organic solution was reduced to a small volume (2–3 mL) under reduced pressure before being partitioned between CH_2Cl_2 and H_2O. The organic layer was separated, dried, filtered, and concentrated under reduced pressure. When necessary, the product was isolated from any remaining coproducts by chromatography on a silica gel column.

Acknowledgment. The financial support of the Natural Sciences and Engineering Research Council and Queen's University is gratefully acknowledged.

Registry No. 1 (R = MeO, R^1 = Me, R^2 = Me), 6622-76-0; 1 (R = MeO, R^1 = Me, R^2 = Et), 1567-14-2; 1 (R = MeO, R^1 = Me, R^2 = *n*-Pr), 16493-96-2; 1 (R = MeO, R^1 = Me, R^2 = *i*-Pr), 20515-18-8; 1 (R = MeO, R^1 = Et, R^2 = Me), 101226-85-1; 1 (R = MeO, R^1 = Me, R^2 = $(CH_2)_4OH$), 101226-86-2; 1 (R = MeO, R^1 = Me, R^2 = $(CH_2)_3OH$), 101226-87-3; 1 (R = $NHCH_2Ph$, R^1 = Me, R^2 = Me), 83375-42-2; **2A**, 101019-17-4; **2B**, 101226-73-7; **2C**, 101019-21-0; **2D**, 101019-23-2; **2E**, 101226-74-8; **2F**, 101226-75-9; **2G**, 101226-76-0; **2H**, 101226-77-1; **2J**, 101019-24-3; **2K**, 101019-25-4; **2L**, 101226-78-2; **2M**, 101019-18-5; **2N**, 101019-19-6; **2P**, 101019-22-1; **2Q**, 101019-20-9; **3A**, 39788-68-6; **3D**, 39788-58-4; **3F**, 101226-79-3; **3G**, 101226-80-6; **3J**, 88222-48-4; **3K**, 88222-58-6; **3L**, 101226-81-7; **3M**, 101019-26-5; **3N**, 101019-28-7; **3P**, 101019-32-3; **3Q**, 101019-30-1; **4A**, 39788-67-5; **4D**, 39788-59-5; **4F**, 101226-82-8; **4G**, 101226-83-9; **4J**, 88222-47-3; **4K**, 88222-57-5; **4L**, 101226-84-0; **4M**, 101019-27-6; **4N**, 101019-29-8; **4P**, 101019-33-4; **4Q**, 101019-31-2; **5**, 38512-74-2; **6**, 75768-12-6; **7**, 75768-11-5; 9-BBN, 280-64-8; $Hg(OAc)_2$, 1600-27-7; $HgCl_2$, 7487-94-7; $Hg(O_2CCF_3)_2$, 13257-51-7; $HgBr_2$, 7789-47-1; $NaBH_4$, 16940-66-2; $Na(MeO)_3BH$, 16940-17-3; $Na(AcO)_3BH$, 56553-60-7; $LiBH_4$, 16949-15-8; $NaBH_3CN$, 25895-60-7; BH_3, 13283-31-3; $Br_2BH{\cdot}Me_2S$, 55671-55-1; DIBAL-H, 1191-15-7; $LiAlH_4$, 16853-85-3; Li(*sec*-Bu)$_3$BH, 38721-52-7; Ph_3SiH, 789-25-3; *n*-Bu_3SnH, 688-73-3; $(n\text{-}Bu)_4NBH_4$, 33725-74-5; $NaBH_2S_3$, 27735-90-6; $HS(CH_2)_2SH$, 540-63-6; $HS(CH_2)_3SH$, 109-80-8; $HS(CH_2)_4SH$, 1191-08-8; $HO(CH_2)_2SH$, 60-24-2; HO_2CCH_2SH, 68-11-1; CH_3CH_2SH, 75-08-1; $NaS(CH_2)_3SH$, 101248-11-7; Na_2CS_3, 534-18-9.

