d, $J = 11.6$ Hz), 6.73 (C_2H, d of d, $J = 10.1, 11.6$ Hz), 7.26–8.12 (Ph), 9.35 (C_1H, d of d, $J = 0.8, 10.1$ Hz); ^{13}C NMR 31.6 (Me), 128.7, 130.0 (Ph C), 132.6, 133.7 (Ph C, C_2 and C_3, overlapping), 154.3 (C=N), 163.7 (ester CO), 198.1 ppm (keto CO); EIMS gave no parent ion, but CIMS gave $(M + 1)^+$ at 218. Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10, N, 6.45. Found: C, 66.31; H, 5.23; N, 6.69.

When attempts were made to purify the ester **32** on a silica column a low yield of it was eluted. It was followed by the more polar hydrolysis product, the oxime **33** (see below). When a basic alumina column was used cleavage to **33** was complete, no **32** being eluted.

The oxime **33** from the column (0.033 g, 0.29 mmol) was dissolved in $CDCl_3$ (0.5 mL) in an NMR tube, and pyridine (0.24 mL, 0.29 mmol) and benzoyl chloride (0.041 g, 0.29 mmol) were added. The ^1H spectrum, run within 30 s, showed the reaction to be already complete. The solution was worked up with ether and aqueous $NaHCO_3$, the ethereal solution giving the ester **32** identical with the material from the benzohydroxamic acid oxidation.

Synthesis of 1-Oximino-2-penten-4-one (33). To a solution of NaOH (0.094 g, 2.35 mmol) and hydroxylamine hydrochloride (0.18 g, 2.57 mmol) in water (3 mL) was added *cis*-1-oxo-2-penten-4-one[54] (0.230 g, 2.34 mmol). After being stirred for 5 min, the solution was saturated with NaCl and extracted with methylene chloride, giving the product (0.054 g, 11%) as an oil from the organic phase: ^1H NMR δ 2.33 (Me, s), 6.25–6.70 (C_2H, C_3H, m), 8.85 (C_1H, m), 10.1 (OH, br s).

When the oxime was benzoylated with benzoyl chloride and pyridine and the mixture worked up, all as described above, the benzoate was identical with the product of the benzohydroxamic acid oxidation.

X-ray Analysis of 5f. Crystals of **5f**, $C_{20}H_{21}NO_3$, M_r 323.40, are triclinic, space group $P\bar{1}$ with $a = 6.101$ (1) Å, $b = 10.652$ (1) Å, $c = 14.552$ (2) Å, $\alpha = 106.69$ (1)°, $\beta = 101.22$ (1)°, $\gamma = 100.20$ (1)°, $V = 860.8$ (2) Å^3, $Z = 2$, $\rho_c = 1.248$ g cm^{-3}, $F(000) = 344$, $\lambda = 0.71069$ Å, μ (Mo Kα) = 0.905 cm^{-1}. Intensity data were collected on a crystal of dimensions ≈ 0.4 mm^3 by using θ–2θ scans ($3.2° < 2\theta \leq 45°$) with a variable scan speed of 2.93–29.30° min^{-1} and a scan width of 0.95° below Kα_1, to 0.95° above Kα_2 on a Syntex P2_1 diffractometer. From a total of 2273 independent reflections measured, 1874 had intensities $I \leq 3\sigma(I)$ and were used in the structure refinement. Two standard reflections (128, 050), monitored after every 100 measurements, showed only minor fluctuations. The data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct methods (MULTAN80) and refined by full-matrix least-squares methods. After two cycles of anisotropic refinement, all hydrogen atoms were located from a difference Fourier synthesis. The final R and R_w values were 0.031 and 0.034, respectively ($R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum_w||F_o| - |F_c||^2/\sum_w|F_o|^2]^{1/2}$). An empirical weighting scheme of the form $w^{-1} = 2.94 - 0.078|F_o| + 0.007|F_o|^2$ was employed in the final cycles to give constant error in the various ranges of F_{obsd}. A final difference map was featureless with maximum residuals of 0.14 e Å^{-3}. Scattering factors were taken from the "International Tables for X-ray Crystallography",[60] and for hydrogen, the data of Stewart et al.[61] were used. Computer programs used have been described elsewhere.[62] Bond lengths and angles of **5f** are shown in Table III.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for support of this work.

Registry No. (±)-**2b**, 100909-74-8; (±)-**2b**, 100910-05-2; (±)-**5a** (isomer 1), 100909-75-9; (±)-**5a** (isomer 2), 100910-06-3; **5b**, 100909-76-0; (±)-**5c** (isomer 1), 100909-77-1; (±)-**5c** (isomer 2), 100910-07-4; (±)-**5d** (isomer 1), 100909-78-2; (±)-**5d** (isomer 2), 100910-08-5; (±)-**5e** (isomer 1), 100909-79-3; (±)-**5e** (isomer 2), 100910-09-6; (±)-**5f**, 100909-80-6; (±)-**5g** (isomer 1), 100927-99-9; (±)-**5g** (isomer 2), 100910-10-9; (±)-**5i** (isomer 1), 100909-81-7; (±)-**5i** (isomer 2), 100910-11-0; (±)-**5j** (isomer 1), 100909-82-8; (±)-**5j** (isomer 2), 100910-12-1; (±)-**5k** (isomer 1), 100909-83-9; (±)-**5k** (isomer 2), 100910-13-2; (±)-**5l** (isomer 1), 100909-84-0; (±)-**5l** (isomer 2), 100910-14-3; **8**, 100909-85-1; (±)-**10a**, 100909-86-2; (±)-**10d**, 100909-87-3; (±)-**10e**, 100910-15-4; (±)-**10l**, 100909-88-4; (±)-**10g**, 100909-89-5; (±)-**10i**, 100909-90-8; (±)-**10j**, 66296-80-8; **17**, 17559-81-8; **18**, 820-69-9; **19a**, 100909-91-9; **19d**, 100909-92-0; **19e**, 19842-57-0; **19f**, 100909-93-1; **19l**, 100909-94-2; **19m**, 100909-95-3; (±)-**21** (isomer 1), 100909-96-4; (±)-**21** (isomer 2), 100909-97-5; (±)-**23a**, 100909-98-6; (±)-**23b**, 100992-07-2; (±)**25**, 100909-99-7; **26**, 100910-00-7; (±)-**27**, 100910-01-8; **28**, 100910-02-9; **32**, 100910-03-0; **33**, 100910-04-1; butyric anhydride, 106-31-0; 3-butyryl-2,5-dimethylfuran, 82873-11-8; *cis*-1-oxo-2-penten-4-one, 34218-22-9; diethyl malonate, 105-53-3; ethyl cyanoacetate, 105-56-6; *p*-bromotoluene, 106-38-7; 2,5-dimethylfuran, 625-86-5; 2,5-diethylfuran, 10504-06-0; benzohydroxamic acid, 495-18-1; 2-methylfuran, 534-22-5.

