resolution mass spectrum, m/z calcd for $C_{20}H_{24}O_3S$ 344.1446, found 344.1435.

Similarly, 0.50 g (3.4 mmol) of *l*-carvone and 0.94 g (4.6 mmol) of *p*-chlorophenyl vinyl sulfone (**20**) gave a 4% (GC) yield of the tricyclic ketone **23** and a 20% recovery of carvone.

4-Isopropenyl-5,7-dimethyltricyclo[3.2.1.0^{2,7}]octan-6-one (27). By the standard bicycloannulation procedure, 0.51 g (3.1 mmol) of (5*R*)-2,6-dimethyl-5-isopropenylcyclohex-2-en-1-one (**25**) and 0.73 g (4.3 mmol) of phenyl vinyl sulfone (**10**) gave (GC 170 °C) a 15% recovery of the starting cyclohexenone (partially deconjugated) and the tricyclooctanone **27**: 0.101 g (17%); colorless oil; IR 1726, 1646 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ [relative LIS with added Eu(fod)$_3$ in brackets] 4.69 [0.4] (m, 1 H), 4.62 [0.75] (m, 1 H), 2.61 [1.0] (dd, 1 H, J = 10, 6 Hz), 2.49–1.60 (m, 6 H), 1.53 [1.2] (bs, 3 H), 1.24 [1.0] (s, 3 H), 0.87 [1.5] (s, 3 H); ^{13}C NMR (25.2 MHz, CDCl$_3$) δ 215.5 (s), 146.4 (s), 113.6 (t), 57.1 (d), 44.7 (s), 37.8 (t), 34.4 (s), 34.0 (d), 30.7 (d), 24.1 (t), 19.0 (q), 17.2 (q), 12.9 (q);[37] mass spectrum, m/z (relative intensity) 190 (M$^+$, 25), 175 (24), 161 (8), 148 (11), 136 (100), 122 (21), 119 (20), 105 (33), 95 (37), 91 (35), 79 (45), 67 (48), 54 (7); high-resolution mass spectrum, m/z calcd for $C_{13}H_{18}O$ 190.1358, found 190.1355.

Similarly, 0.51 g (3.1 mmol) of (5*R*)-2,6-dimethyl-5-isopropenylcyclohex-2-en-1-one (**25**) and 0.89 g (4.4 mmol) of *p*-chlorophenyl vinyl sulfone (**20**) gave a 21% recovery of the starting cyclohexenone (partially deconjugated) and 0.120 g (20%) of the same tricyclic ketone, **27**. Reaction of 0.25 g (1.5 mmol) of **25** with 0.39 g (1.8 mmol) of *p*-nitrophenyl vinyl sulfone (**40**) under the same conditions gave only 3 mg (1%) of **27** and 17 mg (7%) of recovered **25**.

***syn*- and *anti*-4-Isopropenyl-1,5,7-trimethyltricyclo[3.2.1.0^{2,7}]octan-6-one (29 and 30).** By the standard bicycloannulation procedure, 0.50 g (3.1 mmol) of (5*R*)-2,6-dimethyl-5-isopropenylcyclohex-2-en-1-one (**25**) and 0.81 g (3.7 mmol) of *p*-chlorophenyl isopropenyl sulfone (**28**) gave (preparative GC on OV-225 at 175 °C) a 3% recovery of the starting cyclohexenone and the two diastereomeric tricyclooctanones: **29**: 0.126 g (20%); colorless oil; IR 1715, 1642 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.53 (m, 2 H), 2.70–1.73 (m, 5 H), 1.50 (bs, 3 H), 1.26 (s, 3 H), 1.18 (s, 3 H), 0.90 (s, 3 H); mass spectrum, m/z (relative intensity) 204 (M$^+$, 78), 189 (57), 176 (62), 161 (41), 149 (54), 136 (100), 121 (100), 109 (100), 96 (100), 94 (100), 82 (56), 68 (36), 51 (78); high-resolution mass spectrum, m/z calcd for $C_{14}H_{20}O$ 204.1514, found 204.1508. **30**: 13 mg (2%); colorless oil; IR 1720, 1640 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.60 (m, 2 H), 2.7–1.0 (m, 15 H), 0.89 (s, 3 H); mass spectrum, m/z (relative intensity) 204 (M$^+$, 43), 190 (57), 176 (32), 162 (39), 147 (38), 136 (100), 121 (70), 109 (91), 106 (50), 96 (100), 92 (67), 80 (55), 70 (42), 55 (40), 41 (75); high-resolution mass spectrum, m/z calcd for $C_{14}H_{20}O$ 204.1514, found 204.1510.

5-Isopropyl-2-methyltricyclo[3.2.1.0^{2,7}]octan-6-one (32). By the standard bicycloannulation procedure, 0.50 g (3.3 mmol) of piperitone (**31**) and 0.67 g (4.0 mmol) of phenyl vinyl sulfone (**10**) gave (GC 190 °C) tricyclooctanone **32**: 6 mg (1%); colorless oil; IR 1723 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.70–1.15 (m, 9 H), 1.10 (s, 3 H), 0.85 (d, 3 H, J = 7 Hz), 0.78 (d, 3 H, J = 7 Hz); mass spectrum, m/z (relative intensity) 178 (M$^+$, 43), 163 (11), 150 (40), 135 (43), 108 (100), 96 (63), 85 (83), 68 (43), 49 (83), 41 (49).

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

Registry No. 8, 78-59-1; 10, 5535-48-8; 11, 58738-47-9; 12, 91781-44-1; 13, 91781-45-2; 17, 76380-14-8; 18, 76380-15-9; 19, 1193-18-6; 20, 5535-51-3; 21, 82667-39-8; 23, 91840-33-4; 24, 91840-34-5; 25 (isomer 1), 91781-46-3; 25 (isomer 2), 91840-35-6; 27, 91840-36-7; 28, 91781-47-4; 29, 91781-48-5; 30, 91840-37-8; 31, 89-81-6; 32, 91781-49-6; 40, 5535-55-7; PhC(O)CH$_2$SO$_2$Ph, 3406-03-9; PhC(O)CH$_2$SO$_2$-*p*-C$_6$H$_4$Cl, 36603-45-9; PhC(O)CH(CH$_3$)SO$_2$Ph, 27839-91-4; PhC(O)CH(CH$_3$)SO$_2$-*p*-C$_6$H$_4$Cl, 91781-50-9; *l*-carvone, 6485-40-1; 3,5,5-trimethyl-2-[2-(phenylsulfonyl)ethyl]cyclohex-2-en-1-one, 91781-51-0; 5-[2-[(*p*-chlorophenyl)sulfonyl]ethyl]-2,4,4-trimethyltricyclo[3.2.1.0^{2,7}]octan-6-one, 91781-52-1.

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[37] For a comprehensive study of the ^{13}C NMR properties of tricyclo[3.2.1.0^{2,7}]octan-6-ones and the corresponding tricyclooctanes see: Cory, R. M.; Stothers, J. B. *Org. Magn. Reson.* **1978**, *11*, 252.

Carbon–Carbon Bond-Forming Reactions Using Cerium Metal or Organocerium(III) Reagents

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Carbon–carbon bond-forming reactions using cerium metal or organocerium(III) reagents have been investigated. Cerium amalgam is an effective reagent for the chemoselective preparation of homoallylic alcohols from allyl halides and carbonyl compounds. The same reagent can also be satisfactorily employed for the Reformatsky-type reaction of α-halo esters with carbonyl compounds. It has been shown that organocerium(III) reagents are conveniently generated by the reaction of organolithiums with cerium(III) iodide or cerium(III) chloride. The reagents are less basic than organolithiums and Grignard reagents, and they react cleanly at −78 to −65 °C with various carbonyl compounds to afford the addition products in high yields, even though the substrates are susceptible to enolization or metal–halogen exchange with simple organolithiums. The same reagents react also with α,β-unsaturated carbonyl compounds to yield 1,2-addition products in high selectivity.

The elements of the rare earth series having f orbitals exhibit unique electronic and stereochemical properties, and they possess intriguing potential as reagents and catalysts.[1-4] Recently, considerable efforts have been made on the utilization of these elements in organic reactions, and many interesting synthetic procedures have been developed.[5,6] However, relatively few reports may

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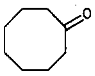
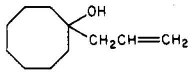
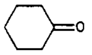
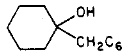
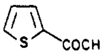
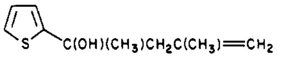
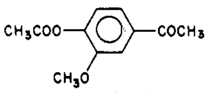
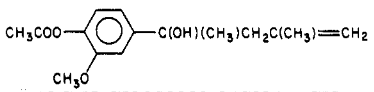
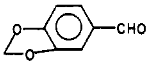
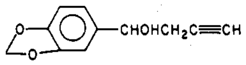
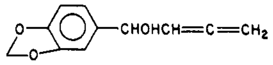
Table I. Cerium Amalgam Mediated One-Step Synthesis of Homoallylic Alcohols

