Allyl Alcohols and Organocerium Reagents, II[+] Mechanism and Extensibility of the Reaction

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Alkylcerium reagents add to the multiple bonds of allyl and propargyl alcohols in good yields and under mild conditions. The double bond can be reduced with lithium aluminum hydride in the presence of cerium trichloride. The regiochemistry of the attack depends on electronic factors.

Introduction

The observation that organometallic compounds can add to allyl alcohols dates back many years.[1] This reaction has not yet found general synthetic applications, however, since it is restricted to a few reactants and substrates, and often requires extreme reaction conditions. Moreover the regio- and stereochemical outcomes of the reaction are not easily generalized.

Two mechanisms were proposed for the reaction of Grignard reagents. The first one involves an intramolecular rearrangement of an alkenoxy(alkyl)magnesium derivative,[2] followed by an electrophilic attack of the magnesium atom at the olefinic linkage and transfer of the alkyl framework to the farthest terminus of the double bond to form a five-membered magnesacyclic derivative. In such a mechanism the greater the electronic density available in the R−Mg bond, the more readily the alkyl group would migrate to the olefinic bond. A very similar mechanism was also proposed for the addition of organolithium reagents to allyl alcohols in the presence of TMEDA as catalyst.[3] The TMEDA should promote a more facile coordination of RLi to the alcoholate function, removing the counterion from the oxygen, followed by electrophilic addition of the lithium to the double bond and transfer of the alkyl framework to give a noncyclic dianonic species. The second mechanism involves a magnesium halide catalysis in which the magnesium atom, acting as an electrophile, weakens the double bond and favors an intermolecular addition of the Grignard reagent, releasing a magnesium halide molecule.[3]

Recently we reported that alkylcerium reagents add to the double bond of aliphatic, straight chain allyl alcohols to give alkenes with elimination of water.[4] These findings open up an interesting and new window on the synthetic application of organocerium reagents which, until now, were employed mainly in the addition to electrophilic double bonds.[5] These organocerium reagents promise to overcome most of the drawbacks of the previously reported reactions as the regiochemistry of the reaction is easily predictable and the reaction conditions are very mild.

In this paper we report on the extension of this reaction to triple bonds and aryl-substituted double bonds, and the chance to reduce the double bond of allyl alcohols by means of the reducing system $LiAlH_4$ and $CeCl_3$. Moreover, on attempting to explain the reaction pathway we realized that many different cerium species are involved, each with a peculiar reactivity pattern. The exact nature of organocerium compounds is still unknown and has proved to be resistant to all attempts at elucidation,[6][7] although the different reactivity of cerium species, which appear at first sight to be very similar, under different generation conditions, has been demonstrated by Reetz.[8] For example, in the reaction of aldehydes with organocerium compounds, the same $[CH_3Ce(OiPr)_3]^-$ species gave different yields or chemoselectivities when generated from $CeCl_3/3iPrOH/3BuMgBr/CH_3Li$, $Ce(OiPr)_3/CH_3Li$ or $CeCl_3/3iPrOH/4CH_3MgBr$.

Results and Discussion

The reaction was carried out as reported previously,[4] i.e. the lithium alcoholate, preformed from the alcohol and lithium hydride at 0°C, was added to the organocerium reagent, also preformed from a threefold excess of organolithium with respect to dry cerium trichloride, at −78°C. The reaction was allowed to stand at −20°C overnight before quenching with 4% aqueous HCl and submitting the mixture to the usual workup.