Supplementary Material Available: Physical and spectroscopic data (IR, Ms, ^1H, and ^{13}C NMR) for the α,β-unsaturated carbonyl compounds, the organomercurials **2A–Q** and the demercuration products **3A–Q** and **4A–Q** (10 pages). Ordering information is given on any current masthead page.

Alkylmetal Asymmetric Reduction. 17.[1] Stereochemical Course of Ketone Reduction by β-Branched Alkyl Derivatives of Beryllium and Aluminum

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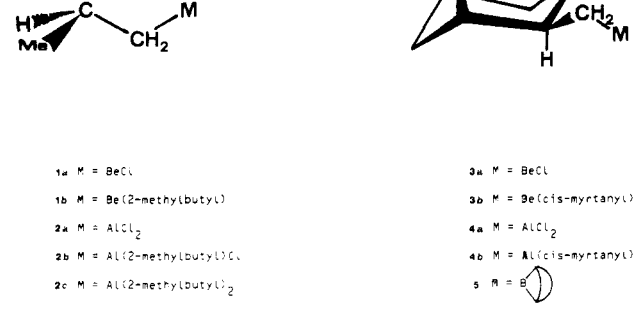
(*R*)-(2-Methylbutyl)beryllium chloride and tri-*cis*-myrtanylaluminum have been prepared; both these new organometallic derivatives are able to provide enantioselective reduction of prochiral ketones. Further investigations on the use of *cis*-myrtanylberyllium chloride, di-*cis*-myrtanylberyllium, and bis[(*R*)-2-methylbutyl]beryllium as reducing agents of ketones are also reported. The extent of enantioselectivity, along with the stereochemistry of the process, was found to depend mainly on the nature of metal atom and on the structure of the ketone employed. The stereochemical results obtained are discussed on the basis of previous reports too.

One of the most widely investigated aspects in the field of asymmetric induction has been the synthesis of optically active carbinols from enantioselective reduction of prochiral ketones.[2]

Recently we have studied the asymmetric reduction of alkyl phenyl and α-alkynyl ketones using [(*S*)-2-methylbuty]aluminum derivatives **2a–c**[3] and *cis*-myrtanylaluminum dichloride (**4a**).[4] This procedure affords optically active carbinols in short reaction times, good chemical and sometimes high optical yields. We have also noted that 2-methylbutyl derivatives reduce phenyl and α-alkynyl ketones with the same stereochemical course:[3] phenyl and α-alkynyl carbinols being recovered with *S* and *R* absolute configuration, respectively. On the other hand, using *cis*-myrtanylaluminum dichloride (**4a**) we observed a reversal of the stereochemistry of the process on passing from phenyl to α-alkynyl ketones: in fact, all carbinols recovered had *R* absolute configuration. At present, we have extended our studies to beryllium derivatives,[5] to look for the origin of this discrepancy in the stereochemical behavior of this kind of enantioselective reducing agent. Therefore we have prepared *cis*-myrtanylberyllium chloride (**3a**) and di-*cis*-myrtanylberyllium (**3b**), and we have checked their ability to reduce enantioselectively prochiral ketones:[5] we preliminarly found that both **3a** and **3b** had the same stereochemical trend shown by **4a**.



1a M = $BeCl$
1b M = Be(2-methylbutyl)
2a M = $AlCl_2$
2b M = Al(2-methylbutyl)Cl
2c M = Al(2-methylbutyl)$_2$
3a M = $BeCl$
3b M = Be(cis-myrtanyl)
4a M = $AlCl_2$
4b M = Al(cis-myrtanyl)$_2$
5 M = B

In the present work we report the data concerning the reduction of ketones by cis-myrtanyl organometallic derivatives **3a,b**[5] and **4b** and [(*R*)-2-methylbutyl]beryllium derivatives (**1a**,[6]**b**).