entry	halide	carbonyl compound	conditn	product(s)	yield,[a] %
1	$CH_2{=}CHCH_2I$	p-$BrC_6H_4COCH_3$	0 °C, 5 h; rt,[b] 1 h	p-$BrC_6H_4C(OH)(CH_3)CH_2CH{=}CH_2$	95
2	$CH_2{=}CHCH_2I$		0 °C, 2 h; rt, 1 h		58
3	$C_6H_5CH_2I$	$C_6H_5COCH_3$	0 °C, 3 h; rt, 15 h	$C_6H_5C(OH)(CH_3)CH_2C_6H_5$	84
4	$C_6H_5CH_2I$		0 °C, 4 h		59
5	$C_6H_5CH_2I$	p-ClC_6H_4CHO	0 °C, 2 h	p-$ClC_6H_4CHOHCH_2C_6H_5$ p-$ClC_6H_4COOCH_2C_6H_4Cl$-p	35 42
6	$CH_2{=}C(CH_3)CH_2I$	p-$IC_6H_4COCH_3$	0 °C, 4.5 h	p-$IC_6H_4C(OH)(CH_3)CH_2C(CH_3){=}CH_2$	88
7	$CH_2{=}C(CH_3)CH_2I$		0 °C, 4.5 h		59
8	$CH_2{=}C(CH_3)CH_2I$		0 °C, 3.5 h		79
9	$CH_2{=}C(CH_3)CH_2I$	p-NCC_6H_4CHO	0 °C, 4 h	p-$NCC_6H_4CHOHCH_2C(CH_3){=}CH_2$	69
10	$CH_2{=}C(CH_3)CH_2I$	C_6H_5CHO	0 °C, 4 h; rt, 1 h	$C_6H_5CHOHCH_2C(CH_3){=}CH_2$ $C_6H_5C(OH)[CH_2C(CH_3){=}CH_2]_2$	79 5
11	$CH_2{=}C(CH_3)CH_2I$	p-ClC_6H_4CHO	0 °C, 2 h	p-$ClC_6H_4CHOHCH_2C(CH_3){=}CH_2$ p-$ClC_6H_4C(OH)[CH_2C(CH_3){=}CH_2]_2$	71 4
12	$CH_2{=}CHCH_2Br$	$C_{10}H_9COCH_3$-β	rt, 48 h	$C_{10}H_9C(OH)(CH_3)CH_2CH{=}CH_2$	71
13	$CH_2{=}CHCH_2Br$	p-$CH_3OC_6H_4COCH_3$	rt, 49 h	p-$CH_3OC_6H_4C(OH)(CH_3)CH_2CH{=}CH_2$	85
14	$CH_2{=}CHCH_2Br$	$C_6H_5CH{=}CHCOCH_3$	rt, 74 h	$C_6H_5CH{=}CHC(OH)(CH_3)CH_2CH{=}CH_2$	44
15	$CH_2{=}CHCH_2Br$	p-ClC_6H_4CHO	rt, 22 h	p-$ClC_6H_4CHOHCH_2CH{=}CH_2$ p-$ClC_6H_4CH_2OH$	35 41
16	$C_6H_5CH{=}CHCH_2Br$	p-$BrC_6H_4COCH_3$	rt, 62 h	p-$BrC_6H_4C(OH)(CH_3)CH_2CH{=}CHC_6H_5$ p-$BrC_6H_4C(OH)(CH_3)CH(C_6H_5)CH{=}CH_2$	47 31[c]
17	$HC{\equiv}CCH_2I$	p-$BrC_6H_4COCH_3$	0 °C, 4 h; rt, 17 h	p-$BrC_6H_4C(OH)(CH_3)CH_2C{\equiv}CH$ p-$BrC_6H_4C(OH)(CH_3)CH{=}C{=}CH_2$	71[d] 13[d]
18	$HC{\equiv}CCH_2I$	$C_6H_5CH{=}CHCOCH_3$	0 °C, 12 h; rt, 6 h	$C_6H_5CH{=}CHC(OH)(CH_3)CH_2C{\equiv}CH$ $C_6H_5CH{=}CHC(OH)(CH_3)CH{=}C{=}CH_2$	69[d] 20[d]
19	$HC{\equiv}CCH_2I$	p-ClC_6H_4CHO	0 °C, 5 h; rt, 14 h	p-$ClC_6H_4CHOHCH_2C{\equiv}CH$ p-$ClC_6H_4CHOHCH{=}C{=}CH_2$	65[d] 27[d]
20	$HC{\equiv}CCH_2I$		0 °C, 10 h; rt, 6 h	 	62[d] 23[d]

[a] Isolated yield. [b] rt = room temperature. [c] A mixture of stereoisomers. [d] The isomer ratio was determined by ^1H NMR. Each isomer was not separated.

be found concerning carbon–carbon bond formation with organolanthanoids.[6a,b,7–10] The methods reported hitherto employ a few selected and expensive elements (Sm, Eu, Yb), have limited applicability, and are consequently not always suited to practical organic synthesis.

We have been deeply interested in the largely unexplored field of organolanthanoid chemistry and intended to exploit new synthetic reactions which are not achievable with the organometallic reagents of main group and d block elements. For this purpose, our attention has been focused on the utilization of cerium metal and cerium halides in organic reactions, since elemental cerium is of highest natural abundance in the rare earth series and cerium metal and its major inorganic salts are commercially available at moderate prices. In this paper, we report cerium metal mediated Barbier-type and Reformatsky-type reactions. Furthermore, generation and reactivities of organocerium(III) reagents are described.

Results and Discussion

Barbier-Type Reaction. Our initial investigation was undertaken with the treatment of commercially available cerium ingot for use in organic reactions. At first, cerium ingot was carefully scraped with a rasp, and the obtained cerium turnings (ca. 20–50 mesh) were treated with an alcoholic solution of mercury(II) chloride under argon. The cerium amalgam thus prepared was pyrophoric and burned spontaneously in contact with air. Using this activated cerium we carried out preliminary experiments for carbon–carbon bond formations and observed that benzyl iodide, on treatment with cerium amalgam in tetrahydrofuran (THF), was converted into 1,2-diphenylethane in almost quantitative yield. On the basis of this observation, Barbier-type reactions of allyl and benzyl iodides with various ketones were attempted in the presence of cerium amalgam. The reaction proceeded smoothly at 0

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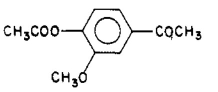
Table II. The Reaction of 3-Iodo-2-methyl-1-propene with Esters in the Presence of Cerium Metal

entry	ester	conditn	product	yield,[a] %
1[b]	$C_6H_5COOC_2H_5$	0 °C, 1 h	$C_6H_5C(OH)[CH_2C(CH_3){=}CH_2]_2$	79
2[b]	$C_6H_5CH{=}CHCOOC_2H_5$	−20 °C, 12 h	$C_6H_5CH{=}CHC(OH)[CH_2C(CH_3){=}CH_2]_2$	79
3[b]	$C_6H_5(CH_2)_2COOCH_3$	0 °C, 6 h	$C_6H_5(CH_2)_2C(OH)[CH_2C(CH_3){=}CH_2]_2$	86
4[c]	$CH_3CO{-}C_6H_4{-}(CH_2)_2COOCH_3$	0 °C, 5 h	$CH_2{=}C(CH_3)CH_2C(OH)(CH_3){-}C_6H_4{-}(CH_2)_2COOCH_3$	89

[a] Isolated yield. [b] $CH_2{=}C(CH_3)CH_2I$/ester = 3. [c] $CH_2{=}C(CH_3)CH_2I$/ester = 2.

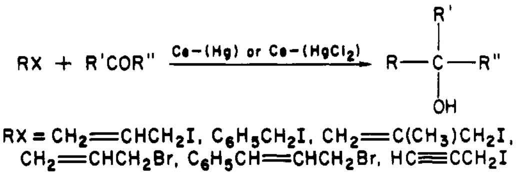
Table III. The Reformatsky-Type Reaction Using Cerium Metal

α-halo ester	carbonyl compound	reagent	temp	time, h	β-hydroxy ester yield, %
$ICH_2COOC_2H_5$	*n*-C_3H_7CHO	Ce–($HgCl_2$)	0 °C	19	63
$ICH_2COOC_2H_5$	2-furaldehyde	Ce–($HgCl_2$)	−70 °C	5.5	76
$ICH_2COOC_2H_5$	C_6H_5CHO	Ce–(Hg)	0 °C	3.5	81
$ICH_2COOC_2H_5$	$C_2H_5CH(CH_3)COCH_3$	Ce	0 °C	20	55[a]
$ICH_2COOC_2H_5$	cyclododecanone	Ce	0 °C	0.8	75
$ICH_2COOC_2H_5$	$IC_6H_4COCH_3$	Ce	−10 °C	1.3	70
$ICH_2COOC_2H_5$	*p*-$NCC_6H_4COCH_3$	Ce–(Hg)	0 °C	5	79
$ICH_2COOC_2H_5$	*p*-$O_2NC_6H_4COCH_3$	Ce–($HgCl_2$)	−40 °C	1.3	74
$ICH_2COOC_2H_5$		Ce–($HgCl_2$)	0 °C	17	89
$CH_3CHICOOC_2H_5$	C_6H_5CHO	Ce–($HgCl_2$)	−30 °C	4	91[b]
$CH_3CHICOOC_2H_5$	$C_6H_5COCH_3$	Ce–($HgCl_2$)	−40 °C	5	92[a]
$CH_3CHICOOC_2H_5$	$C_6H_5COCH(CH_3)_2$	Ce–($HgCl_2$)	0 °C	28	48[a]
$BrCH_2COOC_2H_5$	C_6H_5CHO	Ce–($HgCl_2$)	rt[e]	17	49
$BrCH_2COOC_2H_5$	$C_6H_5COCH_3$	Ce–($HgCl_2$)	rt	46	60
$BrCH_2CH{=}CHCOOCH_3$	C_6H_5CHO	Ce–($HgCl_2$)	rt	19	51[c]
$C_6H_5CHBrCOOC_2H_5$	C_6H_5CHO	Ce–($HgCl_2$)	−18 °C	3.5	96[d]

[a] A mixture of stereoisomers. [b] Erythro:threo = 50:50. [c] The isolated product was $C_6H_5CHOHC(COOCH_3){=}CHCH_3$. [d] Erythro:threo = 57:43. [e] rt = room temperature.

°C through to room temperature and the corresponding homoallylic and homobenzylic alcohols were isolated in satisfactory yields.[11] Some typical results are described in Table I.

This reaction was then extended to various combinations of carbonyl compounds with 3-iodo-2-methyl-1-propene, allyl bromide, cinnamyl bromide, and propargyl iodide. In some cases, a catalytic amount of mercury(II) chloride was added as initiator in place of cerium amalgam. These results are added in Table I.



$$RX + R'COR'' \xrightarrow{Ce-(Hg)\ \text{or}\ Ce-(HgCl_2)} R{-}C(R')(OH){-}R''$$

$$RX = CH_2{=}CHCH_2I,\ C_6H_5CH_2I,\ CH_2{=}C(CH_3)CH_2I,\ CH_2{=}CHCH_2Br,\ C_6H_5CH{=}CHCH_2Br,\ HC{\equiv}CCH_2I$$

The following are the characteristic features of this method. (1) The reaction proceeds in the presence of carbonyl compounds giving homoallylic alcohols in satisfactory yields. (2) The reaction is chemoselective; ketones react smoothly, while other functional groups such as vinylic iodide (entry 6), alkoxycarbonyl (entry 8), and cyano (entry 9) remained unaffected under the employed conditions. (3) Propargyl iodide, whose organometallic derivatives are not easily available, also reacts with carbonyl compounds to afford the addition products in 60–70% yields, although isomeric allenyl alcohols are produced as the minor products. In these respects, this method for the preparation of homoallylic alcohols may be favorably compared with previously existed methods.[12]

The reactions of aromatic aldehydes with allyl halides are worth noting. In these reactions some byproducts were isolated along with the corresponding homoallylic alcohols. Ester (entry 5) is probably formed by the Tischchenko-like reaction which is induced competitively under the reaction conditions.[13] Bis(homoallyl) alcohols (entries 10 and 11) may be produced by the reaction of initially formed esters.

In order to confirm this postulate, several esters were treated with excess 3-iodo-2-methyl-1-propene in the presence of cerium metal. The results are listed in Table II. These results indicate apparently that esters react with 3-iodo-2-methyl-1-propene to yield bis(homoallyl) alcohols in good yields. These reactions of esters, however, seem to be slower than those of ketones. This is exemplified in entry 4, in that the ketone carbonyl moiety is preferentially subjected to nucleophilic attack while the ester function remains intact.