As shown in Table 1, the reaction works well with both allyl (entries 1−12) and propargyl alcohols (entries 13−15) with a large variety of substituents at the positions R^1, R^2 and R^3. Among the organocerium species, the most remarkable finding from this reaction is the addition of hydrides under the same experimental conditions (entries 1, 8, 15). The regiochemistry of the reaction is easily predicted, except for the addition of hydrides. In fact, in all the reactions with R^1 = alkyl or H (entries 2−7), the alkyl

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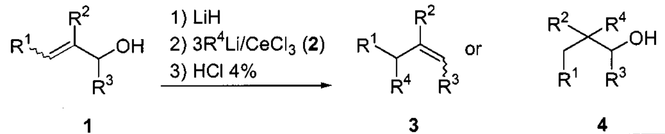
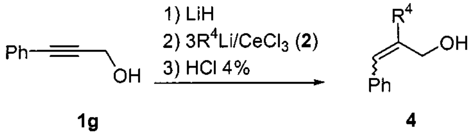
Table 1. Reaction of allyl and propargyl alcohols with various alkylcerium reagents at −78 °C



Entry	Alcohol	R^2	R^1	R^3	Cerium Compound	R^4	Yield (%) 3	Yield (%) 4
1	**1a**	H	H	C_5H_{11}	**2a**	H[a]	-	74
2	**1a**	H	H	C_5H_{11}	**2b**	Bu	92[b]	-
3	**1b**	H	-$(CH_2)_3$-		**2b**	Bu	53	-
4	**1b**	H	-$(CH_2)_3$-		**2c**	Ph	60	-
5	***c*-1c**	H	*cis*-Pr	H	**2b**	Bu	69	-
6	***t*-1c**	H	*trans*-Pr	H	**2b**	Bu	53	-
7	**1d**	Ph	H	Et	**2b**	Bu	55	-
8	**1e**	H	*trans*-Ph	H	**2a**	H[a]	-	74
9	**1e**	H	*trans*-Ph	H	**2b**	Bu	-	97
10	**1e**	H	*trans*-Ph	H	**2d**	Me	-	60
11	**1e**	H	*trans*-Ph	H	**2e**	C_6H_{13}	-	70
12	**1f**	H	*trans*-Ph	Ph	**2b**	Bu	-	55



Entry	Cerium Compound	R^4	Yield (%)
13	**2b**	Bu	48
14	**2d**	Me	49
15	**2a**	H[a]	54

[a] Mixture $LiAlH_4/CeCl_3$. – [b] See ref.[4]

framework of the organocerium reagent binds to the double bond terminus farthest from the alcohol function, while with R^1 = aryl (entries 9–14), it is linked to the nearest one.