Supplementary Material Available: Tables of atomic coordinates and isotropic thermal parameters for non-hydrogen and hydrogen atoms, anisotropic thermal parameters, and structure factors (14 pages). Ordering information is given on any current masthead page.

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Low Valent Titanium Induced Cross-Coupling of Chiral α,β-Unsaturated Ketones with Acetone[1]

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The cross-coupling of chiral (*R*)-(−)-(4-methylcyclohexylidene)acetone and (*R*)-(−)-(4-methylcyclohexylidene)acetophenone with acetone, on a Ti(0) surface, leads, inter alia, to the corresponding chiral (*R*)-(−)-(4-methylcyclohexylidene)-2-substituted-3-methyl-2-butene. By contrast, due to steric acceleration, chiral (*S*)-(+)-(2,2,4,6,6-pentamethylcyclohexylidene)acetone, (*S*)-(+)-(4-(dimethyl-*tert*-butylsiloxy)-2,2,6,6-tetramethylcyclohexylidene)acetone, and (*S*)-(+)-(4-(dimethyl-*tert*-butylsiloxy)-2,2,6,6-tetramethylcyclohexylidene)acetophenone yield only achiral cross-coupled products with acetone on a Ti(0) surface.

Ti(0) surfaces have been prepared by reduction of $TiCl_3$ or $TiCl_4$ with metals[2-7] such as magnesium, zinc, zinc–copper couple, alkali metals (Li, Na, K), and metal hydrides ($LiAlH_4$). The surfaces have been used in the pi-

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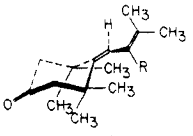
nacol coupling of carbonyls,[2] reductive elimination of vicinal glycols to olefins,[4] cyclization of 1,3-glycols to cyclopropanes,[5,6] and the formation of 1,3-dienes by 1,4-reductive elimination of 2-ene-1,4-diols and 2-yne-1,4-diols.[7]

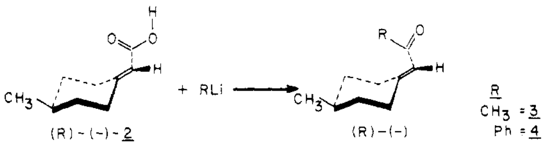
The Ti(0)-induced reductive coupling of carbonyls[2c–f,4,8] to olefins is of special interest since it provides a convenient method for the preparation of sterically crowded olefins[3c] such as tetraisopropylethylene,[9] tetraneopentylethylene,[10] 1-(1-indanylidene)indane,[11] 1-(1-tetralinylidene)tetralin,[11] and 9-(9-fluorenylidene)fluorene.[11]

Our interest in this reaction stems from our desire to prepare a chiral 1,3-diene, such as 1, in order to investigate its atropisomeric and chiroptical properties. Attempts to synthesize this molecule from suitable precursors such as α,β-unsaturated carbonyls by converting them to 1,3-dienes by the usual methods failed, due largely to steric effects. The success enjoyed by others[9–11] in the use of Ti(0)-induced coupling of hindered carbonyl compounds prompted us to investigate this reaction.


1

Results

Syntheses. The α,β-unsaturated methyl and phenyl ketones needed for the cross-coupling with acetone in our pilot study were prepared by the addition of methyl- and phenyllithium to the chiral α,β-unsaturated acid of known absolute configuration. Thus, the addition of phenyl- and methyllithium to (*R*)-(−)-(4-methylcyclohexylidene)acetic acid[13] (2) produced the corresponding (*R*)-(−)-methyl ketone 3 and the (*R*)-(−)-phenyl ketone 4. However, the latter ketone was obtained in poor yields and the procedure described below for the 2,2,6,6-tetramethylcyclohexylidene system was used for its preparation.



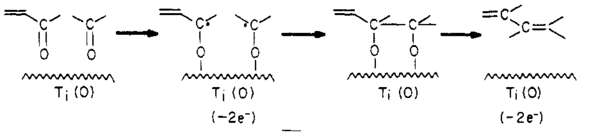
Because of the failure of the sterically hindered (2,2,4,6,6-pentamethylcyclohexylidene)acetic acid to yield ketonic product when treated with methyl- or phenyllithium, the following procedure was developed. Aluminum hydride reduction of the methyl ester of the cyclohexylidene system followed by MnO_2 oxidation gave the α,β-unsaturated aldehyde. The aldehyde was treated with phenylmagnesium bromide or methylmagnesium iodide and the carbinols were oxidized with MnO_2. In this manner (*R*)-(−)-(4-methylcyclohexylidene)acetophenone 4 as well as the chiral (2,2,4,6,6-pentamethylcyclohexylidene)acetone 5 and the chiral (4-(dimethyl-*tert*-butylsiloxy)-2,2,6,6-cyclohexylidene) derivatives of acetone 6 and acetophenone 7 were obtained.

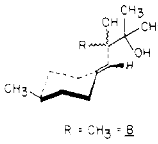
Table I. Cross-Coupling of Chiral α,β-Unsaturated Ketone with Acetone[a,b]

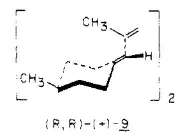
entry	α,β-unsaturated ketone	temp, °C	time, h	product	yield, %
1	(*R*)-(−)-3	0	1	(*R*)-(−)-8 (*R*,*R*)-(+)-9	52 4
2	(*R*)-(−)-4	25	3.5	(*R*)-(−)-10 (*R*)-(−)-11	40 24
3	(*S*)-(+)-5	25	72	(±)-12 (±)-13	28 67
4	(*S*)-(+)-5	65	20	(±)-12	53[c]
5	(*S*)-(+)-6	65	20	(±)-14	73[c]
6	(*S*)-(+)-7	0	5	(±)-15 (±)-16	10 77
7	(*S*)-(+)-7	65	20	(±)-15	85

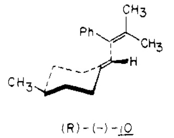
[a] α,β-Unsaturated ketone to acetone, 1:4. [b] Ketone to Ti(0) 1:20. [c] Polar fraction not analyzed.

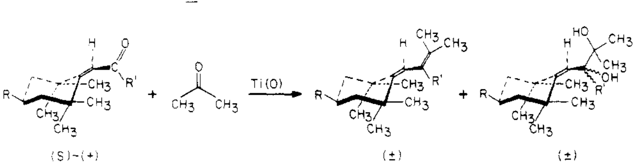
Scheme I




R = CH3 = 8
Ph = 11


(R,R)-(+)-9


(R)-(−)-10



	R	R′		
5	CH_3	CH_3	12	13
6	*t*-Bu$(CH_3)_2$SiO	CH_3	14	
7	*t*-Bu$(CH_3)_2$SiO	Ph	15	16

Reaction on Ti(0) Surface. Low valent titanium was prepared as a slurry in THF by the reduction of $TiCl_4$ with $LiAlH_4$ in a 2:1 ratio. To this mixture was added the chiral α,β-unsaturated ketone and acetone with stirring. The conditions and results are tabulated in Table I.