Reformatsky-Type Reaction. The Barbier-type reaction described above was then extended to the Refor-

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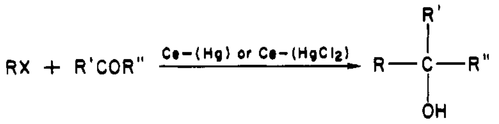
(11) A preliminary account of a portion of this work has appeared: Imamoto, T.; Hatanaka, Y.; Tawarayama, Y.; Yokoyama, M. *Tetrahedron Lett.* **1981**, *22*, 4987.

(12) For allylation of carbonyl compounds to yield homoallylic alcohols, see the following: (a) Katzenellenbogen, J. A.; Lenox, R. S. *J. Org. Chem.* **1973**, *38*, 326. (b) Barbot, F.; Miginiac, Ph. *Tetrahedron Lett.* **1975**, 3829. (c) Hosomi, A.; Sakurai, H. *Ibid.* **1976**, 1295. (d) Deleris, G.; Dunogues, J.; Cales, R. *Ibid.* **1976**, 2449. (e) Ruppert, J. F.; White, S. D. *J. Org. Chem.* **1976**, *41*, 550. (f) Kramer, G. W.; Brown, H. C. *Ibid.* **1977**, *42*, 2292. (g) Yamaguchi, M.; Mukaiyama, T. *Chem. Lett.* **1980**, 993. (h) Okude, Y.; Hirano, S.; Hiyama, T.; Nozaki, H. *J. Am. Chem. Soc.* **1977**, *99*, 3179. (i) Hiyama, T.; Kimura, K.; Nozaki, H. *Tetrahedron Lett.* **1981**, *22*, 1037. (j) Naruta, Y.; Ushida, S.; Maruyama, K. *Chem. Lett.*, **1979**, 919. (k) Yatagai, H.; Yamamoto, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 4548. (l) Mukaiyama, T.; Harada, T.; Shoda, S. *Chem. Lett.* **1981**, 1527. (m) Reference 23.

(13) Some preliminary experiments were made on the Tischchenko-type reaction induced by cerium compounds. It was observed that several aromatic aldehydes were converted into the corresponding esters in 49–98% yields, on treatment with the catalyst (ca. 10 mol%) which was prepared by the reaction of iodobenzene with cerium turnings at 50 °C for several hours under argon. On the other hand, no reaction occurred when the aldehydes were treated with cerium(III) chloride or cerium(III) iodide.

matsky-type reaction. The reaction of α-halo esters with carbonyl compounds in the presence of cerium turnings proceeded at 0 °C through to room temperature, but a long induction period was required in several cases. Use of cerium amalgam or addition of a catalytic amount of mercury(II) chloride to a mixture of the reactants facilitated markedly the initiation of this reaction, such that the reaction could now be performed at low temperature. For example, ethyl iodoacetate reacted with 2-furaldehyde even at −70 °C.



RX = $ICH_2COOC_2H_5$, $CH_3CHICOOC_2H_5$, $BrCH_2COOC_2H_5$, $C_6H_5CHBrCOOC_2H_5$, $BrCH_2CH{=}CHCOOCH_3$

As is shown in Table III, this method is applicable to a wide variety of carbonyl compounds, even to compounds bearing other functional groups, and thus it represents one of the useful methods for the preparation of β-hydroxy esters.[14,15]

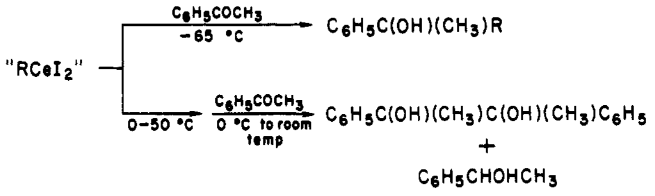
Generation and Reactivities of Organocerium(III) Reagents. Another area of interest to us was the investigation of the reactivities of trivalent σ-bonded organocerium compounds. Only a few π-bonded ionic cerium complexes are known for the trivalent organoceriums,[16] and there have been no reports on organocerium(III) compounds involving covalent bonding, except Evans' attempt at the generation of phenylcerium iodide by the oxidative addition of metallic cerium to iodobenzene.[7,17] We have tried the generation of organocerium(III) reagents by transmetalation of cerium(III) halides with organolithiums and examined their reactivities toward carbonyl compounds.

Our first trial of the generation of organocerium(III) reagents was the reactions of organolithiums with 1 equiv of cerium iodide (CeI_3). The cerium iodide used here was prepared in situ by the reaction of cerium metal with iodine in THF at 0 °C through to room temperature, and to the resulted suspension was added 1 equiv of an organolithium reagent at −65 °C. The color of the suspension turned from orange to ocher, and the generated cerium reagent was then allowed to react with a series of carbonyl compounds at varying temperatures. At the same time organolithiums were also treated with carbonyl compounds under the same conditions for comparison.[18] The results obtained are summarized in Table IV.

$$RLi + CeI_3 \rightarrow \text{“}RCeI_2\text{”}^{19} \xrightarrow{R'COR''} R'R''C(OH)R$$
$$R = n\text{-}C_4H_9,\ sec\text{-}C_4H_9,\ C_2H_5,\ CH_3,\ C_6H_5$$

It should be noted that the cerium reagents reacted smoothly at −65 °C with carbonyl compounds to afford the corresponding alcohols in excellent yields, even though the substrates are readily subjected to enolization or possess halogen atoms in vinylic positions.[20] The results are in sharp contrast to those obtained by the use of organolithiums only, in that the yields of the addition products are remarkably lowered due to competitive enolization or metal–halogen exchange. The most striking contrasts are shown in the reactions of 1,3-diphenyl-2-propanone (entries 5 and 6) and p-iodoacetophenone (entries 7 and 8).

The effect of reaction temperature is also worth mentioning. When the reagents having β-hydrogens were warmed to temperatures higher than 0 °C and then treated with acetophenone, reductive coupling and/or reduction proceeded to afford 2,3-dihydroxy-2,3-diphenylbutane and/or α-phenethyl alcohol.[21,22] In contrast, the reagent prepared from methyllithium or phenyllithium underwent exclusive nucleophilic addition to carbonyl group even at room temperature. The reductive coupling and reduction of carbonyl compounds are probably induced by low-valent cerium[23] and cerium hydride species which are generated through β-hydrogen elimination process.[24]



R = n-C_4H_9, sec-C_4H_9, C_2H_5

Next, we examined the use of commercially available lanthanoid chlorides ($CeCl_3{\cdot}7H_2O$, $LaCl_3{\cdot}7H_2O$, $NdCl_3{\cdot}6H_2O$, $PrCl_3{\cdot}7H_2O$, $SmCl_3{\cdot}6H_2O$, $YbCl_3{\cdot}6H_2O$). These hydrated salts were dried in vacuo at 140 °C for 2 h[25] and treated with n-butyllithium at −78 °C. And, the resulting reagents were subjected to reaction with carbonyl compounds.

As is shown in Table V, excellent results were obtained in the cases of cerium chloride, lanthanum chloride, neodymium chloride, and ytterbium chloride, while the use

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(14) For reviews, see: (a) Shriner, R. L. "Organic Reactions"; Wiley, New York, 1942; Vol. 1, p 1. (b) Rathke, M. W. "Organic Reactions"; Wiley: New York, 1975; Vol. 22, p 423.

(15) Modified Reformatsky reactions have been reported recently: (a) Rieke, R. D.; Uhm, S. J. *Synthesis* **1975**, 452. (b) Maruoka, K.; Hashimoto, S.; Kitagawa, Y.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1977**, *99*, 7705. (c) Santhaniells, E.; Manzocchi, A. *Synthesis* **1977**, 698. (d) Harada, T.; Mukaiyama, T. *Chem. Lett.* **1982**, 161.

(16) (a) Birmingham, J. M.; Wilkinson, G. *J. Am. Chem. Soc.* **1956**, *78*, 42. (b) Hodgson, K. O.; Raymond, K. N. *Inorg. Chem.* **1972**, *11*, 171. (c) Hodgson, K. O.; Raymond, K. N. *Ibid.* **1972**, *11*, 3030.

(17) For trivalent σ-bonded organometallic compounds of lanthanide elements, the derivatives of lutetium, ytterbium, erbium, and samarium have been reported. (a) Evans, W. J.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 292. (b) Atwood, A. L.; Hunter, W. E.; Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1981**, *20*, 4115. (c) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276. (d) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337. (e) Watson, P. L; Roe, D. C. *Ibid.* **1982**, *104*, 6471. (f) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1980**, 652. (g) Cotton, S. A.; Hart, F. A.; Hursthouse, M. B.; Welch, A. J. *Ibid.* **1972**, 1225. (h) Evans, W. J.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *Ibid.* **1981**, 706. (i) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *105*, 1401.

(18) Imamoto, T.; Kusumoto, T.; Yokoyama, M. *J. Chem. Soc., Chem. Commun.* **1982**, 1042.

(19) This formulation merely expresses the basic stoichiometry, and some other species may be present in equilibrium.

(20) A stoichiometric amount of cerium iodide (n-C_4H_9Li:CeI_3 1:1) was necessary to achieve high yield of the addition products.

(21) Similar tendency was also observed in the reaction using SmI_3–n-C_4H_9Li reagent system, although reductive coupling prevailed over the reduction.

(22) The use of n-butylmagnesium chloride instead of n-butyllithium afforded the corresponding addition product, 2-phenyl-2-hexanol, in almost quantitative yield, even at room temperature. These results indicate that an organocerium reagent is not formed from a Grignard reagent and cerium iodide.

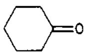
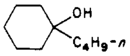
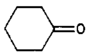
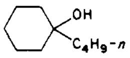
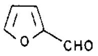
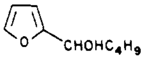
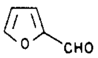
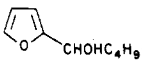
(23) For low valent cerium promoted pinacolic coupling, see: Imamoto, T.; Kusumoto, T.; Hatanaka, Y.; Yokoyama, M. *Tetrahedron Lett.* **1982**, *23*, 1353.

(24) β-Hydrogen elimination reactions of σ-bonded organometallic derivatives of lutetium and erbium have been reported: (a) Reference 17e. (b) Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2008. (c) Evans, W. J.; Meadows, J. H.; Wayada, A. L.; Hunter, W. E.; Atwood, J. L. *Ibid.* **1982**, *104*, 2015.

(25) According to the literature,[16a,26] anhydrous lanthanoid chlorides are generally prepared by heating the lanthanoid oxides (Ln_2O_3) with ammonium chloride at ca. 300 °C or by treatment of hydrated lanthanoid chlorides ($LnCl_3{\cdot}nH_2O$) with thionyl chloride. In this work, we preferred a more conventional method for drying in consideration of experimental convenience.

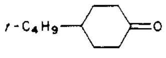
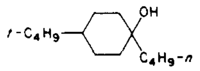
(26) Reed, J. B.; Hopkins, B. S.; Andrieth, L. F. *Inorg. Synth.* **1961**, *1*, 28.