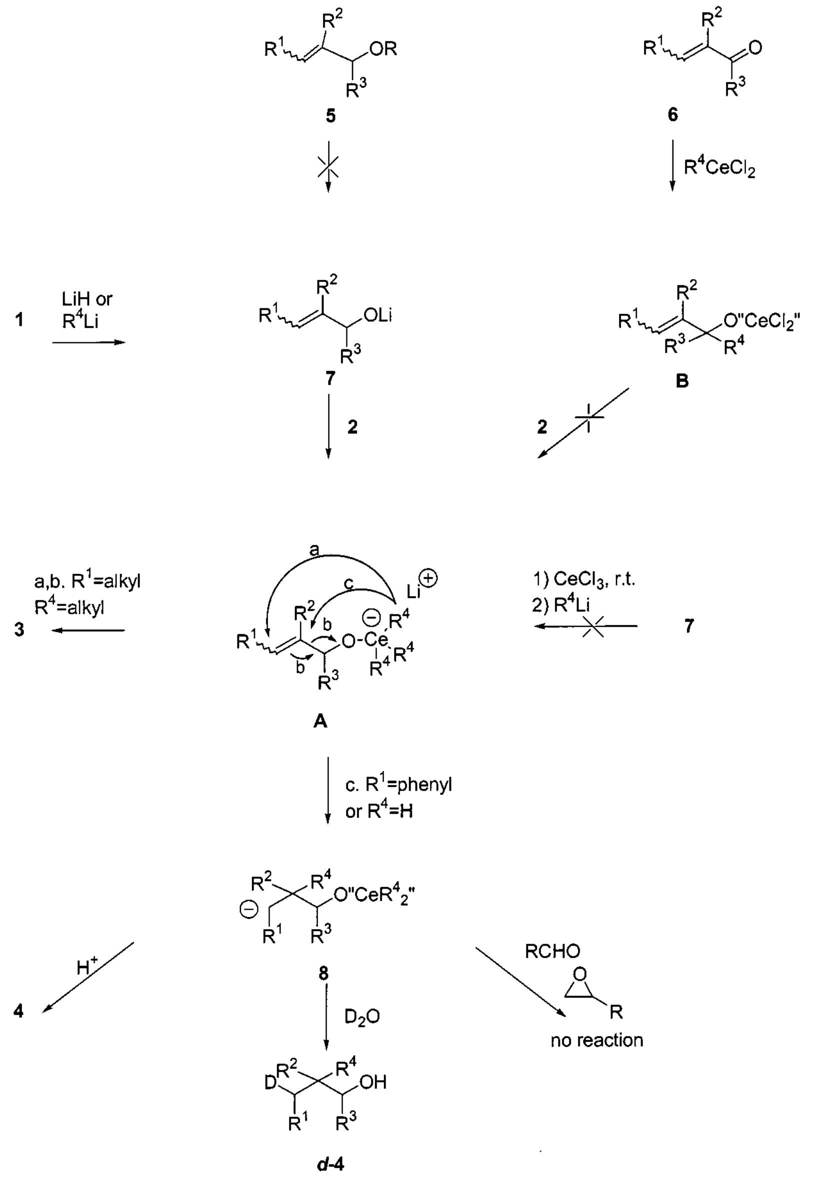
The optimum reaction conditions require a molar ratio of 1:1:3 for alcoholate, cerium trichloride and organolithium reagent, while a molar ratio of 1:1:1 leaves large amounts of unreacted starting materials,[4] thus indicating that the "R^4CeCl_2" species commonly reported in the reaction of organocerium reagents[5k] cannot be the reactive species. Denmark has reported that an $[(R^4)_3CeCl_3]^{3-}$ species may be present at −78 °C.[7]

The formation of a negatively charged oxygen-containing species is essential for the reaction to proceed. In fact, the allyl ethers **5** do not react with organocerium reagents and starting material is quantitatively recovered. If the alcoholate **7** is not preformed by treatment with lithium hydride, it can be formed in situ from deprotonation of the alcohol by the organometallic reagent and thus a further equivalent is required.[4]

Coordination to the oxygen atom of the cerium species, in analogy with the proposal of Eisch for lithium or magnesium,[2] should be the key intermediate step in the reaction. However, although magnesium forms a classical salt, cerium should form an "ate" complex, and assuming that the species proposed by Denmark is correct,[7] the complex might be tentatively described as $[(R^4)_3CeCl_2OR']^{3-}$ or $[(R^4)_3CeOR']^-$ (**A**, Scheme 1).

Species such as $[R^4Ce(OR')_3]^-$ and the addition of R^4Li to $R'OCeCl_2$ are discarded for the following reasons. It has been reported that $Ce(OR')_3$ species are able to form "ate" complexes at −78 °C.[6][8] However, the preparation of cerium octen-3-olate (**7a**) at room temperature, in analogy with Mehorotra's procedure for lanthanide alcoholates,[9] followed by addition of butyllithium (1:3:3 cerium trichloride/alcoholate/butyllithium ratio) at −78 °C gave no reaction. Moreover, the ability of cerium reagents to undergo 1,2-addition to α,β-unsaturated carbonyl compounds **6** is well-known.[5] The intermediates of these reactions are allylcerium alcoholates described as $ROCeCl_2$ (**B**) and they do not undergo further alkylation reactions with the excess of organometallic reagent always present in the reaction mixture.