The condensation of 3 was performed with a fourfold excess of acetone to yield mainly the glycol 8. No 1,3-diene could be detected (Table I). The side reaction was the self-condensation of (*R*)-(−)-3 to yield (*R*,*R*)-(+)-9. However, the cross-coupling of (*R*)-(−)-4 with an excess of

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(1) The support of this work by grants from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and The National Science Foundation is gratefully acknowledged.

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acetone was successful and yielded 40% of the corresponding 1,3-diene, (*R*)-(−)-**10**, as well as 24% of glycol mixture **11**.

Encouraged by the result with **4** that one obtained cross-coupling and that the cross-coupled product was chiral, condensation of **5**, **6**, and **7** with acetone was carried out. In each case conditions were found which produced cross-coupling in satisfactory yield but in each case the cross-coupled 1,3-diene product was *racemic*. Also of significance was the observation that the intermediate glycols **13** and **16** are also racemic in contrast to the chiral glycols **8** and **11** which were obtained in the condensation of (*R*)-(−)-**3** and (*R*)-(−)-**4**.

Discussion

The question to be answered is why does one observe optically active products in the cross-coupling of *R*-(−)-**3** and (*R*)-(−)-**4** with acetone but optically inactive products in the analogous cross-coupling of (*S*)-(+)-**5**, (*S*)-(+)-**6**, and (*S*)-(+)-**7**?

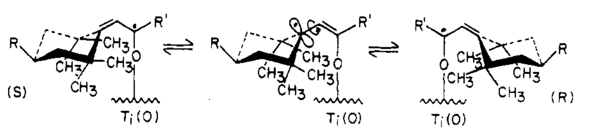
McMurry[8] views the condensation (Scheme I) as occurring on the Ti(0) surface by single electron transfer to the carbonyls of the α,β-unsaturated ketone and acetone. The initially formed anion radicals coupled in a carbon–carbon bond-forming step on the surface of Ti(0) in a manner similar to the pinacol reaction.[14] The intermediate thus formed undergoes an nonstereospecific reductive elimination to yield an olefin. When one of the ketones is α,β-unsaturated, a 1,3-diene is formed.

Electron transfer to the α,β-unsaturated ketone gives rise to a resonance-stabilized allylic radical anion which must maintain its configuration to some degree since the 1,3-diene formed as the final product is chiral. Moreover, chirality is obtained in spite of the fact that the deoxygenation step is only stereoselective, not stereospecific.[8] For example, *R*-(−)-**4**, upon condensation with acetone, gave the corresponding 1,3-diene, (*R*)-(−)-**10**, and a 1:1 mixture of diastereomeric glycols[11] which was further separated by chromatography into pure diastereomers. Their optical purity was determined to be 72% by means of their 270-MHz ^{1}H NMR spectra using a chiral shift reagent (see Experimental Section). This is a maximum value for the 1,3-diene **10** since we cannot estimate the extent of chirality lost in the deoxygenation step. However, this does demonstrate that the initial coupling (pinacol) occurs with a *high degree of retention of configuration.*

The high retention means that the surface bound allyl radical (Scheme I) maintains its configuration to a large extent. Allyl radicals have been shown to maintain their configuration; Walling and Thaler[15] have reported that the complete retention of cis–trans stereochemistry is observed in the photoinduced radical chain chlorination of *cis*- and *trans*-2-butene with *tert*-butyl hypochlorite. In our system cis–trans isomerization is equivalent to racemization.

Why then is complete racemization observed in the reactions of **5**, **6**, and **7**? In these cases one is observing a steric acceleration to racemization due to hindrance exerted by the 2,2,6,6-tetramethyl groups. These groups provide a steric inhibition to the delocalization of the allyl radical system; and in order to relieve the steric interaction, the radical resides at C-1 of the cyclohexane ring. An equilibrium exists between this intermediate and the original radical-site intermediate (Scheme II). The C-1 radical-site intermediate has a plane of symmetry and therefore racemization is observed.

Scheme II



Another interesting observation made during the course of this work is that deoxygenation of glycols to yield dienes is an exceedingly slow reaction compared to the formation of the diene in the original cross-coupling reaction of the ketones. This implies that oxidative addition of the glycols to Ti(0) to yield the oxygen-bound intermediate is a very slow step.

Experimental Section

Infrared (IR) spectra were measured with Perkin-Elmer Model 257 grating spectrophotometer using the polystryrene 1601-cm^{-1} band for calibration. Nuclear magnetic resonance (NMR) spectra were recorded on a Brucker 200-MHz or 270-MHz spectrometer. The solvent used was $CDCl_3$, unless noted otherwise, with Me_4Si and $CHCl_3$ (7.26 ppm) as internal standards. Mass spectra (MS) were obtained with a Finnigan high resolution instrument. Microanalyses were performed by Beller Laboratories, Gottingen, Germany.

(*R*)-(−)-(4-Methylcyclohexylidene)acetone (3). To a stirred solution of (*R*)-(−)-(4-methylcyclohexylidene)acetic acid[16] (91% optically pure) (4.0 g, 26 mmol) in 175 mL of dry ether, maintained at 0 °C under an argon atmosphere, was added methyllithium in ether (52 mL of 1.0 M, 52 mmol) over a period of 20 min. After stirring at 0 °C for another 20 min, the reaction mixture was poured into water. The organic phase was separated, washed with water, dried over Na_2SO_4, and evaporated to obtain 3.9 g of a product which was found to be a mixture of two compounds. The crude product was chromatographed (silica gel; hexane, ether) to obtain, after complete removal of solvents under vacuum, pure **3** (2.95 g, 75%) and 1-(4-methylcyclohexylidene)-2,2-dimethylethanol (0.75 g, 17%) as colorless liquids.

(a*R*)-(−)-**3**: $[\alpha]^{26}_{\mathrm{Hg}}$ −94.53 ± 0.73° (*c* 0.7, $CHCl_3$); IR (CCl_4) 3000–2850, 1695, and 1625 cm^{-1}; ^{1}H NMR δ 0.91 (d, 3 H), 0.96–1.2 (m, 2 H), 1.65 (m, 1 H), 1.75–2.0 (m, 4 H), 2.18 (s, 3 H, and m, 1 H), 3.69 (dt, 1 H), and 6.00 (s, 1 H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.85; H, 10.47.