Table IV. The Reaction of Cerium(III) Iodide–Organolithium Reagent Systems or Organolithiums with Carbonyl Compounds

entry	reagent[a]	carbonyl compound	conditn	product(s)	yield,[b] %
1	n-C_4H_9Li–CeI_3, A	$C_6H_5COCH_3$	–65 °C, 3 h	$C_6H_5C(OH)(CH_3)C_4H_9$-n	98
2	n-C_4H_9Li	$C_6H_5COCH_3$	–65 °C, 3 h	$C_6H_5C(OH)(CH_3)C_4H_9$-n	64 (27)
3	n-C_4H_9Li–CeI_3, A	$C_6H_5CH_2COC_6H_5$	–65 °C, 3 h	$C_6H_5CH_2C(OH)(C_6H_5)C_4H_9$-$n$	95
4	n-C_4H_9Li	$C_6H_5CH_2COC_6H_5$	–65 °C, 3 h	$C_6H_5CH_2C(OH)(C_6H_5)C_4H_9$-$n$	63 (29)
5	n-C_4H_9Li–CeI_3, A	$(C_6H_5CH_2)_2CO$	–65 °C, 3 h	$(C_6H_5CH_2)_2C(OH)C_4H_9$-$n$	98
6	n-C_4H_9Li	$(C_6H_5CH_2)_2CO$	–65 °C, 3 h	$(C_6H_5CH_2)_2C(OH)C_4H_9$-$n$	33 (61)
7	n-C_4H_9Li–CeI_3, A	p-$IC_6H_4COCH_3$	–65 °C, 3 h	p-$IC_6H_4C(OH)(CH_3)C_4H_9$-n	99
8	n-C_4H_9Li	p-$IC_6H_4COCH_3$	–65 °C, 3 h	p-$IC_6H_4C(OH)(CH_3)C_4H_9$-n	trace (0)
9	n-C_4H_9Li–CeI_3, A		–65 °C, 3 h		95
10	n-C_4H_9Li		–65 °C, 3 h		74
11	n-C_4H_9Li–CeI_3, A	2,4,6-$(CH_3)_3C_6H_2COCH_3$	–65 °C, 3 h	2,4,6-$(CH_3)_3C_6H_2C(OH)(CH_3)C_4H_9$-$n$	15 (85)[c]
12	n-C_4H_9Li	2,4,6-$(CH_3)_3C_6H_2COCH_3$	–65 °C, 3 h	2,4,6-$(CH_3)_3C_6H_2C(OH)(CH_3)C_4H_9$-$n$	trace (95)[c]
13	n-C_4H_9Li–CeI_3, A	$C_6H_5CH_2CH_2CHO$	–65 °C, 3 h	$C_6H_5CH_2CH_2CHOHC_4H_9$-n	92
14	n-C_4H_9Li	$C_6H_5CH_2CH_2CHO$	–65 °C, 3 h	$C_6H_5CH_2CH_2CHOHC_4H_9$-n	83
15	n-C_4H_9Li–CeI_3, A		–65 °C, 3 h		89
16	n-C_4H_9Li		–65 °C, 3 h		86
17	sec-C_4H_9Li–CeI_3, A	$C_6H_5COCH_3$	–65 °C, 3 h	$C_6H_5C(OH)(CH_3)C_4H_9$-sec	98
18	sec-C_4H_9Li	$C_6H_5COCH_3$	–65 °C, 3 h	$C_6H_5C(OH)(CH_3)C_4H_9$-sec	53 (35)
19	C_2H_5Li–CeI_3, A	$C_6H_5COCH_3$	–65 °C, 3 h	$C_6H_5C(OH)(CH_3)C_2H_5$	93
20	C_2H_5Li	$C_6H_5COCH_3$	–65 °C, 3 h	$C_6H_5C(OH)(CH_3)C_2H_5$	60 (33)
21	CH_3Li–CeI_3, A	$C_6H_5COCH_3$	–65 °C, 3 h	$C_6H_5C(OH)(CH_3)_2$	96
22	CH_3Li	$C_6H_5COCH_3$	–65 °C, 3 h	$C_6H_5C(OH)(CH_3)_2$	86
23	C_6H_5Li–CeI_3, A	$C_6H_5COCH_3$	–65 °C, 3 h	$CH_3C(OH)(C_6H_5)_2$	88
24	C_6H_5Li	$C_6H_5COCH_3$	–65 °C, 3 h	$CH_3C(OH)(C_6H_5)_2$	89
25	n-C_4H_9Li–CeI_3, B	$C_6H_5COCH_3$	0 °C, 5 h	$C_6H_5C(OH)(CH_3)C(OH)(CH_3)C_6H_5$ $C_6H_5C(OH)(CH_3)C_4H_9$-n	92 trace
26	n-C_4H_9Li–CeI_3, C	$C_6H_5COCH_3$	rt, 3 h	$C_6H_5CHOHCH_3$ $C_6H_5C(OH)(CH_3)C(OH)(CH_3)C_6H_5$ $C_6H_5C(OH)(CH_3)C_4H_9$-n	67 15 11
27	n-C_4H_9Li–CeI_3, D	$C_6H_5COCH_3$	rt, 2 h	$C_6H_5CHOHCH_3$ $C_6H_5C(OH)(CH_3)C(OH)(CH_3)C_6H_5$	74 trace
28	sec-C_4H_9Li–CeI_3, B	$C_6H_5COCH_3$	0 °C, 4 h	$C_6H_5C(OH)(CH_3)C(OH)(CH_3)C_6H_5$ $C_6H_5CHOHCH_3$ $C_6H_5C(OH)(CH_3)C_4H_9$-sec	51 22 12
29	sec-C_4H_9Li–CeI_3, D	$C_6H_5COCH_3$	rt, 4 h	$C_6H_5CHOHCH_3$ $C_6H_5C(OH)(CH_3)C(OH)(CH_3)C_6H_5$	52 29
30	C_2H_5Li–CeI_3, D	$C_6H_5COCH_3$	rt, 4 h	$C_6H_5CHOHCH_3$	54 (27)
31	CH_3Li–CeI_3, D	$C_6H_5COCH_3$	rt, 4 h	$C_6H_5C(OH)(CH_3)_2$	95
32	C_6H_5Li–CeI_3, C	$C_6H_5COCH_3$	rt, 4 h	$CH_3C(OH)(C_6H_5)_2$	94
33	C_6H_5Li–CeI_3, D	$C_6H_5COCH_3$	rt, 4 h	$CH_3C(OH)(C_6H_5)_2$	trace (62)

[a] The alphabets in parentheses indicate the conditions for the preparation of cerium reagents: A, –65 °C, 30 min; B, –65 °C, 30 min, then 0 °C, 15 min; C, –65 °C, 30 min, then room temperature, 15 min; D, –65 °C, 30 min, then 50 °C, 15 min. [b] The figures in parentheses indicate the yields of recovered ketone. [c] Determined by ^1H NMR analysis.

Table V. The Reaction of n-C_4H_9Li-LnX_3 with Carbonyl Compounds[a]

reagent	carbonyl compound	product	yield,[b] %
n-C_4H_9Li–$CeCl_3$	$(C_6H_5CH_2)_2CO$	$(C_6H_5CH_2)_2C(OH)C_4H_9$-$n$	96
n-C_4H_9Li–$LaCl_3$	$(C_6H_5CH_2)_2CO$	$(C_6H_5CH_2)_2C(OH)C_4H_9$-$n$	96
n-C_4H_9Li–$NdCl_3$	$(C_6H_5CH_2)_2CO$	$(C_6H_5CH_2)_2C(OH)C_4H_9$-$n$	98
n-C_4H_9Li–$PrCl_3$	$(C_6H_5CH_2)_2CO$	$(C_6H_5CH_2)_2C(OH)C_4H_9$-$n$	85
n-C_4H_9Li–$SmCl_3$	$(C_6H_5CH_2)_2CO$	$(C_6H_5CH_2)_2C(OH)C_4H_9$-$n$	60
n-C_4H_9Li–$YbCl_3$			97

[a] All reactions were carried out in THF at –78 °C for 3 h. [b] Isolated yield.

of praseodymium chloride and samarium chloride resulted in relatively lower yields probably owing to insufficient dehydration of the salts.[27] Screening of the lanthanoid salts revealed that cerium chloride is the best for the reaction as it is readily available at moderate price and its anhydrous salt can be easily obtained. Lanthanum chloride and neodymium chloride can be also employed in practical organic synthesis since their prices are not prohibitive.

On the basis of the facts described above, the $CeCl_3$–n-C_4H_9Li reagent system was treated with a variety of carbonyl compounds in order to examine the scope of the reaction. The results summarized in Table VI apparently demonstrate that the cerium reagent exhibits strong carbonylophilic character and reacts selectively with carbonyl

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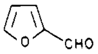
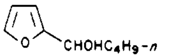
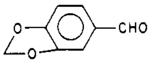
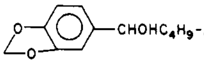
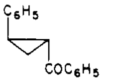
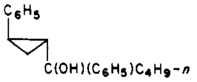
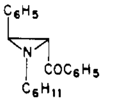
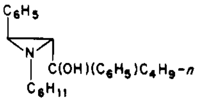
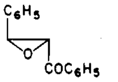
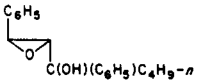
[27] High yields of the addition products may be achieved in these reactions, if completely dry salts are employed.