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0022-3263/86/1951-2030$01.50/0

Table I. Enantioselective Reduction of Ketones by Alkylberyllium Derivatives 1a,b (R = 2-Methylbutyl)

run	ketone	reducing agent	temp, °C	reacn time, h	solvent	optically active carbinol: yield,[a] %	optically active carbinol: $[\alpha]^{25}_D$, deg (c, solvent)	optically active carbinol: ee, %
1	acetophenone	RBeCl	20	2	ether	100 (79)	−0.06 (neat)	<0.1 (*S*)[b]
2		R_2Be	20	4		100 (83)	−1.50 (neat)	3 (*S*)
3	ethyl phenyl ketone	RBeCl	20	2		98 (90)	−1.28 (neat)	4.5 (*S*)
4		R_2Be[c]	0	1	pentane	89 (80)	−1.56 (neat)	15 (*S*)
5	isopropyl phenyl ketone	RBeCl	20	2	ether	99 (90)	−12.08 (8.78, ether)	25 (*S*)
6		R_2Be[c]	0	1	pentane	97 (88)	−8.02 (4.55, ether)	46 (*S*)
7			20	5	ether	98 (66)	−13.90 (8.80, ether)	29 (*S*)
8	*tert*-butyl phenyl ketone	RBeCl	20	12		78 (69)	−5.55 (8.29, ether)	15 (*S*)
9		R_2Be[c]	0	1	pentane	90 (78)	−4.07 (8.01, ether)	31 (*S*)
10	4-octyn-3-one	RBeCl	20	2	ether	100 (80)	+2.01 (7.97, ether)	5 (*R*)
11		R_2Be	20	2		100 (78)	+2.95 (10.86, ether)	7.5 (*R*)
12	4-nonyn-3-one	RBeCl	20	2		100 (74)	+1.94 (12.91, hexane)	12.5 (*R*)
13		R_2Be	20	2		100 (69)	+2.02 (13.32, hexane)	13 (*R*)
14	2,2-dimethyl-4-nonyn-3-one	RBeCl	20	2		100 (89)	+3.35 (neat, 1 = 1)	21 (*R*)
15		R_2Be	20	2		100 (75)	+3.30 (neat, 1 = 1)	20 (*R*)

[a] GLC yields after hydrolysis. The number in parentheses refer to isolated yield. [b] HPLC on the csp showed a racemic product. [c] From ref 6.

Table II. Enantioselective Reduction of Ketones by Alkylberyllium Derivatives 3a,b (R = *cis*-Myrtanyl)

run	ketone	reducing agent	temp, °C	reacn time, h	solvent	optically active carbinol: yield,[a] %	optically active carbinol: $[\alpha]^{25}_D$, deg (c, solvent)	optically active carbinol: ee, %[b]
16	acetophenone	RBeCl	20	14	ether	67	*d*	[4] (*S*)
17		R_2Be[c]	20	4		95	+8.12 (neat)	19 [21] (*R*)
18	ethyl phenyl ketone	RBeCl	20	3		55	+6.35 (neat)	22 (*R*)
19		R_2Be	20	4		92	+6.96 (neat)	24 (*R*)
20			−35	4		98	+11.09 (neat)	39 [41] (*R*)
21	isopropyl phenyl ketone	RBeCl[c]	20	3		35	+18.66 (3.91, ether)	39 (*R*)
22			20	40		73	+18.02 (7.55, ether)	38 (*R*)
23			20	44	hexane	54	+15.76 (7.17, ether)	33 (*R*)
24		R_2Be[c]	20	4	ether	94	+12.51 (12.71, ether)	26 (*R*)
25			−17	4		96	+15.81 (4.24, ether)	33 (*R*)
26			−35	4		99	+17.25 (5.45, ether)	36 [34] (*R*)
27	*tert*-butyl phenyl ketone	RBeCl[c]	20	3		35	+14.24 (3.58, ether)	39 (*R*)
28		R_2Be[c]	20	4		86	+8.90 (5.17, ether)	25 (*R*)
29		R_2Be[c]	−17	4		94	+12.32 (3.90, ether)	34 (*R*)
30	2-methyl-4-nonyn-3-one	RBeCl	20	3		40	+0.70 (neat, 1 = 1)	8.5 (*R*)
31			20	14	hexane	88	+1.60 (neat, 1 = 1)	19.5 (*R*)
32		R_2Be	−35	4	ether	100	−0.74 (6.78, hexane)	9 (*S*)
33	2,2-dimethyl-4-nonyn-3-one	RBeCl[c]	20	3		40	+4.90 (neat, 1 = 1)	30 (*R*)
34			20	44	hexane	75	+4.70 (neat, 1 = 1)	29 (*R*)
35		R_2Be[c]	−17	4	ether	100	+4.40 (neat, 1 = 1)	27 (*R*)
36			−35	4		100	+6.70 (neat, 1 = 1)	41 (*R*)