(*R*)-(−)-(4-Methylcyclohexylidene)acetophenone (4). To a stirred solution of (*R*)-(−)-(-methylcyclohexylidene)acetaldehyde[16] (91% optically pure) 2.0 g, 14.5 mmol) in 50 mL of dry THF, maintained at 0 °C under argon atmosphere, was added phenyllithium in ether (20.7 mL of 0.70 M, 14.5 mmol) over a period of 10 min. The solution was stirred at 0 °C for 15 min., hydrolyzed by adding it to ice, and extracted with ether. The ether solution was washed with water, dried over Na_2SO_4, and evaporated to obtained a quantitative yield of a mixture of two diastereomeric alcohols. The crude product was dissolved in 150 mL of hexane and stirred with 20 g of active MnO_2. After an hour of stirring, MnO_2 was filtered off and washed throughly with ether, and the combined solution was evaporated to give a quantitative yield of the product. Trace impurities were removed by radial chromatography to obtain, after removal of solvents under vacuum, **4** as a colorless liquid; $[\alpha]^{25}_{\mathrm{Hg}}$ −39.27 ± 0.83° (*c* 0.5, $CHCl_3$); IR (CCl_4) 3100–2850, 1670, and 1620 cm^{-1}, ^{1}H NMR δ 0.95 (d, 3 H), 0.95–1.35 (m, 2 H), 1.55–2.15 (m, 4 H), 2.2–2.5 (m, 2 H), 3.56 (d, 1 H), 6.62 (s, 1 H), 7.35–7.60 (m, 3 H), and 7.95 (dd, 2 H).

Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.07; H, 8.43.

(*S*)-(+)-(2,2,4,6,6-Pentamethylcyclohexylidene)acetone (5). To a stirred suspension of methylmagnesium iodide (50 mmol) in 50 mL of dry ether was added at 0 °C 1.94 g (10 mmol) of (*S*)-(+)-(2,2,4,6,6-pentamethylcyclohexylidene)acetaldehyde[17] ($[\alpha]_{\mathrm{Hg}}^{32}$ +71.22 ± 0.15°, 46.50% ee) in 10 mL of ether. The

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[14] Cross-coupling or homocoupling will depend on the reduction potential for the carbonyl systems involved. Excess acetone is necessary to promote efficient cross-coupling in these systems.

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reaction mixture was stirred at 25 °C for 1 h and at reflux for 1 h, then cooled to 0 °C. Aqueous NH_4Cl was added and the product was extracted into ether (3 × 100 mL). The ether layer was washed with water, dried (Na_2SO_4), and concentrated to give 1.90 g of crude product. Purification by column chromatograpy on 50 g of silica gel using hexane-ether gave pure (*S*)-(+)-1-(2,2,4,6,6-pentamethylcyclohexylidene)-2-hydroxypropane as a gum, 1.82 g (87%): $[\alpha]_{Hg}^{30}$ +9.33 ± 0.06° (*c* 1.08, C_2H_5OH); IR (film) 3330 (br), 3000–2840, 1630, 1465, 1400–1370, 1330–1200, 1140, 1110, 1070, 960, and 880 cm^{-1}; NMR δ 0.89 (d, J = 7 Hz, 3 H), 1.00–1.60 (m, 19 H, including ring methyls), 1.67 (br s, 1 H, OH) 1, 80 (m, 1 H), 4.85–5.06 (m, 1 H), and 5.30, 5.35 (2 d, J = 8 Hz, in the ratio of 1:1, 1 H).

Anal. Calcd for $C_{14}H_{26}O$: C, 80.00; H, 12.38. Found: C, 79.95; H, 12.43.

Using active MnO_2 (15 g), the above carbinol (1.80 g, $[\alpha]^{30}_{Hg}$ +9.33 ± 0.06°, 46.50% ee) dissolved in 70 mL of hexane was oxidized to the corresponding ketone. Workup and purification by column chromatography on 60 g of silica gel using hexane–ether gave 1.60 g (90%) of pure (*S*)-(+)-(2,2,4,6,6-pentamethylcyclohexylidene)acetone (**5**) as a liquid: $[\alpha]^{25}_{Hg}$ +114.71 ± 0.08° (*c* 1.18, C_2H_5OH); IR (0.05 M solution in CCl_4) 2950 (m), 1690, 1618, 1470, 1390, 1375, 1360, 1233, 1203, 1190, 1065, 980, and 950 cm^{-1}; ^{1}H NMR δ 0.89 (d, J = 6.70 Hz, 3 H), 1.00–1.60 (m, 4 H), 1.13 (s, 3 H), 1.16 (s, 3 H), 1.17 (s, 3 H), 1.35 (s, 3 H), 1.88 (m, 1 H), 2.25 (s, 3 H), and 5.97 (s, 1 H); ^{13}C NMR 22.72 (CH_3), 22.92 (CH), 23.94 (CH_3), 30.10 (CH_3), 31.69 (CH_3), 32.58 (CH_3), 32.92 (CH_3), 37.59 (C), 38.31 (C), 49.05 (CH_2), 51.51 (CH_2), 124.83 (CH), 162.79 (C), and 205.16 (C=O) ppm.

Anal. Calcd for $C_{14}H_{24}O$: C, 80.77; H, 11.54. Found: C, 80.62; H, 11.63.

(*S*)-(+)-(4-(Dimethyl-*tert*-butylsiloxy)-2,2,6,6-tetramethylcyclohexylidene)acetone (6). A solution of (*S*)-(+)-(4-(dimethyl-*tert*-butylsiloxy)-2,2,6,6-tetramethylcyclohexylidene)acetaldehyde[17] (4.03 g, 13 mmol) $[\alpha]_D^{30}$ +23.61 ± 0.80°, 37.52% ee) in 25 mL of the THF was added to a cooled (0 °C) slurry of methylmagnesium iodide (65 mmol) in 150 mL of ether. After stirring for 30 min. at 25 °C, the reaction mixture was allowed to reflux for 1 h and then cooled to 0 °C. Aqueous NH_4Cl was added and the product extracted with ether (3 × 100 mL). The combined ether solution was washed with water, dried (Na_2SO_4), and concentrated. The crude product on purification on a silica gel column (80 g) using hexane–ether gave a diastereomeric mixture of (*S*)-(–)-1-(4-(dimethyl-tert-butylsiloxy)-2,2,6,6-tetramethylcyclohexylidene)-2-hydroxypropane as a gum (4 g): $[\alpha]^{32}_D$ –0.80 ± 0.41° (*c* 2, C_2H_5OH); IR (film) 3580 (sharp), 3330 (br), 2900 (m), 1630, 1470, 1390, 1370, 1265, 1080, and 1020–790 cm^{-1}; ^{1}H NMR δ 0.03 (s, 6 H), 0.88 (s, 9 H), 1.00–1.80 (m, 20 H, including OH and methyl signals), 3.92 (m, 1 H), 4.87 (m, 1 H), and 5.24–5.26 (2 d, J = 9 Hz, 1 H).

Anal. Calcd for $C_{19}H_{38}O_2Si$: C, 69.93; H, 11.65. Found: C, 69.87; H, 11.78.