Table VI. The Reaction of n-C_4H_9Li–$CeCl_3$ Reagent System with Carbonyl Compounds

carbonyl compd	conditn[a] time, h	product	yield,[b] %
$C_6H_5(CH_2)_2CHO$	1.5	$C_6H_5(CH_2)_2CHOHC_4H_9$-*n*	80
	3		85
p-$(CH_3)_2NC_6H_4CHO$	2	*p*-$(CH_3)_2NC_6H_4CHOHC_4H_9$-*n*	87
o-$CH_3OC_6H_4CHO$	3	*o*-$CH_3OC_6H_4CHOHC_4H_9$-*n*	97
	1		94
$C_6H_5COCH_3$	3	$C_6H_5C(OH)(CH_3)C_4H_9$-*n*	98
p-$BrC_6H_4COCH_3$	3	*p*-$BrC_6H_4C(OH)(CH_3)C_4H_9$-*n*	96
p-$IC_6H_4COCH_3$	3	*p*-$IC_6H_4C(OH)(CH_3)C_4H_9$-*n*	93
p-$NCC_6H_4COCH_3$	3	*p*-$NCC_6H_4C(OH)(CH_3)C_4H_9$-*n*	48
p-$CH_3OC_6H_4COCH_3$	1.5	*p*-$CH_3OC_6H_4C(OH)(CH_3)C_4H_9$-*n*	99
	3		87[c]
	5		93[c]
	4		52[c]
$C_6H_5CH{=}CHCHO$	1	$C_6H_5CH{=}CHCHOHC_4H_9$-*n*	96
$C_6H_4CH{=}CHCOCH_3$	3	$C_6H_5CH{=}CHC(OH)(CH_3)C_4H_9$-*n*	95
$C_6H_5CH{=}CHCOC_6H_5$	0.5	$C_6H_5CH{=}CHC(OH)(C_6H_5)C_4H_9$-*n*	42
		$C_6H_5CH(C_4H_9$-*n*$)CH_2COC_6H_5$	40

[a] All reactions were carried out at −78 °C in THF. [b] Isolated yield. [c] Mixture of stereoisomers.

group.[28] Various alcohols including an epoxy alcohol can be obtained by this method. It is noted that α,β-unsaturated carbonyl compounds are subjected to 1,2-addition selectively except chalcone. This selective 1,2-addition is comparable with the 1,2-reduction of α,β-enone with sodium borohydride in the presence of cerium chloride.[6d]

Comparison of Cerium(III) Reagents with Grignard Reagents. It is very interesting to compare organocerium(III) reagents with Grignard reagents in their reactivities. The Grignard reaction is well-known as one of the most versatile reactions in organic syntheses and has wide spread synthetic applications.[29] Nevertheless, in some cases so-called abnormal reactions such as enolization,[30] reduction,[31] and conjugate addition[32] become major rather than the addition to carbonyl group, and the desired 1,2-addition products are not obtained in satisfactory yields. Our aim was to examine whether the cerium reagents react normally or abnormally with such substrates. For this purpose several selected carbonyl compounds (cyclopentanone, cyclohexanone, 1,3-diphenyl-2-propanone, β-tetralone, 2,4,6-trimethylacetophenone, and 2-cyclohexenone) were treated with *n*-butyl- and *tert*-butylcerium reagents, and the results were compared with those of Grignard reagents.

Table VII. Comparison of the Reactivities of Cerium Chloride–Organolithium Reagent Systems with Those of Grignard Reagents

entry	carbonyl compd	reagent	conditions	yield,[a] %
1	cyclopentanone	*n*-C_4H_9Li–$CeCl_3$	−78 °C, 3 h	77
2	cyclopentanone	*n*-C_4H_9MgBr	0 °C, 5 h	60[b]
3	cyclohexanone	*n*-C_4H_9Li–$CeCl_3$	−78 °C, 3 h	98
4	cyclohexanone	*n*-C_4H_9MgBr	0 °C, 5 h	70[b]
5	β-tetralone	*n*-C_4H_9Li–$CeCl_3$	−78 °C, 3 h	88
6	β-tetralone	*n*-C_4H_9MgBr	0 °C, 4 h	6
7	1,3-diphenyl-2-propanone	*n*-C_4H_9Li–$CeCl_3$	−78 °C, 3 h	96
8	1,3-diphenyl-2-propanone	*n*-C_4H_9MgBr	0 °C, 6 h	10[b]
9	2,4,6-trimethylacetophenone	*n*-C_4H_9Li–$CeCl_3$	−78 °C, 4 h	57
10	2,4,6-trimethylacetophenone	*n*-C_4H_9MgBr	0 °C, 8 h	10[b]
11	2-cyclohexenone	*n*-C_4H_9Li–$CeCl_3$	−78 °C, 3 h	98
12	2-cyclohexenone	*n*-C_4H_9MgBr	0 °C, 5 h	48 + 21[c]
13	cyclopentanone	*t*-C_4H_9Li–$CeCl_3$	−78 °C, 3 h	27
14	cyclopentanone	*t*-C_4H_9MgCl	0 °C, 4 h	5[b]
15	cyclohexanone	*t*-C_4H_9Li–$CeCl_3$	−78 °C, 3 h	55
16	cyclohexanone	*t*-C_4H_9MgCl	0 °C, 8 h	10
17	1,3-diphenyl-2-propanone	*t*-C_4H_9Li–$CeCl_3$	−78 °C, 3 h	65
18	1,3-diphenyl-2-propanone	*t*-C_4H_9MgCl	0 °C, 8 h	trace

[a] Isolated yield of 1,2-addition product unless otherwise stated. [b] Determined by ^1H NMR. [c] Yield of 1,4-addition product.

As is shown in Table VII, cerium reagents reacted with the above ketones to give the corresponding addition products in good to high yields. In contrast, the use of Grignard reagents resulted in relatively lower yields. The most striking examples are shown in the reactions of β-tetralone and 1,3-diphenyl-2-propanone which are susceptible to enolization (entries 5, 6, 7, 8, 17, and 18). Another prominent feature of cerium reagent is exemplified by the reaction of 2-cyclohexenone; cerium reagent afforded 1,2-addition product in 98% yield, while *n*-butylmagnesium bromide produced 1,2- and 1,4-addition products in 48% and 21% yields, respectively.

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(28) In order to examine the reactivities of cerium reagent toward ester and thiol ester, (*p*-methoxycarbonyl)benzoic acid *S*-ethyl ester was treated with $CeCl_3$-*n*-C_4H_9Li reagent system at −78 °C for 3 h, however the compound was recovered unchanged.

(29) For excellent reviews, see the following: (a) Kharasch, M. S.; Reinmuth, O. "Grignard Reactions of Nonmetallic Substances" Prentice-Hall: New Yor, 1954. (b) Houben-Weyl "Methoden der Organischen Chemie" Georg Thieme Verlag: Stuttgart, 1973; Vol. XIII-2a, p 49. (c) Ashby, E. C. *Q. Revs.* **1967**, *21*, 259. (d) Thayer, J. S. *Adv. Organomet. Chem.* **1975**, *13*, 1.

(30) (a) Kohler, E. P.; Thompson, R. B. *J. Am. Chem. Soc.* **1937**, *59*, 887. (b) Whitmore, F. C.; Block, L. P. *Ibid.* **1942**, *64*, 1619. (c) Whitmore, F. C.; George, R. S. *Ibid.* **1942**, *64*, 1239. (d) Smith, L. I.; Guss, C. *Ibid.* **1937**, *59*, 804.

(31) (a) Morrison, J. D.; Lambert, G. *J. Org. Chem.* **1972**, *37*, 1034. (b) Morrison, J. D.; Mosher, H. S. "Asymmetric Organic Reactions"; Prentice Hall: New Yor, 1971; Chapter 5.

(32) Kohler, E. P.; Peterson, W. D. *J. Am. Chem. Soc.* **1933**, *55*, 1073.

These characteristic reactivities of organocerium reagents are mainly ascribed to low basicity of the reagents and to a strong affinity of trivalent cerium for oxygen atom.[33] We believe that organocerium(III) reagents have potential synthetic utility in their applicability to a variety of organic syntheses.

Experimental Section

Infrared spectra were recorded on a Hitachi 215 spectrometer. The ^{1}H NMR spectra were determined with JEOL FX-100 and C-60 HL. Microanalyses were performed with a Perkin-Elmer 240 elemental analyzer at the Chemical Analysis Center of Chiba University.

All experiments were carried out under an atmosphere of dry argon. For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 F_{254}, 0.25 mm) were used. The products were purified by preparative TLC on silica gel (Wakogel B-5F).

Rare earth metals (cerium and samarium, purity 99.9%) were purchased from Rare Metallic Co. Ltd. Cerium chloride, lanthanum chloride, neodymium chloride, samarium chloride, and ytterbium chloride were purchased from Wako Pure Chemicals Ltd. and praseodymium chloride was obtained from Kanto Chemicals Co. Ltd. Other simple chemicals were purchased and purified before use. THF and ether were distilled from sodium benzophenone.

Preparation of Cerium Amalgam. Cerium ingot was very carefully scraped by the use of a rasp[34] and obtained cerium turnings (280 mg, 2 mmol) were treated with a solution of mercury(II) chloride (250 mg) in ethanol (2 mL) for 2 min under argon. The alcoholic medium was removed by a squirt and the residue was washed with ethanol several times under argon and finally dried in vacuo. This amalgam was very sensitive to air and it spontaneously burned in contact with air.

Preparation of Homoallylic Alcohols (General Procedure). To the cerium amalgam prepared above was added a solution of allyl halide (2 mmol) and carbonyl compound (1 mmol) in dry THF (3 mL) under argon usually at 0 °C–room temperature. After disappearance of the starting carbonyl compound, the reaction mixture was treated with a saturated aqueous ammonium chloride solution and then extracted with chloroform. The combined organic extracts were dried over sodium sulfate and the solvent was evaporated. The residue was purified by preparative TLC on silica gel.

Spectral and analytical data of new homoallylic alcohols prepared are as follows.[35]

2-(4-Bromophenyl)-4-penten-2-ol: IR (neat) 3400 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.46 (s, 3 H), 2.17 (s, 1 H), 2.35–2.60 (m, 2 H), 4.8–6.0 (m, 3 H), 7.10–7.60 (m, 4 H). Anal. Calcd for $C_{11}H_{13}BrO$: C, 54.79; H, 5.43. Found: C, 54.80; H, 5.46.

2-(4-Iodophenyl)-4-methyl-4-penten-2-ol: IR (neat) 3420 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.47 (s, 6 H), 2.37 (s, 1 H), 2.43 (d, J = 13 Hz, 1 H), 2.51 (d, J = 13 Hz, 1 H), 4.60–4.75 (m, 1 H), 4.75–4.90 (m, 1 H), 7.13 (d, J = 8 Hz, 2 H), 7.60 (d, J = 8 Hz, 2 H). Anal. Calcd for $C_{12}H_{15}IO$: C, 47.70; H, 5.00. Found: C, 47.69; H, 4.94.

4-Methyl-2-(2-thienyl)-4-penten-2-ol: IR (neat) 3400 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.53 (s, 3 H), 1.55 (s, 3 H), 2.28 (br s, 1 H), 2.52 (br s, 2 H), 4.60–4.75 (m, 1 H), 4.75–4.90 (m, 1 H), 6.70–7.10 (m, 3 H).

2-(4-Acetoxy-3-methoxyphenyl)-4-methyl-4-penten-2-ol: IR (neat) 3450, 1750 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.45 (s, 3 H), 1.48 (br s, 3 H), 2.21 (s, 3 H), 2.45 (br s, 2 H), 2.55 (br s, 1 H), 3.72 (s, 3 H), 4.50–4.70 (m, 1 H), 4.70–4.90 (m, 1 H), 6.83 (br s, 2 H), 7.30 (br s, 1 H). Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.46; H, 7.66.

1-(4-Cyanophenyl)-3-methyl-3-buten-1-ol: mp 40–41 °C; IR (KBr) 3370, 2225 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.75 (s, 3 H), 2.32 (d, J = 6 Hz, 2 H), 3.12 (br s, 1 H), 4.55–4.90 (m, 3 H), 7.40 (d, J = 8 Hz, 2 H), 7.50 (d, J = 8 Hz, 2 H). Anal. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.95; H, 7.03; N, 7.37.