On the other hand, some abnormal results in the reactions of organocerium species can now be rationalized. The only reported complete reduction of an unsaturated compound is the formation of 3-(2-hydroxyphenyl)-1-propanol from the cerium-mediated lithium aluminum hydride reduction of coumarin (Equation B, Scheme 2).[10] This result can be rationalized supposing the intervention of the alcoholate function at the aromatic ring which is formed after the first reduction step. While the aliphatic oxygen is al-

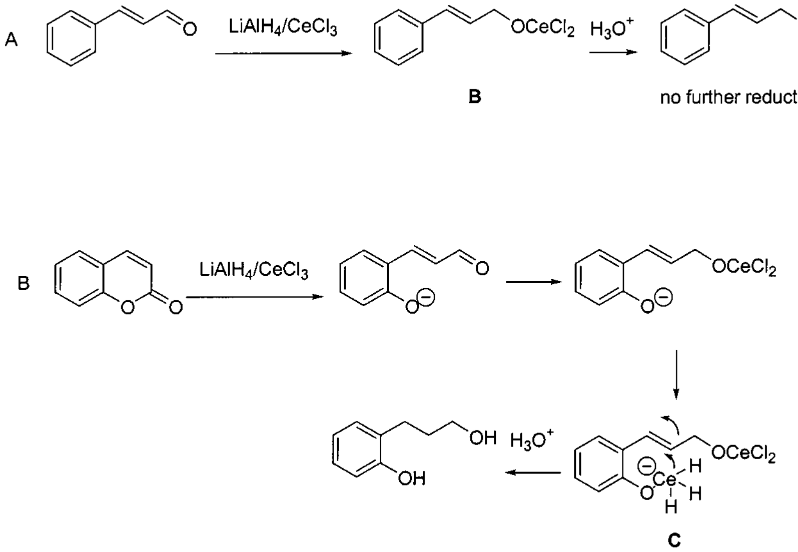


Scheme 1. General mechanism of the reaction

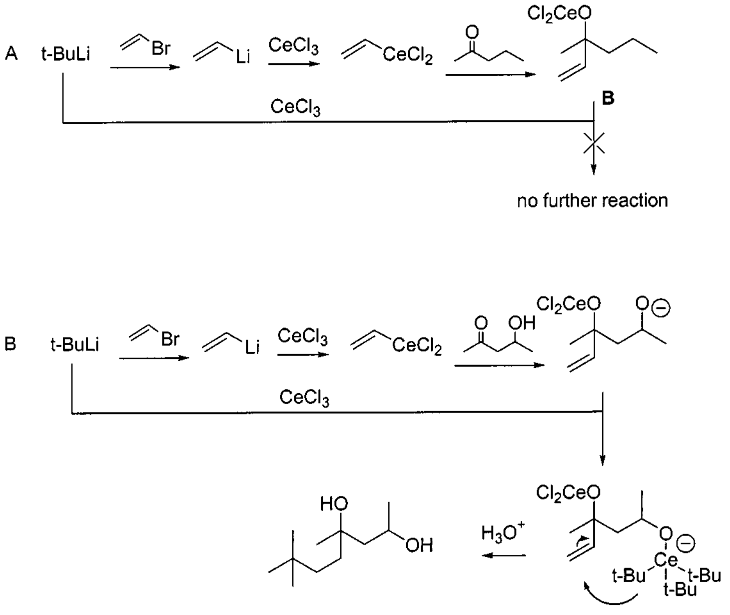
ready busy, the aromatic one may form an "ate" complex similar to **A** (**C**, Scheme 2) which should promote the second addition of hydride. Moreover, we have found the formation of 4,7,7-trimethyl-2,4-octanediol as a by-product[11] in the cerium-mediated addition of vinyllithium to 4-hydroxy-2-pentanone,[5g] although 4,7,7-trimethyl-2-octanol was not observed in the reaction of 2-pentanone under the same experimental conditions (Scheme 3).