[a] GLC yields after hydrolysis. [b] The numbers in brackets refer to value obtained by HPLC on the csp. [c] From ref 5. [d] Not determined.

The asymmetric reductions have been carried out, unless otherwise specified, in ethereal solvent by following previously published procedures[4,5] and using a slight excess (about 20%) of reducing agents with respect to the carbonyl compound. [(*R*)-2-Methylbutyl]beryllium chloride (**1a**) was prepared by adding anhydrous $BeCl_2$ to the Grignard reagent of (*S*)-2-methylbutyl chloride and, after purification, was characterized by ^1H NMR spectroscopy as its diethyl etherate.

Enantiomeric excesses of the carbinols obtained as reduction products were evaluated by purifying the alcohols by flash chromatography[7] and measuring the rotatory power of each sample. However, recent progresses in the field of direct separation of enantiomers by chromatography using chiral stationary phases (csp)[8] provide a rapid and more accurate method for determining enantiomeric compositions.[9] Therefore, the enantiomeric composition of the phenylalkylcarbinols was also determined by direct chromatographic separation of the antipodes on (*R*)-*N*-(3,5-dinitrobenzoyl)phenylglycine bonded to 3-aminopropyl silanized silica.[10] This csp is quite efficient in the resolution of this class of compounds. In addition, it is known[10] that the *S* enantiomer of simple alkyl phenyl carbinols is eluted first.

Compound **1a** is able to reduce phenyl and α-alkynyl ketones (Table I) to the corresponding optically active carbinols within short times and in high yields, except for *tert*-butyl phenyl ketone (run 8). The enantiomeric excesses are moderate (up to 25%, run 5) and in some cases very low (<0.1%, run 1). The extent of asymmetric reduction seems to increase with increasing steric hindrance of the alkyl groups on the carbonyl moiety (i.e., runs 10, 12, 14). It is interesting to note that while (*S*)-alkylphenylcarbinols are obtained, the reduction of α-alkynyl ketones affords *R* alcohols.

Table I also shows the data concerning the reduction carried out with bis[(*R*)-2-methylbutyl]beryllium (**1b**).[6] This reagent exhibits the same stereochemical trend shown by **1a** and **2a–c**.[3] The data reported also show that the

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(9) Pirkle, W. H.; Hyun, M. H. *J. Chromatogr.* **1985**, *322*, 309.
(10) Pirkle, W. H.; Finn, J. M. *J. Org. Chem.* **1981**, *46*, 2932.

Table III. Enantioselective Reduction of Ketones by Tri-*cis*-myrtanylaluminum (4b)[a]

run	ketone	optically active carbinol: yield,[b] %	[α]$^{25}_{D}$, deg (c, solvent)	ee, %
37	isopropyl phenyl ketone	98 (87)	+42.73 (2.85, ether)	90 (*R*)
38	*tert*-butylphenyl ketone	99 (90)	+35.48 (3.06, ether)	98 (*R*)
39	2-methyl-4-nonyn-3-one	95 (65)	+1.98 (8.21, hexane)	24 (*R*)
40	2,2-dimethyl-4-nonyn-3-one	97 (70)	+5.11 (neat)	31 (*R*)

[a] Reactions carried out in ether at 20 °C for 1 h. [b] GLC yields after hydrolysis. The numbers in parentheses refer to isolated yield.

use of hydrocarbon solvent increases the extent of asymmetric induction (runs 6, 7).