A solution of a diastereomeric mixture of the above alcohols (4 g, $[\alpha]^{32}_D$ –0.80 ± 0.41°, 37.52% ee) in 100 mL of pentane was treated with 20 g of MnO_2 at 25 °C for 24 h. The product was filtered free of MnO_2 using ether, and the combined solution was evaporated. The crude ketone, after purification on silica gel (70 g) with hexane–ether, afforded 3.96 g of (*S*)-(+)-(4-(dimethyl-*tert*-butylsiloxy)-2,2,6,6-tetramethylcyclohexylidene)acetone (**6**) as a colorless liquid: $[\alpha]^{29}_D$ +66.41 ± 0.50° (*c* 1.13, C_2H_5OH); IR (0.05 M solution in CCl_4) 2950, 2920, 2880, 2850, 1690, 1604, 1470, 1390–1350, 1260, 1225, 1195,1180, 1090, and 1010–800 cm^{-1}; ^{1}H NMR δ 0.03 (s, 6 H), 0.87 (s, 9 H), 1.14 (s, 3 H), 1.16 (s, 3 H), 1.17 (s, 3 H), 1.29 (s, 3 H), 1.25–1.80 (m, 4 H), 2.22 (s, 3 H), 4.00 (m, 1 H), and 5.96 (s, 1 H); ^{13}C NMR 4.70 ($2CH_3$), 18.04 (C), 25.81 ($3CH_3$), 30.15 (CH_3), 31.13 (CH_3), 31.58 (CH_3), 32.53 (CH_3), 32.70 (CH_3), 37.93 (C), 38.76 (C), 48.17 (CH_2), 50.47 (CH_2), 64.68 (CH), 124.83 (CH), 162.63 (C), and 204.41 (C=O) ppm.

Anal. Calcd for $C_{19}H_{36}O_2Si$: C, 70.37; H, 11.11. Found: C, 70.35; H, 11.13.

(*S*)-(+)-(4-(Dimethyl-*tert*-butylsilyloxy)-2,2,6,6-tetramethylcyclohexylidene)acetophenone (7). To a cooled slurry of 80 mmol of phenylmagnesium bromide in 120 mL of THF was added 4.96 g (16 mmol) of (*S*)-(+)-(4-(dimthyl)-*tert*-butylsiloxy)-2,2,4,4-tetramethylcyclohexylidene)acetaldehyde[17] ($[\alpha]^{30}_D$ +23.61 ± 0.80°, 37.52% ee) in 20 mL of THF. The reaction mixture was stirred at 25 °C for 1 h, at reflux for 1 h, and then cooled to 0 °C. Aqueous NH_4Cl was added and the product extracted with ether. The ether solution was washed with water, dried (Na_2SO_4), and concentrated. Purification by column chromatography on silica gel (80 g) using hexane–ether gave 5 g (80%) of a diastereomeric mixture of (*S*)-(–)-1-(4-(dimethyl-*tert*-butylsiloxy)-2,2,4,4-tetramethylcyclohexylidene)-2-hydroxy-2-phenylethane as a viscous liquid: $[\alpha]^{29}_D$ –13.31 ± 0.31° (*c* 2.15, C_2H_5OH); IR (film) 3330 (br), 3070 (w), 3050 (w), 3020 (w), 2900 (m) 1945 (w), 1870 (w), 1800 (w), 1630, 1600, 1495, 1470, 1390, 1370, 1260, 1200, 1175, 1085 and 1050–760 cm^{-1}; ^{1}H NMR δ 0.08 (s, 6 H), 0.90 (s, 9 H), 1.00–1.90 (m, 17 H, including sevral CH_3 singlets and OH), 4.00 (m, 1 H), 5.58 (br d, 1 H), 5.83 (br d, 1 H), and 7.20–7.50 (m, 5 H).

Anal. Calcd for $C_{24}H_{40}O_2Si$: C, 74.22; H, 10.31. Found: C, 74.33; H, 10.39.

A mixture of the above carbinols (5 g, $[\alpha]^{29}_D$ –13.31 ± 0.31°, 37.52% ee) and 20 g of MnO_2 in 150 mL pentane was stirred for 12 h. The product was filtered, concentrated, and purified by column chromatography on 80 g of silica gel using hexane–ether to give 4.90 g of (*S*)-(+)-(4-(dimethyl-*tert*-butylsiloxy)-2,2,6,6-tetramethylcyclohexylidene)acetophenone (**7**) as a liquid: $[\alpha]^{29}_D$ +40.31 ± 0.20° (*c* 1.08, C_2H_5OH): IR (0.05 M solution in CCl_4) 3070 (w), 3050 (w), 2950, 2920, 2885, 2860, 1950 (w), 1900 (w), 1810 (w), 1770 (w), 1662, 1615, 1595, 1580, 1475, 1468, 1453, 1390, 1375, 1316, 1260, 1235, 1185, 1090, and 1030–800 cm^{-1}; ^{1}H NMR δ 0.01 (s, 3 H), 0.02 (s, 3 H), 0.83 (s, 9 H), 1.12 (s, 3 H), 1.21 (s, 3 H), 1.25 (s, 3 H), 1.27 (s, 3 H), 1.30–1.80 (m, 5 H), 4.01 (m, 1 H), 6.25 (s, 1 H), 7.30–7.55 (m, 3 H), and 7.88 (br d, 2 H); ^{13}C NMR 4.90 ($2CH_3$), 18.11 (C), 25.87 ($3CH_3$), 30.76 (CH_3), 32.13 (CH_3), 32.52 (CH_3), 33.10 (CH_3), 38.39 (C), 39.04 (C), 48.75 (CH_2), 50.84 (CH_2), 64.83 (CH), 122.88 (olefinic HC), 128.40 (2CH), 128.87 (2CH), 132.90 (CH), 137.72 (C), 162.28 (olefinic C), and 198.03 (C=O) ppm.

Anal. Calcd for $C_{24}H_{38}O_2Si$: C, 74.61; H, 9.84. Found: C, 74.46; H, 9.86.

Cross-Coupling Reaction between Optically Active Ketones and Acetone with Low Valent Titanium Reagent: General Procedure. Under an argon atmosphere, a stirred mixture of dry THF (60 mL) and $TiCl_4$ (5.10 mL, 8.85 g; 46.60 mmol) at 0 °C was treated with $LiAlH_4$ (0.94 g, 24.8 mmol) in small portions. The resulting black slurry was allowed to reflux for an hour and then cooled to room temperature or 0 °C. To this mixture was added a mixture of acetone (0.53 g, 9.2 mmol) and optically active ketone (2.30 mmol) in 5 mL of dry THF. The mixture was stirred at the required temperature for the appropriate reaction time. The reaction mixture was poured onto a slurry of silica gel, Na_2CO_3, and ice, diluted with ether, stirred well, and filtered. The solid portion was washed twice with ether and the combined ether solution was washed with water, dried over K_2CO_3, and evaporated to give the crude product. The crude product was purified by the use of radial chromatography (silica gel plate, 2 mm thickness), eluting with hexane followed by hexane–ether or by column chromatography on silica gel.