This result provides further evidence for our hypothesis. In fact, since vinyllithium was prepared by metal-halogen exchange from an excess of *tert*-butyllithium and vinyl bromide, the diol arises from addition of the adventitious *tert*-butylcerium to the allyl alcoholate intermediate promoted by the second hydroxy function, which acts as the alkoxy function able to give the "ate" complex.

The "ate" complex can evolve following different patterns depending on the substitution at the double bond. When R^1 is an alkyl group, the "ate" complex transfers the R^4 alkyl group to the farthest terminus of the double bond (Scheme 1, pattern a). At the same time, the cerium species still bound to the oxygen is able to cause spontaneous elimination of the alkene in an S_N2'-type mechanism (Scheme 1, pattern b). No evidence for the formation of an anionic intermediate which might dehydrate during acidic workup, such as that proposed by Felkin for the TMEDA-catalyzed addition of RLi to allyl alcohols,[3] was found. In fact, all attempts to trap anionic intermediates either by quenching the reaction with deuterium oxide or by performing tandem reactions were unsuccessful. The transfer most likely occurs from above or below the double bond plane due to the better overlap of the appropriate molecular orbitals, therefore the substitution at the carbon atom carrying the hydroxy function (entries 1−4, 7, 12) or both *cis* and *trans* substitution of the double bond (entries 5, 6) cannot influence



Scheme 2. Abnormal behaviour in the reduction of coumarin[10]

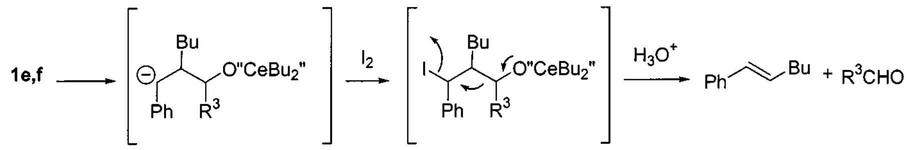


Scheme 3. Abnormal addition of *t*BuLi to β-hydroxy ketones[11]

the reaction. However, when both R^1 and R^3 are not hydrogen, as in compound **1f**, a 10:1 mixture of diastereomers is obtained. When the group to be transferred is the small hydride ion, it links to the terminus of the double bond nearest to the hydroxyl function without elimination (Scheme 1, pattern c), leading to a carbanionic intermediate, as demonstrated by quenching the reaction with deuterium oxide; 1-*d*-3-octanol (***d*-4a**) was isolated in yields similar to those reported in Table 1 (entry 1). When R^1 is a phenyl group, pattern c is also followed by the reaction (table: entries 8−12), but it is likely that electronic factors due to the presence of a charge-stabilizing substituent (the phenyl group) reverse the regiochemistry. As expected, the anionic intermediate can be trapped by reaction with deuterium oxide, but tandem reactions with benzaldehyde or styrene oxide were unsuccessful.

With iodine as the electrophile a reaction occurs, but the expected iodo derivative is not recovered. The products of the reaction are an alkene and an aldehyde, most likely arising from β-elimination from the iodo derivative (Scheme 4). To the best of our knowledge, no similar reactions are reported for other β-iodoalcoholates.

In conclusion the addition reaction of organoceriums to allyl alcohols appears to be widely applicable. It represents a vast improvement in the chemistry of the addition of organometallic reagents to functionalized double bonds. In fact, at present, this reaction seems to have no drawbacks and, moreover, employs easily available starting materials



Scheme 4. Attempted trapping of anionic intermediates with S_2

and mild experimental conditions. Studies are in progress to understand how long the chain between the oxygen atom and the double bond might be.

These results have also shown that the reactivity of organoceriums is very complex. The organocerium species shown to be the same in many reaction schemes for the sake of simplicity are actually very different and behave differently. The discovery of the exact nature of these compounds is a very stimulating field of organometallic chemistry.

