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Asymmetric Reduction of Acetophenone with Lithium Aluminum Hydride Complexes of Terpenic Glycols†

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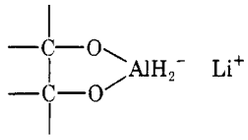
Optically active 1,2-glycols derived from (+)-1-menthene, (+)-α-terpineol, and (+)-α- and (−)-β-pinene formed chiral complexes with lithium aluminum hydride. The complexes were used to reduce acetophenone in different solvents and at various temperatures. The solvents included dioxane, diethyl ether, ethylene glycol dimethyl ether, and tetrahydrofuran, and temperatures ranged from −50 to 66 °C. Enantiomeric excess was maximum when the solvent was diethyl ether and the temperature was 15–20 °C. Various glycol complexes reduced the ketone in enantiomeric excesses ranging from 15% negative rotation to 30% positive rotation.

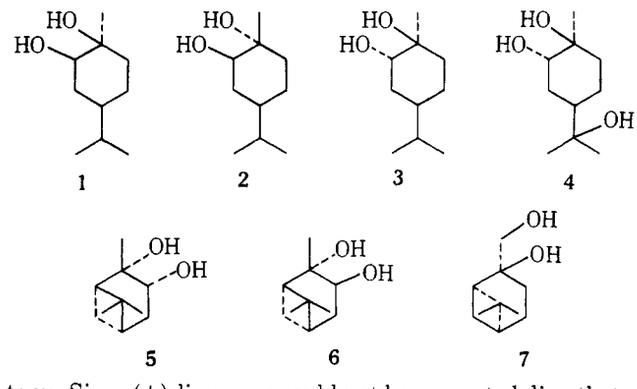
Conversion of abundant optically active terpenes such as limonene and pinene to useful optically active products has been the focus of much research effort. One approach is to synthesize asymmetric reagents from the terpenes.

In previous studies,[1] glycol–lithium aluminum hydride complexes were prepared from monosaccharide derivatives[2] and diol derivatives of tartaric acid[3] and α-pinene.[4,5] In one case, use of a monosaccharide derivative resulted in an enantiomeric excess (optical yield) of 70%.[2c] Enantiomeric excess has been found to depend on the glycol structure, whether ethanol or benzyl alcohol is added to the complex, and other variables, such as temperature and solvent.[1]

We converted glycols 1–7 to hydride complexes



and used them to reduce acetophenone under various conditions. Five of the glycols were prepared from (+)-limonene and (+)-α and (−)-β-pinene by oxidation with $KMnO_4$ (compounds 1 and 4–7); two other glycols (2 and 3) were donated to us. Since (+)-limonene could not be converted directly to a simple 1,2-glycol, it was first converted to (+)-1-menthene and (+)-α-terpineol by procedures which preserved the optical activity.[6,12] The respective products were then oxidized to the 1,2-glycol **1**, and the 1,2,8-triol **4**. The pinane glycols (**5**, **6**, and **7**) were synthesized by the oxidation of α- or β-pinene according to published procedures.[3–6] Acetophenone was chosen as the test ketone because it is frequently so used in the evaluation of asymmetric hydride reducing agents.[1]



Results and Discussion

Tables I and II show that the yields of α-methylbenzyl alcohol from the reduction of acetophenone under various conditions were generally high but that the optical yields were

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Table I. Reduction of Acetophenone with Glycol 1–Lithium Aluminum Hydride Complex

Run	Molar reactant ratio[a] Glycol	Alcohol	$LiAlH_4$	Solvent	Temp, °C Reag prepn	Reaction	Alcohol yield, %[b]	Product rotation, $[\alpha]_D$, deg	Optical yield, %[c]
A	1.1		1.1	Diethyl ether	0	25	99	+6.98	20
B	1.1		1.1	Glyme[d]	0	25	99	+6.42	18
C	1.1		1.1	Dioxane	10	25	99	+2.15	6
D	1.1		1.1	THF	0	25	98	+4.95	14
E	1.1		1.1	THF	0	−50	86	+3.70	11
F	1.1		1.1	THF	0	66	99	+5.99	17
G	1.1		1.1	THF	20	25	99	+6.42	18
H	1.1		1.1	THF	20	66	99	+4.33	12
I	1.1		1.1	THF	66	66	98	+3.89	11
J	1.1		1.1	THF	−50	−50	94	+1.58	4
K	1.1		1.1	Diethyl ether	20	25	99	+8.42	24
L	0.55		0.55	Diethyl ether	20	25	67	+7.56	21
M	1.1	Ethanol 1.0	1.1	THF	20	25	45	−1.99	(−)6
N	1.1	Ethanol 1.1	1.1	THF	20	66	57	+0.64	2
O	1.1	Benzyl alcohol 1.1	1.1	THF	20	66	59	+0.98	3
P	2.0	Ethanol 8.7	4.6	Diethyl ether	20	25	99	+10.7	30