2-(2-Naphthyl)-4-penten-2-ol: IR (neat) 3410 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.54 (s, 3 H), 2.30–2.94 (m, 3 H), 4.70–6.02 (m, 3 H), 7.02–7.92 (m, 7 H). Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.71; H, 7.58.

2-(4-Bromophenyl)-5-phenyl-4-penten-2-ol: mp 81–82 °C; IR (neat) 3410 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.50 (s, 3 H), 2.25 (br s, 1 H), 2.50–2.79 (m, 2 H), 5.61–6.21 (m, 1 H), 6.36 (d, J = 16 Hz, 1 H), 6.90–7.60 (m, 9 H). Anal. Calcd for $C_{17}H_{17}BrO$: C, 64.37; H, 5.40. Found: C, 64.52; H, 5.43.

2-(4-Bromophenyl)-4-pentyn-2-ol: IR (neat) 3400, 3280, 2120 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.56 (s, 3 H), 1.98 (t, J = 2.5 Hz, 1 H), 2.56 (d, J = 2.5 Hz, 2 H), 3.16 (br s, 1 H), 7.37 (d, J = 9 Hz, 2 H), 7.42 (d, J = 9 Hz, 2 H).

2-(4-Bromophenyl)-3,4-pentadien-2-ol: IR (neat) 3400, 1950 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.56 (s, 3 H), 2.56 (br s, 1 H), 4.89 (d, J = 7 Hz, 2 H), 5.44 (t, J = 7 Hz, 1 H), 7.37 (d, J = 9 Hz, 2 H), 7.42 (d, J = 9 Hz, 2 H).

3-Methyl-1-phenyl-1,4,5-hexatrien-3-ol: IR (neat) 3390, 1950 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.45 (s, 3 H), 3.22 (br s, 1 H), 4.84 (d, J = 6.5 Hz, 2 H), 5.38 (t, J = 6.5 Hz, 1 H), 6.29 (d, J = 8 Hz, 1 H), 6.63 (d, J = 8 Hz, 1 H), 7.0–7.5 (m, 5 H).

1-(4-Chlorophenyl)-2,3-butadien-1-ol: IR (neat) 3350, 1950 cm^{-1}; ^{1}H NMR (CCl_4) δ 3.88 (br s, 1 H), 4.7–5.4 (m, 4 H), 7.22 (s, 4 H).

1-[3,4-(Methylenedioxy)phenyl]-2,3-butadien-1-ol: IR (neat) 3380, 1950 cm^{-1}; ^{1}H NMR (CCl_4) δ 3.88 (br s, 1 H), 4.7–5.5 (m, 4 H), 5.90 (s, 2 H), 6.65–6.95 (m, 3 H).

The Reaction of 3-Iodo-2-methyl-1-propene with Esters in the Presence of Cerium. The reaction was carried out in a similar manner as the preparation of homoallylic alcohols described above. In this case cerium turnings were used in place of cerium amalgam, with the addition of a small amount of mercury(II) chloride as initiator.

2,6-Dimethyl-4-phenyl-1,6-heptadien-4-ol:[36] IR (neat) 3490, 1640 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.41 (br s, 6 H), 2.27 (s, 1 H), 2.53 (s, 4 H), 4.50–4.66 (m, 2 H), 4.66–4.83 (m, 2 H), 7.0–7.5 (m, 5 H).

2,6-Dimethyl-4-(α-styryl)-1,6-heptadien-4-ol:[36] IR (neat) 3525, 1645 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.75 (s, 6 H), 2.02 (s, 1 H), 2.34 (s, 4 H), 4.50–4.75 (m, 2 H), 4.75–4.90 (m, 2 H), 6.15 (d, J = 16 Hz, 1 H), 6.53 (d, J = 16 Hz, 1 H), 7.00–7.43 (m, 5 H).

2,6-Dimethyl-4-(α-phenethyl)-1,6-heptadien-4-ol:[36] IR (neat) 3530, 1645 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.74 (s, 1 H), 1.87 (s, 6 H), 1.50–2.00 (m, 2 H), 4.80–5.00 (m, 2 H), 7.13 (s, 5 H).

Methyl 2-[4-(1-hydroxy-1,3-dimethyl-3-butenyl)phenyl]propionate: IR (neat) 3500, 1740, 1645 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.45 (s, 3 H), 1.49 (s, 3 H), 1.87 (s, 1 H), 2.47 (s, 2 H), 2.05–3.08 (m, 4 H), 3.57 (s, 3 H), 4.40–4.65 (m, 1 H), 4.65–4.95 (m, 1 H), 7.02 (d, J = 8 Hz, 2 H), 7.24 (d, J = 8 Hz, 2 H). Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.30; H, 8.41.

Reformatsky-Type Reaction (General Procedure). To a mixture of a carbonyl compound (1 mmol) and cerium turnings (168 mg, 1.2 mmol) in dry THF (2 mL) was added α-halo ester (1.2 mmol) in THF (1 mL) and mercury(II) chloride (10 mg). Stirring was continued until the reaction was complete. The mixture was then treated with aqueous ammonium chloride solution and the product was extracted into chloroform. The combined extracts were dried over sodium sulfate and evaporated. The residue was chromatographed on silica gel TLC.

Ethyl 2-(2-furyl)-2-hydroxypropionate: IR (neat) 3420, 1720 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.20 (t, J = 7.5 Hz, 3 H), 2.75 (d, J = 7.0 Hz, 2 H), 4.14 (q, J = 7.5 Hz, 2 H), 4.10 (br s, 1 H), 5.04 (t, J = 7.0 Hz, 1 H), 6.24 (m, 2 H), 7.33 (m, 1 H). Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.73; H, 6.46.

Ethyl 2-(1-hydroxycyclododecyl)propionate: mp 51.5–52.0 °C; IR (KBr) 3490, 1700 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.28 (t, J = 7.0 Hz, 3 H), 1.10–1.75 (m, 22 H), 2.37 (s, 2 H), 3.25 (s, 1 H), 4.18 (q, J = 7.0 Hz, 2 H). Anal. Calcd for $C_{16}H_{30}O_3$: C, 71.09; H, 11.18. Found: C, 70.98; H, 11.01.

Ethyl 2-hydroxy-2-(4-iodophenyl)butanoate: IR (neat) 3480, 1710 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.15 (t, J = 7.0 Hz, 3 H), 1.45 (s, 3 H), 2.66 (d, J = 13 Hz, 1 H), 2.85 (d, J = 13 Hz, 1 H), 4.05 (q, J = 7.0 Hz, 2 H), 4.18 (br s, 1 H), 7.17 (d, J = 8.5 Hz, 2 H), 7.62

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[33] Further mechanistic studies are now in progress in our laboratory.

[34] The scraping should be carried out slowly and cautiously, since cerium fillings are apt to burn spontaneously.

[35] Some homoallylic alcohols were very unstable and did not give satisfactory elemental analyses.

[36] This compound decomposed during shipment for microanalysis.

(d, J = 8.5 Hz, 2 H). Anal. Calcd for $C_{12}H_{15}IO_3$: C, 43.13; H, 4.52. Found: C, 43.47; H, 4.52.

Ethyl 2-(4-cyanophenyl)-2-hydroxybutanoate: mp 43–45 °C; IR (KBr) 3460, 1710 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.16 (t, J = 7.5 Hz, 3 H), 1.52 (s, 3 H), 2.77 (d, J = 14 Hz, 1 H), 2.93 (d, J = 14 Hz, 1 H), 4.05 (q, J = 7.5 Hz, 2 H), 4.35 (br s, 1 H), 7.60 (s, 4 H). Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00. Found: C, 67.12, H, 6.51; N, 5.92.

Ethyl 2-hydroxy-2-(4-nitrophenyl)butanoate: IR (neat) 3460, 1710 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.17 (t, J = 7.5 Hz, 3 H), 1.52 (s, 3 H), 2.80 (d, J = 17 Hz, 1 H), 2.94 (d, J = 17 Hz, 1 H), 4.05 (q, J = 7.5 Hz, 2 H), 4.48 (br s, 1 H), 7.62 (d, J = 9.0 Hz, 2 H), 8.61 (d, J = 9.0 Hz, 2 H). Anal. Calcd for $C_{12}H_{15}NO_5$: C, 56.91; H, 5.97; N, 5.53. Found: C, 56.92; H, 5.97; N, 5.47.

Ethyl 2-(4-acetoxy-3-methoxyphenyl)-2-hydroxybutanoate: mp 83.0–84.0 °C; IR (KBr) 3480, 1760, 1735 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.10 (t, J = 7.5 Hz, 3 H), 1.49 (s, 3 H), 2.23 (s, 3 H), 2.65 (d, J = 16 Hz, 1 H), 2.87 (d, J = 16 Hz, 1 H), 3.79 (s, 3 H), 4.03 (q, J = 7.5 Hz, 2 H), 4.26 (br s, 1 H), 6.87 (m, 2 H), 7.16 (br s, 1 H). Anal. Calcd for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80. Found: C, 60.86; H, 6.76.

Methyl 1-ethylidene-2-hydroxy-2-phenylpropionate: IR (neat) 3450, 1695 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.96 (d, J = 7.5 Hz, 3 H), 3.69 (s, 3 H), 3.90 (d, J = 11 Hz, 1 H, exchangeable with D_2O), 5.63 (d, J = 11 Hz, 1 H), 7.03 (q, J = 7.5 Hz, 1 H), 7.28 (br s, 5 H). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 69.58; H, 6.85.

Preparation of CeI_3–RLi Reagent System and Reaction with Carbonyl Compounds (General Procedure). To a suspension of cerium turnings (350 mg, 2.5 mmol) in dry THF (7 mL) was added iodine (470 mg, 3.7 mmol) at 0 °C and the mixture was stirred for 1 h at the same temperature under argon. The ice bath was removed and the stirring was continued for 11 h at room temperature. The resulting suspension was cooled to −65 °C and organolithium reagent (2.2 mmol) was added by syringe. After maintaining the temperature at −65 °C with stirring for 30 min, carbonyl compound (1 mmol) was added and the mixture was stirred at −65 °C for 3 h. The reaction mixture was treated with a saturated ammonium chloride solution and the product was extracted into chloroform. The combined extracts were dried (Na_2SO_4) and evaporated. This residue was subjected to preparative TLC on silica gel to give the addition products.

1-Phenyl-2-(phenylmethyl)-2-hexanol: IR (neat) 3540 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.5–1.4 (m, 10 H), 2.56 (s, 4 H), 7.04 (s, 10 H). Anal. Calcd for $C_{19}H_{24}O$: C, 85.03; H, 9.01. Found: C, 84.90; H, 8.93.

2-(4-Iodophenyl)-2-hexanol: IR (neat) 3350 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.6–1.9 (m, 9 H), 1.44 (s, 3 H), 2.09 (s, 1 H), 7.09 (d, J = 8 Hz, 2 H), 7.57 (d, J = 8 Hz, 2 H). Anal. Calcd for $C_{12}H_{17}IO$: C, 47.39; H, 5.63. Found: C, 47.62; H, 5.62.