Experimental Section

General: ^{1}H NMR spectra were recorded at 200 MHz or 300 MHz and ^{13}C NMR at 50.4 MHz or 75.5 MHz with a Varian Gemini 200 instrument or a Bruker WM300 instrument, respectively. Chemical shifts are given in ppm. from Me_4Si. Coupling constants are given in Hz. Assignment of the signals in the ^{13}C NMR spectra was made by DEPT experiments. IR spectra were recorded with a Perkin−Elmer Paragon 1000 PC FTIR spectrometer. MS were recorded with HP 5972 workstation.

THF was dried by refluxing over sodium wire/benzophenone until the blue color of benzophenone ketyl persisted, and then distilling into a dry receiver under nitrogen atmosphere. 1-Octen-3-ol (**1a**), cyclohex-2-en-1-ol (**1b**), *cis* and *trans*-hex-2-en-1-ol (***c*-1c** and ***t*-1c**) and *trans*-cynnamyl alcohol (**1e**) are commercially available (Aldrich). 2-Phenylpent-1-en-3-ol (**1d**) (α-styrylmagnesium bromide and propionaldehyde), *trans*-1-phenylcinnamyl alcohol (**1f**) (phenyllithium and *trans*-cinnamaldehyde), 3-phenylpropargyl alcohol (**1g**) (lithium phenylacetylide and formaldehyde) were obtained by classical Grignard reactions from the reactants in brackets.

Preparation of the Organocerium Reagents 2a−d: Commercial cerium(III) chloride heptahydrate (5.5 mmol) was placed in a flask with a stir bar. The flask was heated in vacuo in an oil bath to 140 °C/0.2 Torr for 2 h. Nitrogen was introduced while the flask was still hot. The flask was cooled in an ice bath and dry THF was introduced from a syringe. The suspension was stirred overnight at room temperature. The resulting white slurry was then cooled to −78 °C and the titrated organolithium reagent (16.5 mmol) was added dropwise from a syringe [or lithium aluminum hydride (7.5 mmol) was poured in] and the mixture allowed to stir for 2 h.

General Procedure for the Addition of Allyl Alcoholates to Organocerium Reagents: Lithium hydride (5.5 mmol) was poured into a THF solution of allyl (or propargyl) alcohol **1a−h** (5 mmol) with stirring at 0 °C under a nitrogen atmosphere. After 1 h the mixture was syringed into the organocerium reagent with stirring at −78 °C under a nitrogen atmosphere. The reaction was allowed to stand in a freezer for 24 h before quenching with 4% HCl solution, extraction with diethyl ether, and washing with water. The dried (Na_2SO_4) extracts were concentrated under reduced pressure and purified by flash chromatography on a silica gel column light petroleum (40−60°)/diethyl ether, 9:1 as eluent]. Yields of the recovered products are listed in Table 1. All compounds were fully characterized by NMR, IR and mass spectroscopy and gave physical data identical to those reported in the literature for 6-dodecene,[12] 3-butylcyclohexene,[13] 3-phenylcyclohexene,[13] 3-propyl-1-heptene,[14] 4-phenyl-3-octene,[15] 2-(phenylmethyl)-1-hexanol,[16] 3-phenylpropanol,[17] 2-methyl-3-phenylpropanol,[18] (*E*)-2-methyl-3-phenylprop-2-en-1-ol,[19] (*E*)-2-butyl-3-phenylprop-2-en-1-ol.[20] 3-Octanol and cinnamyl alcohol (from reaction between **1g** and **2a**) were identical to commercial samples.