Cross-Coupling Reaction between (*R*)-(–)-(4-Methylcyclohexylidene)acetone (3) and Acetone. As described in the general procedure a mixture of **3** $[\alpha]^{26}_{Hg}$ –94.53 ± 0.73° (*c* 0.7, $CHCl_3$), 91% optically pure] (0.76 g, 5 mmol), and acetone (1.16 g, 20 mmol) in 5 mL of dry THF was added to the titanium slurry at 0 °C (prepared from 93 mmol of $TiCl_4$). The reaction mixture was stirred at 0 °C for 1 h and worked up as usual. The crude product was separated by column chromatography, eluting with hexane followed by hexane–ether (60/40).

From the hexane fraction was obtained 0.07 g of a mixture of two hydrocarbons in 1:5 ratio. This mixture was further separated by radial chromatography. The major product, a colorless liquid, was characterized as (*R*,*R*)-(+)-bis(4-methylcyclohexylidene)-*trans*-2,3-dimethylbut-2-ene (**9**): $[\alpha]^{25}_{Hg}$ +35.65 ± 2.0° (*c* 0.25, cyclohexane); IR ($CHCl_3$) 3000–2800 and 1650 cm^{-1}; ^{1}H NMR (C_6D_6) δ 0.85 (d, 3 H), 0.91–1.15 (m, 2 H), 1.26–1.48 (m, 1 H), 1.55–1.85 (m including a CH_3 singlet at 1.82, 6 H), 1.96–2.17 (m, 1 H), 2.17–2.32 (m, 1 H), 2.39–2.62 (m, 1 H), and 5.75 (s, 1 H); ^{13}C NMR 20.59 (q), 22.12 (q), 29.56 (t), 32.73 (d), 35.73 (t), 36.07

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[17] Madhava Reddy, S.; Goedken, V.; Walborsky, H. M. *J. Am. Chem. Soc.*, in press.

(t), 36.87 (t), 123.65 (d), 128.67 (s), and 139.99 (s) ppm; UV (c 1.8 × 10^{-5} M, cyclohexane) λ_{230} (ϵ 9700); MS (high resolution) calcd for $C_{20}H_{32}$ 272.2502, found 272.2512. NMR of the minor product did not correspond to the anticipated 1-(4-methylcyclohexylidene)-2,3-dimethyl-2-butene. Further characterization of this product was not attempted.

From the hexane–ether fractions was obtained, among other minor products which were discharged, a diastereomeric mixture of (*R*)-(−)1-(4-methylcyclohexylidene)-2,3-dihydroxy-2,3-dimethylbutane (**8**) (0.55 g, 52%) as a colorless liquid: $[\alpha]^{26}_{Hg}$ −5.43 ± 0.41° (c 1.2, C_2H_5OH); IR (neat) 3450 (br), 3050–2800, 1655, and 1600 cm^{-1}; ^1H NMR δ 0.91 (d, 3 H), 0.95–2.2 (m including CH_3 signals, 17 H), 3.22 (br d, 1 H), and 5.26, 5.30 (2s, 1H, 1:1 ratio).

Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.63; H, 11.46.

Cross-Coupling Reaction between (*R*)-(−)-(4-Methylcyclohexylidene)acetophenone (4) and Acetone. Following the general procedure, a mixture of acetone (0.53 g, 9.20 mmol) and (*R*)-(−)-(4-methylcyclohexylidene)acetophenone (**4**) (0.50 g, 2.30 mmol) ($[\alpha]^{25}_{Hg}$ −39.27 ± 0.83°; 91% optically pure) in 5 mL of dry THF was added to a slurry of 46.6 mmol of Ti(0) at room temperature with stirring for 3.5 h. After workup the crude product was separated by radial chromatography.

From the hexane fraction was obtained pure (*R*)-(+)-1-(4-methylcyclohexylidene)-3-methyl-2-phenyl-2-butene (**10**) as a colorless liquid: yield 0.225 g (40%); $[\alpha]^{26}_{Hg}$ +33.06 ± 0.37° (c 1.35, $CHCl_3$); IR ($CHCl_3$) 3050–2800, 1940 (w), 1880 (w), 1810 (w), 1760 (w), 1650 and 1600 cm^{-1}; ^1H NMR δ 0.80–1.20 (m, 5 H, including CH_3 doulet at 0.90), 1.40–1.85 (m, 10 H, including isopropylidene methyls), 1.90–2.40 (m, 3 H), 5.73 (s, 1 H), and 7.10–7.35 (m, 5 H).

Anal. Calcd for $C_{18}H_{24}$: C, 89.94; H, 10.06. Found: C, 89.82; H, 10.11.

From the hexane–ether fractions, a total of 0.156 g (24%) of two diastereomeric glycols **11** (1:1 ratio) was obtained. The glycols were separated and characterized. The less polar (−)-1-(4-methylcyclohexylidene)-2,3-dihydroxy-3-methyl-2-phenylbutane: $[\alpha]^{26}_{Hg}$ −5.88 ± 0.58° (c 0.85, C_2H_5OH, 72% optically pure[18]); IR (film) 3450 (br), 3050–2800, 1655 and 1600 cm^{-1}; ^1H NMR δ 0.50–2.40 (m, 20 H, including CH_3 doublet at 0.75, two isopropylidene methyls at 1.10 and 1.22, and two hydroxy protons at 2.08 and 2.35), 6.10 (s, 1 H), and 7.10–7.70 (m, 5 H).

Anal. Calcd for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55. Found: C, 77.91; H, 9.46.

More polar (−)-1-(4-methylcyclohexylidene)-2,3-dihydroxy-3-methyl-2-phenylbutane: $[\alpha]^{26}_{Hg}$ −17.36 ± 0.46° (c 1.08, C_2H_5OH, 72% optically pure[18]); IR ($CHCl_3$) 3550 (br), 3050–2800, 1950, 1880, 1820, 1710, 1650, and 1600 cm^{-1}; ^1H NMR δ 0.20–1.80 (m, 15 H), including CH_3 doublet at 0.68 and two isopropylidene methyls at 1.10 and 1.23), 1.80–2.60 (m, 5 H, including two hydroxy protons at 2.06 and 2.46), 6.10 (s, 1 H), and 7.10–7.60 (m, 5 H).

Anal. Calcd for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55. Found: C, 78.89; H, 9.60.

Other materials present in the crude product were discarded.