The Reaction of $CeCl_3$–RLi Reagent System with Carbonyl Compounds (General Procedure). Cerium chloride ($CeCl_3 \cdot 7H_2O$) (480 mg, 1.3 mmol) was placed in a 30-mL two-necked flask and was heated in vacuo (0.1 mmHg) at 140 °C for 2 h and cooled. Dry THF (5 mL) was added under argon and stirring was continued for 1 h and cooled to −78 °C in dry ice–acetone bath. To this suspension was added alkyllithium (1.3 mmol) with stirring. After stirring was continued for 1 h, carbonyl compound (1 mmol) in THF (2 mL) was added. The reaction mixture was treated in a similar manner described above and the product was isolated by preparative TLC.

1-[4-(*N*,*N*-Dimethylamino)phenyl]-1-pentanol: mp 34.0–35.5 °C; bp 103 °C (0.08 mm); IR (neat) 3350 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.6–2.1 (m, 10 H), 2.72 (s, 1 H), 2.93 (s, 6 H), 4.40 (t, J = 7 Hz, 1 H), 6.65 (d, J = 10 Hz, 2 H), 7.13 (d, J = 10 Hz, 2 H). Anal. Calcd for $C_{13}H_{21}NO$: C, 75.32; H, 10.21; N, 6.76. Found: C, 75.28; H, 10.11; N, 6.65.

1-(2-Methoxyphenyl)-1-pentanol: bp 135 °C (0.5 mm); IR (neat) 3370 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.6–2.0 (m, 9 H), 2.97 (s, 1 H), 3.74 (s, 3 H), 4.80 (t, J = 6 Hz, 1 H), 6.5–7.4 (m, 4 H). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.95; H, 9.34.

1-[3,4-(Methylenedioxy)phenyl]-1-pentanol: bp 105 °C (0.1 mm); IR (neat) 3320 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.7–2.0 (m, 9 H), 2.67 (s, 1 H), 4.35 (t, J = 7 Hz, 1 H), 5.82 (s, 2 H), 6.4–6.8 (m, 3 H). Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74. Found: C, 69.02; H, 7.69.

2-(4-Bromophenyl)-2-hexanol: bp 110 °C (0.2 mm); IR (neat) 3380 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.6–2.0 (m, 9 H), 1.48 (s, 3 H), 2.70 (s, 1 H), 7.45 (d, J = 9 Hz, 2 H), 7.48 (d, J = 9 Hz, 2 H). Anal. Calcd for $C_{12}H_{17}BrO$: C, 56.05; H, 6.66. Found: C, 56.29; H, 6.59.

2-(4-Cyanophenyl)-2-hexanol: bp 145 °C (0.1 mm); IR (neat) 3450, 2235 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.5–2.0 (m, 9 H), 1.57 (s, 3 H), 2.41 (s, 1 H), 7.57 (s, 4 H). Anal. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.53; H, 8.44; N, 6.75.

2-(4-Methoxyphenyl)-2-hexanol: IR (neat) 3400 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.6–2.0 (m, 9 H), 1.44 (s, 3 H), 2.60 (s, 1 H), 3.71 (s, 3 H), 6.73 (d, J = 9 Hz, 2 H), 7.22 (d, J = 9 Hz, 2 H). Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.18; H, 9.58.

1-(2-Phenylcyclopropyl)-1-phenyl-1-pentanol: IR (neat) 3420 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.6–2.2 (m, 14 H), 6.7–7.5 (m, 10 H). Anal. Calcd for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.53; H, 8.62.

1-Cyclohexyl-2-(1-hydroxy-1-phenylpentyl)-3-phenylaziridine: IR (KBr) 3400 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.5–2.1 (m, 20 H), 2.58 (d, J = 3 Hz, 1 H), 3.37 (d, J = 3 Hz, 1 H), 3.82 (s, 1 H), 7.1–7.7 (m, 10 H). Anal. Calcd for $C_{25}H_{33}NO$: C, 82.60; H, 9.15; N, 3.85. Found: C, 82.61; H, 9.08; N, 3.81.

1,2-Epoxy-1,3-diphenyl-3-heptanol: IR (KBr) 3480 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.7–2.3 (m, 9 H), 2.70 (s, 1 H), 3.53 (d, J = 3 Hz, 1 H), 4.21 (d, J = 3 Hz, 1 H), 7.2–8.2 (m, 10 H). Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85. Found: C, 80.67; H, 7.87.

3-Methyl-1-phenyl-1-hepten-3-ol: IR (neat) 3370 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.5–1.8 (m, 9 H), 1.35 (s, 3 H), 2.64 (s, 1 H), 6.34 (d, J = 17 Hz, 1 H), 6.64 (d, J = 17 Hz, 1 H), 7.0–7.6 (m, 5 H). Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.31; H, 9.78.

1,3-Diphenyl-1-hepten-3-ol: IR (neat) 3410 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.6–2.2 (m, 9 H), 1.91 (s, 1 H), 6.51 (s, 2 H), 6.9–7.8 (m, 10 H). Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 85.47; H, 8.35.

2-Butyl-1,2,3,4-tetrahydro-2-naphthol. For easier separation from the starting ketone, the reaction mixture was treated with $NaBH_4$ in ethanol for the conversion of β-tetralone into the corresponding secondary alcohol, and then the product was isolated by preparative TLC (benzene:ethyl acetate 10:1): bp 120 °C (0.08 mm); IR (neat) 3370 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.6–1.8 (m, 11 H), 2.09 (s, 1 H), 2.3–3.0 (m, 4 H), 6.7–7.2 (m, 4 H). Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.31; H, 9.75.

2-Mesityl-2-hexanol. The reaction mixture was treated with 29 mg (0.75 mmol) of $LiAlH_4$ in dry ether for 1 h at room temperature for the conversion of the starting ketone into the corresponding secondary alcohol. The resulting mixture was worked up in the usual manner and the desired product, 2-mesityl-2-hexanol, was isolated by preparative TLC (benzene:ethyl acetate 10:1): bp 90 °C (0.01 mm); IR (neat) 3440 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.6–2.1 (m, 10 H), 1.60 (s, 3 H), 2.18 (s, 3 H), 2.45 (s, 6 H), 6.70 (s, 2 H). Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.93; H, 10.88.

1-*tert*-Butyl-1-cyclopentanol:[36] IR (neat) 3410 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.6–2.5 (m, 9 H), 0.95 (s, 9 H).

3,3-Dimethyl-1-phenyl-2-(phenylmethyl)-2-butanol: mp 61–62 °C (i-C_3H_7OH); IR (KBr) 3560 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.05 (s, 9 H), 1.32 (s, 1 H), 2.83 (d, J = 14 Hz, 2 H), 3.05 (d, J = 14 Hz, 2 H), 6.9–7.4 (m, 10 H). Anal. Calcd for $C_{19}H_{24}O$: C, 85.03; H, 9.01. Found: C, 84.98; H, 8.95.

The Reaction of Grignard Reagents with Ketones. *n*-Butylmagnesium bromide in THF and *tert*-butylmagnesium chloride in ether were prepared by the standard method. These Grignard reagents (1.3 mmol) were allowed to react with ketones (1 mmol) at 0 °C, and products were isolated after usual workup.

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Registry No. $CH_2{=}CHCH_2I$, 556-56-9; $C_6H_5CH_2I$, 620-05-3; $CH_2{=}C(CH_3)CH_2I$, 3756-30-7; $CH_2{=}CHCH_2Br$, 106-95-6; $C_6H_5CH{=}CHCH_2Br$, 4392-24-9; $HC{=}CCH_2I$, 659-86-9; p-$BrC_6H_4COCH_3$, 99-90-1; $C_6H_5COCH_3$, 98-86-2; p-ClC_6H_4CHO, 104-88-1; p-$IC_6H_4COCH_3$, 13329-40-3; p-NCC_6H_4CHO, 105-07-7; C_6H_5CHO, 100-52-7; β-$C_{10}H_7COCH_3$, 93-08-3; p-$CH_3OC_6H_4COCH_3$, 100-06-1; $C_6H_5CH{=}CHCOCH_3$, 122-57-6; $C_6H_5COOC_2H_5$, 93-89-0; $C_6H_5CH{=}CHCOOC_2H_5$, 103-36-6; C_6-