The results obtained with *cis*-myrtanylberyllium chloride (**3a**)[5] and di-*cis*-myrtanylberyllium (**3b**)[5] as reducing agent are shown in Table II. In the case of **3a** the reduction rate drops significantly, and both chemical and optical yields are moderately high. The absolute configurations of the products are *R* in all the cases except in the reduction of acetophenone (run 16). With **3a** the nature of the solvent does not affect to a large extent the value of asymmetric induction (runs 33, 34). Short and long reaction times (runs 21, 22) give the same results: this fact indicates that, according to what previously affirmed,[5] the presence of alkoxide species in the reaction medium does not affect the stereochemical course of the processes.

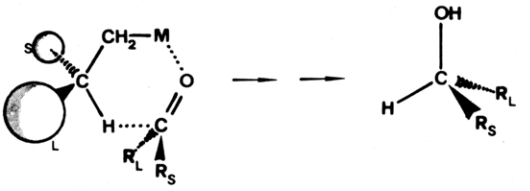
The reduction of ketones using **3b** was carried out at temperatures below 20 °C; in these conditions the reduction processes are still very fast and afford the product in nearly quantitative yields.[11] The capability of enantioface discrimination of **3b** is roughly the same as **3a**, and all the carbinols with the exception for one (run 32) have the *R* absolute configuration.

Results obtained with tri-*cis*-myrtanylaluminum (**4b**) as reducing agent are shown in Table III. The stereochemical behavior of this alane is analogous to that of *cis*-myrtanylaluminum dichloride (**4a**):[4] the absolute configuration of the carbinols recovered are *R* in all the cases, but the enantioface discrimination drops significantly on passing from phenyl to α-alkynyl substrates.

For this kind of reaction, consistent with other authors,[12] we have already proposed[13] a mechanism involving a slightly strained six-membered ring transition state.[14] A comparison of all the data reported shows that the stereochemical behavior of an organometallic chloride derivative is not appreciably different from that of the corresponding organometallic compound. The halogen atom determines only the extent of the asymmetric induction.[3] Undoubtedly the halogen atom can affect the strength of the alkylmetal compound as Lewis acid, and this fact, along with the basicity of the carbonyl moiety, might affect the geometry of the transition state.

The simplest attempt to evaluate the different energies in the diastereomeric transition state can be made, considering only steric interactions among substituent groups

Scheme I



inside the transition state. Thus, we can postulate that, in order to reduce the steric interactions, the substituent groups on the substrate and the reducing agent should be facing larger–smaller and smaller–larger, respectively, as shown in Scheme I. Considering that the steric hindrances of the substituent groups are not always in agreement with their relative priority in IUPAC rules for attributing absolute configuration,[15] we should obtain phenyl- and α-alkynylcarbinols of opposite configurations for the same stereochemical course. All these considerations are effective only in the case of the reductions performed by the 2-methylbutyl derivatives (Table I).[3] On the contrary, using *cis*-myrtanyl derivatives we can note an inversion of the stereochemical course of the reaction on passing from phenyl to α-alkynyl ketones (Table II).[1,4,5] In addition, it is important to note that in the reduction of acetophenone (runs 16, 17) and 2-methyl-4-nonyn-3-one (runs 30–32), reaction products of opposite configuration can be obtained even using reducing agents having very similar structure. Besides, M. Midland has recently shown[2a] that a change in enantioselectivity occurs by reducing acetophenone and 4-methylpentyn-3-one by means of similar organoboranes **5** and organoaluminum **4a**[4] reagents.

In view of the present results, it seems that the nature of the metal atom in the reducing agent is not the only factor which affects the absolute configuration of the products and that the nature of the substrate can play an important role.