[a] Based on 1.0 ratio for acetophenone. [b] Based on relative peak areas of acetophenone and α-methylbenzyl alcohol in GC trace of crude product mixture. [c] Corrected for optical purity of starting glycol. For most glycols, optical purity was based on that of the starting hydrocarbon, assuming no change in optical composition during the subsequent transformations. In some cases, the optical purity of the glycols was actually higher than that of starting material, because of purification during recrystallization. Rotations of the pure hydrocarbons were taken from the literature as follows: 1-menthene, 86°;[6b] limonene, 127°;[16b] α-pinene, 51°;[16b] β-pinene, 21°.[16b] The purity of glycols **2** and **3** was based on the reported rotation of **3**.[10b,11b] On the basis of these data, glycols and optical purities (%) were **1**, 79; **2** and **3**, 86; **4**, 79; **5** and **6**, 76; **7**, 95. [d] Ethylene glycol dimethyl ether.

Table II. Reduction of Acetophenone with Glycol (2–7)–Lithium Aluminum Hydride Complex[a]

Molar reactant ratio[b] Glycol	$LiAlH_4$	Solvent	Alcohol yield, %[c]	Product rotation, $[\alpha]_D$, deg	Optical yield, %[d]
(2) 1.1	1.1	Diethyl ether	99	−5.29	(−)14
(3) 1.1	1.1	Diethyl ether	99	+3.78	10
(3) 1.7	1.1	Diethyl ether	48	+0.90	2
(3) 0.5	1.0	Diethyl ether	99	+2.21	6
(4) 1.1	1.1	THF	55	+1.27	4
(5) 1.1	1.1	Diethyl ether	99	−1.23	(−)4
(6) 1.1	1.1	THF	94	+3.30	10
(6) 1.7	1.1	THF	73	+4.63	14
(6) 0.5	1.0	THF	98	+1.29	4
(7) 1.1	1.1	Diethyl ether	99	−0.98	(−)2

[a] Reaction temperature 25 °C, reagent preparation 20 °C. [b] Based on 1.0 ratio for acetophenone. [c] See footnote *b*, Table I. [d] Corrected for optical purity of starting glycol; see footnote *c*, Table I.

not (maximum was 30%). Optical yield was little affected by variations of solvent and/or reaction temperature. It was noticeably affected by the addition of alcohol to the reagent and variation of the glycol structure.

Data in Table I are for the reduction of acetophenone under various conditions with the complex of glycol **1**. This glycol was one of the easiest to synthesize, and relatively large amounts of the pure starting compound were available. Runs A–D were carried out in solvents representing four different types of ethers. Temperatures for the reagent preparation and reaction steps were arbitrarily kept at 0 and 25 °C, respectively, for three of these runs. Run C required a slightly elevated temperature for the reagent preparation to prevent crystallization of the solvent. The last column shows that optical yield of the alcohol was highest for diethyl ether and glyme (ethylene glycol dimethyl ether). The cyclic ethers THF (tetrahydrofuran) and 1,4-dioxane were less effective.

The effect of varying both reagent preparation and reaction temperature was studied with THF rather than ether or glyme. Tetrahydrofuran was used because its boiling point is higher than that of ether and because of possible interference of glyme during the workup.