2-(Phenylmethyl)-1-octanol: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.87$ (t, $J = 6.7$ Hz, 3 H, CH_3), 1.22−1.37 (m, 10 H, 5 CH_2), 1.76−1.78 (m, 1 H, CH), 1.84 (br. s, 1 H, OH), 2.61 (ABX, $J_{AB} = 15$, $J_{AX} = 3.2$; $J_{BX} = 3.8$ Hz, 2 H, CH_2Ph), 3.48 (d, $J = 5.2$ Hz, 2 H, CH_2OH), 7.14−7.28 (m, 5 H, Ar). − ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 14.30$ (CH_3), 22.87 (CH_2), 27.14 (CH_2), 29.81 (CH_2), 30.95 (CH_2), 32.04 (CH_2), 37.84 (CH_2Ph), 42.76 (CH), 64.96 (CH_2OH), 125.99 (CH, Ar), 128.44 [2 × CH, Ar], 129.38 [2 × CH, Ar], 141.07 (C, Ar). − IR (film) $\tilde{\nu} = 3331$ (OH) cm^{-1}. − MS: *m*/*z* (%) = 220 (8), 202 (15), 131 (16), 117 (43), 104 (78), 91 (100), 77 (7).

2-(Phenylmethyl)-1-phenyl-1-hexanol: mixture of diastereomers: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.78$ (t, $J = 6.71$ Hz, 3 H, CH_3), 1.12−1.40 (m, 6 H, 3 CH_2), 1.89 (br. d, $J = 2.47$ Hz, 1 H, OH), 1.96−2.08 (m, 1 H, CH), 2.66 (ABX, $J_{AB} = 13.76$, $J_{AX} = 4.58$, $J_{BX} = 8.47$ Hz, 2 H, CH_2Ph), 4.60−4.80 (m, 1 H, CHOH), 7.10−7.40 (m, 10 H, Ar). − ^{13}C NMR (50 MHz, $CDCl_3$) major diastereomer: $\delta = 13.87$ (CH_3), 22.75 (CH_2), 29.07 (CH_2) 29.16 (CH_2), 35.01 (CH_2Ph), 46.97 (CH), 75.57 (CHOH), 125.63 (CH, Ar), 126.39 (CH, Ar), 127.27 [2 × CH, Ar], 128.12 [2 × CH, Ar], 128.22 [2 × CH, Ar], 129.27 [2 × CH, Ar] 141.16 (C, Ar), 143.76 (C, Ar). Minor diastereomer (detectable peaks): $\delta = 15.19$ (CH_3), 27.45 (CH_2), 29.24 (CH_2) 36.84 (CH_2), 47.22 (CH_2Ph), 65.76 (CH), 74.70 (CHOH). − IR (film) $\tilde{\nu} = 3408$ (OH) cm^{-1}. − MS: *m*/*z* (%) = 268 (1), 250 (12), 193 (9), 162 (11), 107 (100), 91 (41), 79 (25).

Preparation of Cerium Allyl Alcoholate: Lithium hydride (16.5 mmol) was poured into a THF solution of alcohol **1a** (15 mmol) with stirring at 0 °C under a nitrogen atmosphere. After 1 h the mixture was added to a stirred suspension of dry cerium chloride (5 mmol), prepared as above, by syringe at −78 °C under a nitrogen atmosphere. After 2 h a solution of BuLi (15 mmol) was dropped from a funnel into the mixture at −78 °C. The mixture was then allowed to stir at 0 °C and monitored by GC/MS and TLC. After two days both chromatograms showed the peak for **1a** to be the only product.

Deuterium Oxide Quenching: The reaction between **1a** and **2b** was quenched with D_2O extracted with ether and the organic layer then submitted to GC/MS analysis. No deuterium incorporation was detected since the $M^+/(M^+ + 1)$ ratio of 6-dodoecene remained unchanged with respect to the standard procedure.

The reaction between **1a** and **2a** was quenched with D_2O extracted with ether and the organic layer then submitted to GC/MS analysis. The peak corresponding to 3-octanol showed the following fragmentation pattern: *m*/*z* (%) = 113 (2), 101 (17), 83 (51), 60 (100), 55 (76), 41 (47). 1-*d*-3-Octanol was isolated after column chromatography (72% yield, oil) and submitted to NMR analysis: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.83−0.95$ (m, 5 H, $CH_3 + CH_2D$), 1.20−1.60 (m, 10 H, 5 CH_2), 1.88 (br. s, 1 H, OH), 3.46−3.57 (m, 1 H, *CH*OH). − ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 9.45$ (t, J = 19.3 Hz, CH_2D), 13.89 (Me), 22.56 (CH_2), 25.26 (CH_2), 29.98, (CH_2), 31.88 (CH_2), 36.88 (CH_2), 73.23 (CHOH)