Cross-Coupling Reaction between (*S*)-(+)-(2,2,4,6,6-Pentamethylcyclohexylidene)acetone (5) and Acetone. To a slurry of Ti(0) (40 mmol) in 60 mL of THF was added (*S*)-(+)-(2,2,4,6,6-pentamethylcyclohexylidene)acetone (**5**) (0.41 g, 2 mmol, $[\alpha]^{25}_{Hg}$ +114.71 ± 0.08°, 46.50% ee) and acetone (0.461 g, 8 mmol) in 5 mL of THF at 0 °C. After being stirred for 3 days at room temperature, the reaction mixture gave, on quick workup as earlier, 0.52 g of a crude mixture. Column chromatography of the mixture on silica gel (25 g) using hexane–ether yieled two fractions: the less polar fraction I eluted with hexane (0.13 g, 28%) and was found to be the liquid (±)-1-(2,2,4,6,6-pentamethylcyclohexylidene)-2,3-dimethyl-2-butene (**12**): IR (film) 2900 (m), 1680 (w), 1610 (w), 1470, 1385, 1375, 1305, and 1260–865 cm^{-1}; ^1H NMR δ 0.86 (d, J = 6.50 Hz, 3 H), 1.10 (s, 3 H), 1.13 (s, 3 H), 1.15 (s, 3 H), 1.16 (s, 3 H), 1.61 (br s, 6 H), 1.70 (br s, 3 H), 0.80–1.60 (m, 4 H), 1.88 (m, 1 H), and 4.91 (br s, 1 H); ^{13}C NMR 19.55 (CH_3), 20.26 (CH_3), 22.65 (CH_3), 22.86 (CH_3), 24.34 (CH), 29.35 (CH_3), 31.91 (CH_3), 32.62 (CH_3), 33.83 (CH_3), 37.14 (C), 37.98 (C), 50.53 (CH_2), 52.92 (CH_2), 123.53 (C), 126.62 (CH), 128.84 (C), and 150.24 (C) ppm; UV (c 1.16 × 10^{-4}, cyclohexane) λ_{198} ϵ 14800.

Anal. Calcd for $C_{17}H_{30}$: C, 87.18, H, 12.82. Found: C, 87.26; H, 12.84.

More polar fraction II (0.36 g, 67%) eluted with hexane–ether to give a diastereomeric mixture (5:1) of (±)-1-(2,2,4,6,6-pentamethylcyclohexylidene)-2,3-dihydroxy-2,3-dimethylbutane (**13**) as a colorless liquid: IR (film) 3430 (br), 2900 (m), 1705 (w), 1610 (w), 1470, 1390–1340, 1240–1060, 965, and 910 cm^{-1}; ^1H NMR δ 0.88 (d, J = 7 Hz, 3 H), 1.00–1.60 (m, 25 H, including several CH_3 singlets), 1.82 (m, 1 H), 1.98 (s, 1 H, OH), 1.38 (s, 1 H, OH) and 5.30, 5.45 (2s, 1 H).

Anal. Calcd for $C_{17}H_{32}O_2$: C, 76.12; 11.89. Found: C, 76.07; H, 11.89.

Cross-Coupling Reaction between (*S*)-(+)-5 and Acetone at Refluxing Temperature. A mixture of (*S*)-(+)-(2,2,4,6,6-pentamethylcyclohexylidene)acetone (**5**) (0.624 g, 3 mmol), $[\alpha]^{25}_{Hg}$ +114.71 ± 0.08°, 46.50% ee) and acetone (12 mmo) was allowed to reflux with Ti (0) (60 mmol) for 20 h. After workup, separation gave 0.37 g (53%) of (±)-1-(2,2,4,6,6-pentamethylcyclohexylidene)-2,3-dimethyl-2-butene (**12**) and 0.16 g of polar fractions.

Low Valent Titanium Reaction of (±)-1-(2,2,4,6,6-Pentamethylcyclohexylidene)-2,3-dihydroxy-2,3-dimethylbutane (13). (±)-1-(2,2,4,6,6-Pentamethylcyclohexylidene)-2,3-dihydroxy-2,3-dimethylbutane (**10**) (0.268 g, 1 mmol) was stirred with 20 mmol of Ti(0) in THF at 25 °C for 3 days. Workup and separation gave 12 mg (5%) of (±)-1-(2,2,4,6,6-pentamethylcyclohexylidene)-2,3-dimethyl-2-butene (**12**) and 0.18 g (67%) of starting material **13**.

Cross-Coupling Reaction between (*S*)-(+)-(4-(Dimethyl-*tert*-butylsiloxy)-2,2,6,6-tetramethylcyclohexylidene)acetone (6) and Acetone. A solution of (*S*)-(+)-(4-(dimethyl-*tert*-butylsiloxy)-2,2,6,6-tetramethylcyclohexylidene)acetone (**6**) (0.324 g, 1 mmol), $[\alpha]^{29}_{D}$ +66.41 ± 0.50°, 37.52% ee) and acetone (0.23 g, 4 mmol) in 5 mL of THF was added to Ti(0) (20 mmol) in 30 mL of THF at 0 °C. The reaction mixture was stirred at 25 °C for 1 h and at reflux for 20 h. Hydrolysis and quick workup gave 0.32 g of crude product, which on purification yielded 0.05 g of polar fractions, and 0.256 g (73%) of a less polar fraction identified as (±)-1-(4-(dimethyl-*tert*-butylsiloxy)-2,2,6,6-tetramethylcyclohexylidene)-2,3-dimethyl-2-butene (**14**) as a liquid: IR (film) 2900 (m), 1615 (w), 1470, 1390, 1370, 1265, 1230–1170, 1090, and 1025–795 cm^{-1}; ^1H NMR δ 0.06 (s, 6 H), 0.90 (s, 9 H), 1.13 (s, 3 H), 1.16 (br s, 9 H), 1.00–1.80 (m, 4 H), 1.58 (br s, 6 H), 1.68 (br s, 3 H), 4.00 (m, 1 H), and 5.90 (br s, 1 H), (C_6D_6) 0.11 (s, 6 H), 1.01 (s, 9 H), 1.16 (s, 3 H), 1.18 (s, 3 H), 1.23 (s, 3 H), 1.26 (s, 3 H), 1.55 (br s, 3 H), 1.63 (br s, 1 H), 1.71 (br s, 3 H), 0.90–2.00 (m, 4 H), 4.11 (m, 1 H), and 5.95 (br s, 1 H); UV (c 8 × 10^{-5}, cyclohexane λ_{196} ϵ 15000.

Anal. Calcd for $C_{22}H_{42}OSi$: C, 75.42; H, 12.00. Found: C, 75.54; H, 12.14.

