singlet; d, doublet; t, triplet; m, multiplet. Mass spectra were obtained on a JEOL GC-MS JMS-QH-100 apparatus. Analytical GLC was carried out on a Shimadzu Model GC-3BF gas chromatograph equipped with a flame ionization detector using a 2.5 m × 3 mm stainless steel column packed with silicone OV-17 on Chromosorb W and an internal standard. Peak area integration was performed by a Shimadzu Chromatopac C-R3A. All lanthanoid metals were obtained from Rare Metallic Co. Yb and Sm were 40 and 20 mesh powders, respectively. Eu and Ce were freshly cut from ingots in a dry glovebox filled with nitrogen before use. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under N_2 prior to use. All starting organic compounds used were commercial grades and purified by distillation or recrystallization before use. All reactions were carried out under N_2.

Reaction of an Equimolar Amount of RYbI with α,β-Unsaturated Carbonyl Compounds. In a 50-mL centrifuge tube were placed a magnetic stirring bar and 0.5 mmol of Yb powders under air, and the tube was sealed with a serum cap. After the tube was dried by heating under N_2, 2 mL of THF was added by syringe. Then 0.75 mmol of RI in 2 mL of THF was added slowly to the tube at −30 °C during 5–10 min. After a short induction period (5–10 min), Yb started to react with the iodide, and then the mixture was stirred for several hours at −30 °C. To the resulting red brown solution of RYbI complex was added the substrate (0.5 mmol in THF, 2 mL) by syringe at −30 °C. The mixture was then heated to room temperature and stirred overnight. The products were treated with 2 N HCl and then extracted with ether (4 × 25 mL). The combined organic extracts were washed with saturated $NaHCO_3$ and dried over anhydrous Na_2SO_4. After the solvent was evaporated, the products were identified by ^{1}H NMR, IR, and retention time comparison with authentic materials. The yields of the products (R = Ph and Me) are described in Table I. Physical properties of the products are recorded below.

1,1,3-Triphenylprop-2-en-1-ol (1a:[9] IR (Nujol) 3500, 1604, 1494 cm^{-1}; NMR (CCl_4) δ 2.11 (br s, 1 H), 6.62 (d, J = 1.2 Hz, 2 H), 6.95–7.54 (m, 15 H).

1-Phenylprop-2-en-1-ol (1b):[18] IR (neat) 3450, 1604, 1494 cm^{-1}; NMR (CCl_4) δ 3.99 (br s, 1 H), 4.99 (m, 2 H), 5.87 (m, 1 H), 7.03 (s, 5 H).

2-Phenylbut-3-en-2-ol (1c):[19] IR (neat) 3450, 1604, 1494 cm^{-1}; NMR (CCl_4) δ 1.50 (s, 3 H), 2.11 (br s, 1 H), 5.10 (m, 2 H), 5.90 (m, 1 H), 7.00 (m, 5 H).

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2,4-Diphenylbut-3-en-2-ol (1d):[20] IR (neat) 3400, 1604, 1494 cm^{-1}; NMR (CCl_4) δ 1.54 (s, 3 H), 2.83 (br s, 1 H), 6.38 (d, J = 1.2 Hz, 2 H), 7.10 (m, 10 H).

1-Methylcyclohex-2-en-1-ol (1e):[21] IR (neat) 3450 cm^{-1}; NMR (CCl_4) δ 1.15 (s, 3 H), 1.35–2.15 (m, 7 H), 5.54 (s, 2 H).

Reaction of Excess RLnI with α,β-Unsaturated Carbonyl Compounds and Allylic Alcohols. To a solution of RLnI (Ln/RI = 3.5:3.0 (mmol); THF, 8 mL), which was prepared as above, was added the substrate (1 mmol in 2 mL of THF) at −30 °C. The mixture was stirred at −30 °C for 1 h and then at room temperature overnight. Usually a color change (from red-brown to purple) was observed during this stage. After the workup as described above, the products were isolated by liquid (silica gel) or gas chromatography. Identities with products formed were proved by mixture melting point, IR, NMR, and retention time comparison with those of authentic samples.

***trans*-Stilbene (2a):** mp 124–126 °C (lit.[22] mp 124 °C); NMR (CCl_4) δ 6.99 (s, 2 H), 7.05–7.55 (m, 10 H).

***trans*-*p*-Methylstilbene (2b):** mp 120 °C (lit.[23] mp 119–120 °C); NMR (CCl_4) δ 2.35 (s, 3 H), 6.97 (s, 2 H), 7.03–7.55 (m, 9 H).

1,1,3-Triphenyl-1-propene (3a):[9,24] NMR (CCl_4) δ 3.45 (d, J = 7.8 Hz, 2 H), 6.19 (t, J = 7.8 Hz, 1 H), 6.90–7.40 (m, 15 H).