As far as the structure of the alkyl group bound to the metal atom is concerned, we only postulate that the *cis*-myrtanyl group, stiffer than the 2-methylbutyl one, might permit a closer interaction between reagent and substrate in the transition state. This hypothesis takes into account the values of enantioselectivity higher than those observed with 2-methylbutyl derivatives and the effect of the nature of the substrate in the "choice" of the preferred stereochemical course. These considerations imply an actual nature of the transition state more complex than that we can suppose on the basis of a simple steric model.

Therefore, although many experimental data are now available, any attempt to offer a most satisfactory interpretation of these stereochemical results has to be postponed until further studies on these reactions employing different organometallic compounds of other elements will be completed.

Experimental Section

Boiling points are uncorrected. ^{1}H NMR (60 MHz) spectra were obtained with a Varian T-60 spectrometer on C_6D_6 solutions with Me_4Si as internal standard. (−)-*cis*-Myrtanyl chloride[4] and (+)-(*S*)-methylbutyl chloride[16] were prepared from (−)-β-pinene and (−)-(*S*)-2-methylbutanol, respectively, according to previously reported procedures. Optical rotations were measured on a Perkin-Elmer 142 automatic polarimeter in a 1-dm tube; unless otherwise specified, rotations refer to those of the pure liquid. GLC analyses (Perkin-Elmer 3920B) were peformed with SE-30

(11) The values of $\Delta\Delta G^{\ddagger}$ show that the increase of the extent of enantioselectivity is mainly due to the temperature effect on the freedom degrees of the alkyl substituents on the substrates. For $\Delta\Delta G^{\ddagger}$ calculation, see: Giacomelli, G.; Menicagli, R.; Lardicci, L. *J. Am. Chem. Soc.* **1975**, *97*, 4009.

(12) Ashby, E. C.; Yu, S. H. *J. Org. Chem.* **1970**, *35*, 2849.

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(14) The strain in the ring was confirmed by entropic values in reductions involving aluminum organoderivatives. See ref 11.

(15) IUPAC tentative rules for the nomenclature of organic chemistry: *J. Org. Chem.* **1970**, *35*, 2849.

(16) Lardicci, L. *Gazz. Chim. Ital.* **1961**, *91*, 458.

and Carbowax 20 M as a stationary phase and nitrogen as carrier gas. All new compounds gave satisfactory microanalyses for C and H (within ±0.3%). All solvents were reagent grade materials, purified by standard methods and redistilled before use. All reactions were conducted under argon atmosphere. Alkyl phenyl ketones were obtained by purification of commerical products: the α-alkynyl ketones were prepared according to known procedure.[17,18]

Chromatographic Resolution. The separations were carried out by means of a Jasco Twinkle apparatus equipped with a Uvidec-100 V detector. The Pirkle column, [(*R*)-*N*-(3,5-dinitrobenzoyl)phenylglycine, ionically bonded to a commercial 25 cm 3-aminopropyl silanized silica column from Merk, Darmstadt, West Germany] was prepared in situ, following the procedure reported.[10] The mobile phase was hexane containing 1% of isopropyl alcohol.

[[(1*S*,2*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-yl]methyl]beryllium chloride (3a),[5] bis[[(1*S*,2*S*)-6,6-dimethylbicyclo-[3.1.1]hept-2-yl]methyl]beryllium (3b)[5] and bis[(*R*)-2-methylbutyl]beryllium (1b)[6] were prepared according to previous reported procedures. **3a**: ^{1}H NMR δ 3.90–3.37 (m, 2 H, 2.57–0.73 (m, 15 H). **3b**–diethyl etherate: ^{1}H NMR δ 3.40 (q, 4 H), 2.77–0.70 (m, 36 H). A sample of **3a** (2.03 g, 11.2 mmol) was treated with a stream of air according to published procedure[19] to afford a sample of original (−)-*cis*-myrtanol: bp 125 °C (13 mm); $[\alpha]^{25}_D$ −18.9° (*c* 5.028, $CHCl_3$).[4]