$H_5(CH_2)_2COOCH_3$, 103-25-3; *p*-$CH_3COC_6H_4(CH_2)_2COOCH_3$, 91671-15-7; $ICH_2COOC_2H_5$, 623-48-3; $CH_3CHICOOC_2H_5$, 31253-08-4; $BrCH_2COOC_2H_5$, 105-36-2; $BrCH_2CH{=}CHCOOCH_3$, 1117-71-1; $C_6H_5CHBrCOOC_2H_5$, 2882-19-1; *n*-C_3H_7CHO, 123-72-8; $C_2H_5CH(CH_3)COCH_3$, 565-61-7; *p*-$NCC_6H_4COCH_3$, 1443-80-7; *p*-$O_2NC_6H_4COCH_3$, 100-19-6; $C_6H_5COCH(CH_3)_2$, 611-70-1; $C_6H_5CH_2COC_6H_5$, 451-40-1; 2,4,6-$(CH_3)_3C_6H_2COCH_3$, 1667-01-2; $C_6H_5CH_2CH_2CHO$, 104-53-0; $(C_6H_5CH_2)_2CO$, 102-04-5; *p*-$(CH_3)_2NC_6H_4CHO$, 100-10-7; *o*-$CH_3OC_6H_4CHO$, 135-02-4; $C_6H_5CH{=}CHCHO$, 104-55-2; $C_6H_5CH{=}CHCOC_6H_5$, 94-41-7; *p*-$BrC_6H_4C(OH)(CH_3)CH_2CH{=}CH_2$, 81336-05-2; $C_6H_5C(OH)(CH_3)CH_2C_6H_5$, 5342-87-0; *p*-$ClC_6H_4CHOHCH_2C_6H_5$, 31233-66-6; *p*-$ClC_6H_4COOCH_2C_6H_4Cl$-*p*, 19048-85-2; *p*-$IC_6H_4C(OH)(CH_3)CH_2C(CH_3){=}CH_2$, 91671-28-2; *p*-$NCC_6H_4CHOHCH_2C(CH_3){=}CH_2$, 91671-31-7; $C_6H_5CHOHCH_2C(CH_3){=}CH_2$, 23092-23-1; $C_6H_5C(OH)[CH_2C(CH_3){=}CH_2]_2$, 81925-76-0; *p*-$ClC_6H_4CHOHCH_2C(CH_3){=}CH_2$, 41801-83-6; *p*-$ClC_6H_4C(OH)[CH_2C(CH_3){=}CH_2]_2$, 91671-32-8; β-$C_{10}H_7C(OH)(CH_3)CH_2CH{=}CH_2$, 81336-07-4; *p*-$CH_3OC_6H_4C(OH)(CH_3)CH_2CH{=}CH_2$, 60573-61-7; $C_6H_5CH{=}CHC(OH)(CH_3)CH_2CH{=}CH_2$, 21573-75-1; *p*-$ClC_6H_4CHOHCH_2CH{=}CH_2$, 14506-33-3; *p*-$ClC_6H_4CH_2OH$, 873-76-7; *p*-$BrC_6H_4C(OH)(CH_3)CH_2CH{=}CHC_6H_5$, 91671-33-9; (R^*,R^*)-*p*-$BrC_6H_4C(OH)(CH_3)CH(C_6H_5)CH{=}CH_2$, 91671-34-0; (R^*,S^*)-*p*-$BrC_6H_4C(OH)(CH_3)CH(C_6H_5)CH{=}CH_2$, 91671-47-5; *p*-$BrC_6H_4C(OH)(CH_3)CH_2C{\equiv}CH$, 85014-12-6; *p*-$BrC_6H_4C(OH)(CH_3)CH{=}C{=}CH_2$, 58705-82-1; $C_6H_5CH{=}CHC(OH)(CH_3)CH_2C{\equiv}CH$, 38516-80-2; $C_6H_5CH{=}CHC(OH)(CH_3)CH{=}C{=}CH_2$, 91671-35-1; *p*-$ClC_6H_4CHOHCH_2C{\equiv}CH$, 42249-99-0; *p*-$ClC_6H_4CHOHCH{=}C{=}CH_2$, 91671-36-2; $C_6H_5CH{=}CHC(OH)[CH_2C(CH_3){=}CH_2]_2$, 91671-16-8; $C_6H_5(CH_2)_2C(OH)[CH_2C(CH_3){=}CH_2]_2$, 91671-17-9; $CH_2{=}C(CH_3)CH_2C(OH)(CH_3)C_6H_4$-*p*-$(CH_2)_2COOCH_3$, 91671-18-0; *n*-$C_3H_7CHOHCH_2COOC_2H_5$, 2305-25-1; $C_6H_5CHOHCH_2COOC_2H_5$, 5764-85-2; (R^*,R^*)-$C_2H_5CH(CH_3)C(OH)(CH_3)CH_2COOC_2H_5$, 91671-19-1; (R^*,S^*)-$C_2H_5CH(CH_3)C(OH)(CH_3)CH_2COOC_2H_5$, 91671-20-4; *p*-$IC_6H_4C(OH)(CH_3)CH_2COOC_2H_5$, 91671-21-5; *p*-$NCC_6H_4C(OH)(CH_3)CH_2COOC_2H_5$, 91671-22-6; *p*-$O_2NC_6H_4C(OH)(CH_3)CH_2COOC_2H_5$, 91671-23-7; (R^*,R^*)-$C_6H_5CHOHCH(CH_3)COOC_2H_5$, 17226-82-3; (R^*,S^*)-$C_6H_5CHOHCH(CH_3)COOC_2H_5$, 17226-81-2; (R^*,R^*)-$C_6H_5C(OH)(CH_3)CH(CH_3)COOC_2H_5$, 17226-97-0; (R^*,S^*)-$C_6H_5C(OH)(CH_3)CH(CH_3)COOC_2H_5$, 17226-96-9; (R^*,R^*)-$C_6H_5C(OH)(CH(CH_3)_2)CH(CH_3)COOC_2H_5$, 91671-25-9; (R^*,S^*)-$C_6H_5C(OH)(CH(CH_3)_2)CH(CH_3)COOC_2H_5$, 91671-26-0; $C_6H_5C(OH)(CH_3)CH_2COOC_2H_5$, 2293-60-9; $C_6H_5CHOHC(COOCH_3){=}CHCH_3$, 91671-27-1; (R^*,R^*)-$C_6H_5CHOHCH(C_6H_5)COOC_2H_5$, 14367-01-2; (R^*,S^*)-$C_6H_5CHOHCH(C_6H_5)COOC_2H_5$, 14367-00-1; $C_6H_5C(OH)(CH_3)C_4H_9$-*n*, 4396-98-9; $C_6H_5CH_2C(OH)(C_6H_5)C_4H_9$-*n*, 84735-50-2; $(C_6H_5CH_2)_2C(OH)C_4H_9$-*n*, 84735-51-3; *p*-$IC_6H_4C(OH)(CH_3)C_4H_9$-*n*, 84735-52-4; 2,4,6-$(CH_3)_3C_6H_2C(OH)(CH_3)C_4H_9$-*n*, 84735-53-5; $C_6H_5CH_2CH_2CHOHC_4H_9$-*n*, 19969-03-0; $C_6H_5C(OH)(CH_3)C_4H_9$-*sec*, 33484-93-4; $C_6H_5C(OH)(CH_3)C_2H_5$, 1565-75-9; $C_6H_5C(OH)(CH_3)_2$, 617-94-7; $CH_3C(OH)(C_6H_5)_2$, 599-67-7; $C_6H_5C(OH)(CH_3)C(OH)(CH_3)C_6H_5$, 1636-34-6; $C_6H_5CHOHCH_3$, 98-85-1; *p*-$(CH_3)_2NC_6H_4CHOHC_4H_9$-*n*, 91671-38-4; *o*-$CH_3OC_6H_4CHOHC_4H_9$-*n*, 91671-39-5; *p*-$BrC_6H_4C(OH)(CH_3)C_4H_9$-*n*, 91671-40-8; *p*-$NCC_6H_4C(OH)(CH_3)C_4H_9$-*n*, 91671-41-9; *p*-$CH_3OC_6H_4C(OH)(CH_3)C_4H_9$-*n*, 19523-03-6; $C_6H_5CH{=}CHCHOHC_4H_9$-*n*, 20157-19-1; $C_6H_5CH{=}CHC(OH)(CH_3)C_4H_9$-*n*, 91671-45-3; $C_6H_5CH{=}CHC(OH)(C_6H_5)C_4H_9$-*n*, 53188-81-1; $C_6H_5CH(C_4H_9\text{-}n)CH_2COC_6H_5$, 1454-57-5; $(C_6H_5CH_2)_2C(OH)C_4H_9$-*t*, 75245-71-5; Ce, 7440-45-1; CeI_3, 7790-87-6; $CeCl_3$, 7790-86-5; $LaCl_3$, 10099-58-8; $NdCl_3$, 10024-93-8; $PrCl_3$, 10361-79-2; $SmCl_3$, 10361-82-7; $YbCl_3$, 10361-91-8; *n*-C_4H_9Li, 109-72-8; *sec*-C_4H_9Li, 598-30-1; C_2H_5Li, 811-49-4; CH_3Li, 917-54-4; C_6H_5Li, 591-51-5; *t*-C_4H_9Li, 594-19-4; *n*-C_4H_9Br, 109-65-9; *t*-C_4H_9Cl, 507-20-0; cyclooctanone, 502-49-8; cyclohexanone, 108-94-1; 2-acetylthiophene, 88-15-3; 4-acetoxy-3-methoxyacetophenone, 54771-60-7; piperonal, 120-57-0; 1-allylcyclooctanol, 57670-91-4; 1-benzylcyclohexanol, 1944-01-0; 4-methyl-2-(2-thienyl)-4-penten-2-ol, 91671-29-3; 2-(4-acetoxy-3-methoxyphenyl)-4-methyl-4-penten-2-ol, 91671-30-6; 1-[3,4-(methylenedioxy)phenyl]-3-butyn-2-ol, 91344-61-5; 1-[3,4-(methylenedioxy)phenyl]-2,3-butadien-1-ol, 91671-37-3; 2-furaldehyde, 98-01-1; cyclododecanone, 830-13-7; ethyl 2-(2-furyl)-2-hydroxypropionate, 25408-95-1; ethyl 2-(1-hydroxycyclododecyl)propionate, 72013-81-1; ethyl 4-acetoxy-α-hydroxy-3-methoxy-α-methylbenzeneacetate, 91671-24-8; 1-butylcyclohexanol, 5445-30-7; α-butylfurfuryl alcohol, 30478-77-4; 4-*tert*-butylcyclohexanone, 98-53-3; 1-*n*-butyl-4-*tert*-butylcyclohexanol, 53188-79-7; *trans*-1-benzoyl-2-phenylcyclopropane, 1145-92-2; *trans*-2-benzoyl-1-cyclohexyl-3-phenylaziridine, 2211-61-2; *trans*-2-benzoyl-3-phenyloxirane, 7570-86-7; 1-[3,4-(methylenedioxy)phenyl]-1-pentanol, 5422-01-5; 1-(2-phenylcyclopropyl)-1-phenyl-1-pentanol (isomer 1), 91671-42-0; 1-(2-phenylcyclopropyl)-1-phenyl-1-pentanol (isomer 2), 91740-20-4; 1-cyclohexyl-2-(1-hydroxy-1-phenylpentyl)-3-phenylaziridine (isomer 1), 91671-43-1; 1-cyclohexyl-2-(1-hydroxy-1-phenylpentyl)-3-phenylaziridine (isomer 2), 91740-21-5; 1,2-epoxy-1,3-diphenyl-3-heptanol (isomer 1), 91671-44-2; 1,2-epoxy-1,3-diphenyl-3-heptanol (isomer 2), 91740-22-6; cyclopentanone, 120-92-3; β-tetralone, 530-93-8; 2-cyclohexenone, 930-68-7; 1-butylcyclopentanol, 1462-97-1; 2-butyl-1,2,3,4-tetrahydro-2-naphthol, 91671-46-4; 1-butyl-2-cyclohexenol, 88116-46-5; 1-*tert*-butylcyclopentanol, 69745-48-8; 1-*tert*-butylcyclohexanol, 20344-52-9.

Dimethylboron Bromide and Diphenylboron Bromide: Cleavage of Acetals and Ketals

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The cleavage of various acetal and ketal derivatives by the use of dialkyl- and diarylboron halides is described. Acetals and ketals readily react with dimethylboron bromide or diphenylboron bromide at −78 °C to give the corresponding carbonyl compounds in excellent yield. Under similar reaction conditions MEM, MOM, and MTM ethers are smoothly converted to alcohols. Acetonides are also cleaved with dimethylboron bromide while THP and THF ethers and methyl glycosides react at room temperature. Mechanistic considerations of the cleavage reactions are presented. The chemoselective virtues of dimethylboron bromide are summarized.

Acetals and ketals are two of the most useful and versatile functionalities in organic chemistry. They find application, for instance, in the protection of carbonyl, hydroxyl, and diol functions.[1] As such they represent a major component of the available protecting groups which can be used in the elaboration of complex or polyfunctional organic structures.

The only unified approach for the cleavage of an acetal or ketal derivative involves treatment with acids or Lewis acids.[1] Unfortunately the use of strong acids is often required but these may sometimes be precluded by the

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[1] Greene, T. W. "*Protective Groups in Organic Synthesis*"; Wiley-Interscience: New York, 1981.

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