Cross-Coupling Reaction between (*S*)-(+)-(4-(Dimethyl-*tert*-butylsiloxy)-2,2,6,6-tetramethylcyclohexylidene)acetophenone (7) and Acetone. A mixture of (*S*)-(+)-(4-(dimethyl-*tert*-butylsiloxy)-2,2,6,6-tetramethylcyclohexylidene)acetophenone (**7**) (0.386 g, 1 mmol), $[\alpha]_D^{29}$ +40.31 ± 0.20°, 37.52% ee) and acetone (0.232 g, 4 mmol) in 5 mL of THF was added to the Ti (0) reagent (20 mmol) at 0 °C and stirred for 5 h at the same temperature. Workup and separation gave two fractions: fraction a eluted with hexane and gave 44 mg (10%) of (±)-1-(4-(dimethyl-*tert*-butylsiloxy)-2,2,6,6-tetramethylcyclohexylidene)-3-methyl-2-phenyl-2-butene (**15**) as a colorless liquid: IR (film) 3070 (w), 3050 (w), 2700 (m), 1940 (w), 1870 (w), 1800 (w), 1745 (w), 1640 (w), 1600, 1580, 1492–1448, 1390, 1373, 1265, 1230–1160, 1090, and 1050–795 cm^{-1}; ^1H NMR δ 0.33 (s, 6 H), 0.71 (s, 3 H), 0.86 (s, 9 H), 1.09 (s, 3 H), 1.18 (s, 3 H), 1.26 (s, 3 H), 1.30–1.80 (m, 4 H), 1.77 (dd, or 2d, J = 2.93 Hz, J = 3.66 Hz, 6 H), 3.95 (m, 1 H), 6.40 (br s, 1 H), and 7.10–7.32 (m, 5 H); UV (c 9.46 × 10^{-5}, cyclohexane) λ_{248} ϵ 8100.

Anal. Calcd for $C_{27}H_{44}OSi$: C, 78.64; H, 10.68. Found: C, 78.82; H, 10.79.

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(18) Optical purities of each of the glycols (**11**) were determined by NMR spectroscopy using the chiral shift reagent (+)-tris[3-[(heptafluoropropyl)hydroxymethylene]-*d*-camphorato]europium(III) in $CDCl_3$. The dimethyl signals at 1.10 and 1.22 and 1.10 and 1.23 ppm, in the less polar and more polar glycols, respectively, were split in the 270-MHz NMR spectrum. Enantiomeric excess was determined by integration.

Polar fraction b eluted with hexane–ether and yielded 0.345 g (77%) of a diastereomeric mixture of (±)-1-(4-(dimethyl-*tert*-butylsiloxy)-2,2,6,6-tetramethylcyclohexylidene)-2,3-dihydroxy-3-methyl-2-phenylbutane (**16**) as a viscous oil: IR (film) 3500, 3070 (w), 3050 (w), 3025 (w), 2900 (m), 1940 (w), 1870 (w), 1800 (w), 1600, 1470 (m), and 1400–725 cm^{-1}; ^{1}H NMR δ 0.07 (s, 3 H), 0.08 (s, 3 H), 0.75, 0.80 (2 s, 3 H, in the ratio of 1:3), 0.90, 0.91 (2 s, 9 H), 1.10–1.90 (m, 23 H, including several CH_3 singlets), 3.02, 3.28 (2 br s, 1 H, OH), 4.04 (m, 1 H), 6.22, 6.30 (2 s, 1 H, in the ratio of 3:1), and 7.18–7.50 (m, 5 H).

Anal. Calcd for $C_{27}H_{46}O_3Si$: C, 72.64; H, 10.31. Found: C, 72.61; H, 10.31.

Cross-Coupling Reaction between (*S*)-(+)-7 and Acetone at Refluxing Temperatures. (*S*)-(+)-(4-(Dimethyl-*tert*-butylsiloxy)-2,2,6,6-tetramethylcyclohexylidene)acetophenone (**7**) (0.386 g, 1 mmol), $[\alpha]^{29}_{D}$ +40.31 ± 0.20°, 37.52% ee) and acetone (0.232 g, 4 mmol) in 30 mL of THF was allowed to reflux with 20 mmol of Ti(0) reagent for 20 h. Workup and separation as described earlier gave 0.35 g (85%) of (±)-1-(4-(dimethyl-*tert*-butylsiloxy)-2,2,6,6-tetramethylcyclohexylidene)-3-methyl-2-phenyl-2-butene (**15**) and a mixture of polar fractions (0.06 g).

Low Valent Titanium Reaction of (+)-1-(4-(Dimethyl-*tert*-butylsiloxy)-2,2,6,6-tetramethylcyclohexylidene)-2,3-dihydroxy-3-methyl-2-phenylbutane (16). The title compound glycol **16** (0.223 g, 0.5 mmol) and Ti(0) reagent (10 mmol) in 15 mL of dry THF was stirred at 0 °C for 5 h. Workup and separation gave only a trace of less polar fraction and 0.20 g (90%) of recovered starting material **16**.

Notes

1,1,1-Trifluoro-2-penten-4-one as a Building Block of Trifluoromethyl-Substituted Compounds

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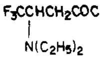
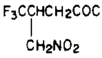
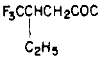
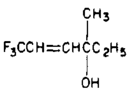
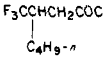
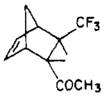
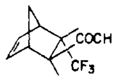
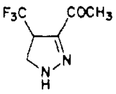
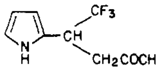
Partially fluorinated organic molecules are receiving increasing attention from the viewpoint of biological activity. Much effort has recently been paid to the development of trifluoromethylation, or perfluoroalkylation in general, of organic compounds.[1-6] An alternative general method involves chemical conversion of a simple CF_3-containing building block.[7] This approach would be more suited for the selective CF_3 functionalization of complicated organic molecules. Thus, reactions of CF_3-containing olefins[8-10] and carbonyl compounds[11-16] have been under active investigation. In the present work we have taken up a β-CF_3-α,β-unsaturated ketone and found that it is an excellent building block for the preparation of a variety of CF_3-containing compounds.

Table I. Reactions of 1,1,1-Trifluoro-2-penten-4-one (1) with Various Reagents

reagnt [solv]	condn	product	yield (%)
$(C_2H_5)_2NH$ $[(C_2H_5)_2NH]$	room temp 1 min	 $F_3C\underset{N(C_2H_5)_2}{\underset{\mid}{C}}HCH_2COCH_3$ **2**	56
CH_3NO_2, Na_2CO_3 $[CH_3NO_2–H_2O]$	60 °C 1 h	 $F_3C\underset{CH_2NO_2}{\underset{\mid}{C}}HCH_2COCH_3$ **3**	86
CH_3CH_2MgI $[(C_2H_5)_2O]$	room temp 1 h	 $F_3C\underset{C_2H_5}{\underset{\mid}{C}}HCH_2COCH_3$ **4**	13
CH_3CH_2MgI $[(C_2H_5)_2O]$	room temp 1 h	 $F_3CCH{=}CH\overset{CH_3}{\underset{OH}{C}}C_2H_5$ **5**	48
$(n\text{-}C_4H_9)_2CuLi$ $[(C_2H_5)_2O]$	room temp 1 h	 $F_3C\underset{C_4H_9\text{-}n}{\underset{\mid}{C}}HCH_2COCH_3$ **6**	44
cyclopentadiene [benzene]	80 °C 1 h	 **7**	62
cyclopentadiene [benzene]	80 °C 1 h	 **8**	18
CH_2N_2 $[(C_2H_5)_2O]$	room temp 1 min	 **9**	91
pyrrole $[CH_2Cl_2]$	40 °C 7 h	 **10**	65

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