[(*R*)-2-Methylbutyl]beryllium Chloride (1a). To an ether solution (250 mL) of the Grignard reagent obtained from (*S*)-2-methylbutyl chloride [10.66 g, 100 mmol, $[\alpha]^{25}_D$ +1.60° (neat)] was added anhydrous $BeCl_2$ (7.85 g, 98 mmol) at 0 °C. The mixture was then refluxed with stirring for 4 h and the upper liquid phase transferred under argon to a suitable container. After removal of the solvent under reduced pressure, the crude product was stirred at 0.001 mm for 1 h to eliminate any remaining volatile product. Diethyl etherate–**1a** (17.4 g, 90%) was recovered and stored in anhydrous ether, at room temperature: ^{1}H NMR δ 3.61–3.13 (m, 2 H), 3.22 (q, 4 H), 1.88–1.58 (m, 1 H), 1.52–1.28 (m, 2 H), 1.22–0.72 (m, 12 H).

Tris[[(1*S*,2*R*)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]-methyl]aluminum (4b). To an ether solution (250 mL) of the Grignard reagent obtained from *cis*-myrtanyl chloride [25.90 g, 150 mmol, $[\alpha]^{25}_D$ −10.31° (*c* 2.2, $CHCl_3$)] anhydrous $AlCl_3$ (6.13 g, 46 mmol) was added at 0 °C. The mixture was then refluxed with stirring for 4 h and the upper liquid phase transferred under argon to a suitable container. After removal of the solvent under reduced pressure, the crude product was stirred at 0.005 mm for 4 h to eliminate any remaining volatile product. Chemically pure **4b** (18.86 g, 93%) was recovered and stored in anhydrous ether, at room temperature.

Asymmetric Reduction of Ketones. The following procedures are representative of all the experiments with the same reactive in the same conditions.

(A) With [(*R*)-2-Methylbutyl]beryllium Chloride (1a). Run 5. Isopropyl phenyl ketone (1.47 g, 9.75 mmol) in anhydrous ether (10 mL) was added rapidly at room temperature to an etheral solution of **1a** (1.50 g, 13 mmol). A pale yellow coloration developed immediately and faded fast. After 2 h, the resulting mixture was cautiously hydrolyzed with dilute H_2SO_4, extracted with ether, washed with a dilute $NaHCO_3$ solution, and dried (Na_2SO_4). Removal of the solvent and purification by distillation afforded (−)-isopropylphenylcarbinol: 1.34 g (90%); $[\alpha]^{25}_D$ −12.08 (*c* 8.776, ether); pure by GLC.

(B) With Bis[(*R*)-2-Methylbutyl]beryllium (1b). Run 7. Isopropyl phenyl ketone (1.48 g, 10 mmol) in anhydrous ether (10 mL) was added rapidly at room temperature to an ethereal solution of **1b** (2.06 g, 13.6 mmol). A pale yellow coloration developed immediately and faded fast. After 5 h, the resulting mixture was submitted to the standard hydrolytic and extractive workup. Removal of the solvent and purification by distillation afforded (−)-isopropylphenylcarbinol: 0.98 g (66%); $[\alpha]^{25}_D$ −13.90 (*c* 8.804, ether), pure by GLC.

(C) With [[(1*S*,2*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-yl]-methyl]beryllium Chloride (3a). (a) Run 18. Ethyl phenyl ketone (1.74 g, 13 mmol) in anhydrous ether (10 mL) was added rapidly at room temperature to an ethereal solution of **3a** (3.27 g, 18 mmol). An orange coloration developed immediately and faded slowly. After 3 h, the resulting mixture was submitted to the preceeding hydrolytic and extractive workup. Removal of the solvent and purification by flash chromatography[7] (80:20 light petroleum ether/ethyl acetate) afforded (+)-ethylphenylcarbinol: 0.88 g (50%); $[\alpha]^{25}_D$ +6.35° (neat); pure by GLC.