A reaction between **1e** and **2e** was quenched with D_2O extracted with ether and the organic layer then submitted to GC\MS analysis. The peak corresponding to 2-(phenylmethyl)-1-octanol showed the following fragmentation pattern: m/z (%) = 221 (5), 203 (8), 131 (12), 117 (31), 104 (72), 92 (100). 2-(Phenyl-*d*-methyl)-1-octanol was isolated after column chromatography (69% yield, oil) and submitted to NMR analysis: ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.87$ (t, 3 H, J = 6.6 Hz, Me), 1.16−1.36 (m, 10 H, 5 CH_2), 1.55 (t, J = 6.4 Hz, 1 H, OH), 1.7−1.82 (m, 1 H, CH), 2.59 (d, J = 6.5 Hz, 1 H, CHD), 3.50 (d, J = 5.3 Hz, 2 H, CH_2OH), 7.16−7.30 (m, 5 H, Ar). − ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 14.24$ (Me), 22.80 (CH_2), 27.07 (CH_2), 29.74 (CH_2), 30.89 (CH_2), 31.97 (CH_2), 37.5 (t, J = 19.5 Hz, CHD), 42.63 (CH), 64.92 (CHOH), 125.95 (CH, Ar), 128.40 [2 × CH,Ar], 129.30 [2 × CH, Ar].

Attempted Tandem Reaction: When formation of 6-dodecene from the reaction between **1a** and **2b** was detected by GC/MS, styrene oxide (6 mmol) or benzaldehyde (6 mmol) in THF was added. Samples, treated as above, were submitted to GC/MS analyses. No products arising from tandem addition to oct-1-en-3-ol were detected. The only recognizable products by GC/MS were styrene oxide, 6-dodecene, 1-phenyl-1-hexene (from addition of butyl carbanion excess to styrene oxide) in the former reaction and benzaldehyde, 6-dodecene, and 1-phenylpentanol (from addition of butyl carbanion excess to benzaldehyde) in the latter.

When formation of 2-(phenylmethyl)-1-hexanol from the reaction between **1e** and **2b** was detected by GC/MS, styrene oxide (6 mmol) or benzaldehyde (6 mmol) in THF was added. Samples, treated as above, were submitted to GC/MS analyses. No products arising from tandem addition to oct-1-en-3-ol were detected. The only recognizable products by GC/MS were styrene oxide, 2-(phenylmethyl)-1-hexanol, 1-phenyl-1-hexene (from addition of butyl carbanion excess to styrene oxide) in the former reaction and benzaldehyde, 2-(phenylmethyl)-1-hexanol, and 1-phenylpentanol (from addition of butyl carbanion excess to benzaldehyde) in the latter.

Iodine Treatment of the Reaction Between 1e,f and 2b: When formation of 2-(phenylmethyl)-1-hexanol and 2-(phenylmethyl)-1-phenyl-1-hexanol, from the reaction between **1e** and **2b** and **1f** and **2b** respectively, were detected by GC/MS, a THF solution of iodine (6 mmol) was added. The reaction was allowed to stand in a freezer overnight and then treated with HCl (4%) and extracted with ether. The organic layer was washed with HCl (4%), a sodium hydrogen sulfite solution and water, then dried over dry sodium sulfate and evaporated under reduced pressure. After column chromatography from both reactions *trans*-1-phenyl-1-hexene was recovered in 64% and 52% yield respectively. 1-Phenyl-1-hexene was fully characterized and gave physical data identical to those reported in the literature.[21] From the latter reaction a 51% yield of benzaldehyde (identical to the commercial product) was also recovered.

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