***trans*-2,4-Diphenyl-2-butene (3b):**[25] NMR (CCl_4) δ 2.13 (s, 3 H), 3.50 (d, J = 7.2 Hz, 2 H), 5.90 (t, J = 7.2 Hz, 1 H), 7.15 (s, 10 H).

***trans*-1,3-Diphenyl-1-propene (3c):**[26] NMR (CCl_4) δ 3.50 (d, J = 4.8 Hz, 2 H), 6.15–6.96 (m, 2 H), 7.15 (s, 10 H).

1,3-Diphenyl-1-*p*-tolyl-1-propene (3d):[26] mixture of trans and cis isomers; NMR (CCl_4) δ 2.30, 2.37 (a pair of *s*, 3 H), 3.43 (d, J = 7.8 Hz, 2 H), 6.19 (t, J = 7.8 Hz, 1 H), 6.95–7.34 (m, 14 H).

2,3,4-Triphenyl-2-butanol (5a): IR (neat) 3450, 1604, 1494 cm^{-1}; NMR (CCl_4) δ 1.26 (br s, 1 H), 1.58 (s, 3 H), 2.70–3.31 (m, 3 H), 6.60–7.04 (m, 10 H), 7.18 (s, 5 H); mass spectrum, *m/e* (relative intensity) 284 (32, M$^+$ − 18), 193 (100).

1,2,3-Triphenyl-1-propanol (5b): IR (neat) 3380, 1604, 1494 cm^{-1}; NMR (CCl_4) δ 1.80 (br s, 1 H), 2.80–3.40 (m, 3 H), 4.79 (d, J = 7.2 Hz, 1 H), 6.68–7.01 (m, 10 H), 7.10 (s, 5 H); mass spectrum, *m/e* (relative intensity) 270 (51, M$^+$ − 18), 178 (100).

2,3-Diphenyl-1-propanol (5d): IR (neat) 3400, 1604, 1494 cm^{-1}; NMR (CCl_4) δ 1.03 (s, 1 H), 2.71–3.15 (m, 3 H), 3.54–3.85 (m, 2 H), 7.05 (s, 5 H), 7.14 (s, 5 H); mass spectrum, *m/e* (relative intensity) 212 (9, M$^+$), 193 (100).

D_2O Quenching Experiment. After the reaction was carried out as described above, the reaction mixture was first treated with 1 mL of D_2O and then with 2 N HCl. The products were isolated by medium-pressure liquid chromatography (silica gel) and identified by NMR, IR, and GLC comparison with those of the corresponding undeuteriated ones.

2,4-Diphenyl-4-deuteriobut-2-ene (3e): NMR (CCl_4) δ 2.13 (s, 3 H), 3.48 (d, J = 7.2 Hz, 1 H), 5.90 (d, J = 7.2 Hz, 1 H), 7.15 (s, 10 H).

1,1,3-Triphenyl-3-deuterioprop-1-ene (3f): NMR (CCl_4) δ 3.41 (d, J = 7.2 Hz, 1 H), 6.19 (d, J = 7.2 Hz, 1 H), 6.90–7.40 (m, 15 H).

Diphenyldeuteriomethanol (4e): mp 66.5–67.5 °C; NMR (CCl_4) δ 2.25 (s, 1 H), 7.21 (s, 10 H).

2,3,4-Triphenyl-4-deuteriobutan-2-ol (5c): IR (neat) 3450, 1604, 1494, cm^{-1}; NMR (CCl_4) δ 1.26 (br s, 1 H), 1.58 (s, 3 H), 2.74 (d, J = 12 Hz, 1 H), 3.16 (d, J = 12 Hz, 1 H), 6.60–7.04 (m, 10 H), 7.18 (s, 5 H).

Reduction of Olefins by PhYbI. To a PhYbI solution (1.5 mmol) were added the olefin (0.5 mmol in 2 mL of THF) and MeOH (0.5 mL) by syringe at −30 °C. The mixture was then stirred at room temperature overnight and finally a dark slurry was obtained. After workup as described above, the products were isolated by medium-pressure liquid chromatography (silica gel) and identified by NMR and GLC. The products are **6**[27] and **7**.[28]

Reduction of *trans*-Stilbene by Yb Metal. To 1.5 mmol of Yb metal was dropped 2 μL of CH_3I under N_2, and the metal was then warmed slightly with a dryer. Addition of 2 mL of THF gave a colored solution to which 0.5 mmol of *trans*-stilbene with THF (2 mL) and MeOD (0.5 mL) were introduced with a syringe. The mixture was then stirred at room temperature overnight and finally a dark slurry was obtained. Usual workup followed by chromatographic purification (silica gel) gave α,α'-dideuteriobibenzyl (**6a**): mp 52.0–52.5 °C; 86.5 mg (95% yield); NMR (CCl_4) δ 2.87 (s, 2 H), 7.11 (s, 10 H); mass spectrum, *m/e* (relative intensity) 184 (1, M$^+$), 92 (100).

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