(b) Run 21. Isopropyl phenyl ketone (1.20 g, 8.4 mmol) in anhydrous hexane (10 mL) was added rapidly at room temperature to a solution of **3a** in hexane (2.03 g, 11.2 mol). Within few hours a white precipitate developed. After 44 h the resulting mixture was submitted to the preceeding hydrolytic and extractive workup. Removal of the solvent and purification by flash chromatography[7] (80:20 light petroleum ether/ethyl acetate) afforded (+)-isopropylphenylcarbinol: 0.66 g (38%); $[\alpha]^{25}_D$ +18.66° (*c* 3.912, ether); pure by GLC.

(D) With Bis[[(1*S*,2*S*)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]methyl]beryllium (3b). Run 26. Isopropyl phenyl ketone (1.20 g, 8.4 mmol) in anhydrous ether (10 mL) was added rapidly at −35 °C to an ethereal solution of **3b** (3.17 g, 11.2 mmol). A pale orange coloration developed immediately and faded slowly. After 4 h at −35 °C, the resulting mixture was submitted to the above hydrolytic and extractive workup. Removal of the solvent and purification by flash chromatography[7] afforded (+)-isopropylphenylcarbinol: 0.98 g (77%); $[\alpha]^{25}_D$ +17.25 (*c* 5.488, ether); pure by GLC.

(E) With Tris[[(1*S*,2*R*)-6,6-dimethylbicyclo[3.1.1]hept-2-yl]methyl]aluminum (4b). Run 37. Isopropyl phenyl ketone (1.48 g, 10 mmol) in anhydrous ether (10 mL) was added rapidly at room temperature to an ethereal solution of **4b** (4.43 g, 10.1 mmol). A pale orange coloration developed immediately and faded slowly. After 1 h, the resulting mixture was submitted to the previous hydrolytic and extractive workup. Removal of the solvent and purification by flash chromatography[7] afforded (+)-isopropylphenylcarbinol: 1.32 g (89%); $[\alpha]^{25}_D$ +42.73 (*c* 2.848, ether); pure by GLC.

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Registry No. **1a**, 101199-24-0; **1b**, 4023-26-1; **3a**, 98057-65-9; **3b**, 98057-66-0; **4b**, 98104-06-4; $BeCl_2$, 7787-47-5; $AlCl_3$, 7446-70-0; (*s*)-2-methylbutyl chloride, 40560-29-0; *cis*-myrtanyl chloride, 87682-09-5; acetophenone, 98-86-2; ethyl phenyl ketone, 93-55-0; isopropyl phenyl ketone, 611-70-1; *tert*-butyl phenyl ketone, 938-16-9; 4-octyne-3-one, 7299-56-1; 4-nonyne-3-one, 1817-61-4; 2,2-dimethyl-4-nonyn-3-one, 53723-95-8; (*R*)-methylphenylcarbinol, 1517-69-7; (*S*)-methylphenylcarbinol, 1445-91-6; (*R*)-isopropylphenylcarbinol, 14898-86-3; (*S*)-isopropylphenylcarbinol, 34857-28-8; (*R*)-*tert*-butylphenylcarbinol, 23439-91-0; (*S*)-*tert*-butylphenylcarbinol, 24867-90-1; (*R*)-ethyl-1-pentynylcarbinol, 101199-25-1; (*S*)-ethyl-1-pentynylcarbinol, 101199-26-2; (*R*)-ethyl-1-hexynylcarbinol, 87682-12-0; (*S*)-ethyl-1-hexynylcarbinol, 90792-11-3; (*R*)-*tert*-butyl-1-hexynylcarbinol, 87682-14-2; (*S*)-*tert*-butyl-1-hexynylcarbinol, 90792-12-4; (*R*)-ethylphenylcarbinol, 1565-74-8; (*S*)-ethylphenylcarbinol, 613-87-6; (±)-methylphenylcarbinol, 13323-81-4; (*R*)-isopropyl-1-hexynylcarbinol, 87682-13-1; (*S*)-isopropyl-1-hexynylcarbinol, 87682-11-9; 2-methyl-4-nonyn-3-one, 63098-60-2.

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