Runs D–F showed that raising the reaction temperature increased optical yield, but not greatly. The decrease observed with run H as compared with run G is anomalous for the reasons cited below. This behavior is the reverse of that observed for oxazoline carbinol–lithium aluminum hydride reagents, whose asymmetric reduction yields increase with temperature.[7]

A separate temperature effect was found for the reagent preparation step. The reagent was prepared by dropwise addition of the glycol to the lithium aluminum hydride solution so that disproportionation of the complex to lithium aluminum hydride and a lithium aluminum tetraalkoxide[8] would

be minimized. For runs D and G with the reaction temperature at 25 °C and the reagent prepared at 0 and 20 °C, respectively, optical yields increased from 14 to 18%. Similarly, runs E and J showed that an increase in temperature of reagent preparation (−50 to 0 °C) increased optical yield (4 to 11%). However, for runs F, H, and I, with reagent preparation temperatures of 0, 20, and 66 °C, optical yields at 66 °C reaction temperature were 17, 12, and 11%. It seems likely that high reagent preparation temperatures increase the extent of disproportionation and hence reduce optical purity. On the other hand low temperatures appear to result in incomplete reactions and hence reduced optical yields. The similar results from runs H and I suggest that by the time the reagent had been heated to reaction temperature from 20 °C, disproportionation had already occurred to a great extent. At −50 °C, evolution of hydrogen during reagent preparation was not measured, but at 20 °C, the reagent preparation step was completed almost immediately, as indicated by the volume of hydrogen evolved. Thus, for this step, a temperature of about 20 °C was judged optimum for maximum optical yield. In run K, the optical yield was 24%, one of the highest in this series, as expected on the basis of the temperature and solvent effects discussed. In run L, half the amount of reagent relative to ketone was used, so that both active hydrogens in the reagent would have had to be consumed for complete reduction. The optical yield dropped slightly and the alcohol yield went down considerably, as compared to the yields for run K. Apparently, the second hydride hydrogen is not as reactive or as effective in inducing asymmetry as the first.

The addition of 1 equiv of a primary alcohol to the complex has been reported to increase optical yield in some cases.[2c,4] The addition of ethanol at two different reaction temperatures (runs M and N) and of benzyl alcohol (run O) markedly reduced optical yield. The product rotation was a negative value in run M and was a small positive value in run N. Product rotation in run O, with benzyl alcohol, was not significantly different from that of run N. Although the sign reversal associated with removal of one of the hydride atoms has been previously reported,[2c] reversal due to temperature has not. The effect of alcohol addition is preferential conversion of the more reactive hydride to alkoxide. The decrease in alcohol yield for runs M–O is consistent with this theory. In these complexes, the optical yield was also decreased in all three cases.

The final run in Table I, run P, was carried out with the most effective ethanol modified complex described in the monosaccharide study.[2c] The glycol complex was prepared by dropwise addition of glycol solution to a large excess of hydride, and sufficient ethanol was then added dropwise to react with excess hydride. This approach considerably improved optical yield.

Although the reducing agents derived from glycols other than 1 produced generally low optical yields (Table II), the effect of glycol structure was observable. Product rotation was negative for several runs (glycols **2**, **5**, and **7**). None of the glycols listed in Table II were as effective as glycol **1**. The effect of glycol to hydride ratio on optical yields was determined with trans glycols **3** and **6**. Diethyl ether was the solvent in most of the runs, but THF was used for glycols **4** and **6**, because of their insolubility in diethyl ether. The effect of this substitution on optical yield was assumed to be relatively small. To eliminate extraneous effects, we did not use alcohol-modified complexes in evaluating glycols **2–7**.

We attempted to correlate glycol structure with the sign and magnitude of rotation assuming that the hydride complexes of all the glycols except trans glycol **3** were cyclic. A cyclic complex of this glycol would be unlikely because of the diaxial orientation of the hydroxyl groups. In all of the cyclic complexes the bulky part of the glycol group would be held away from the hydride hydrogens. Relatively little interference from groups on the ketone would be expected. This was apparently the reason for the generally low optical yields. In view of the small differences involved, interpretation of the results in terms of asymmetric steric hindrance is difficult.

Experimental Section

Melting points were measured on a capillary melting point apparatus and are corrected. Infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer. Optical rotation were taken with a Rudolph Model 62 visual polarimeter: all samples were dissolved in ethanol and placed in an end-filled 0.5-dm cell, unless otherwise noted; values ± standard deviation are reported. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Ether solvents, except diethyl ether, were purified by passage through a column of activity I basic alumina. Diethyl ether (Fisher E-138) was used directly as received. Acetophenone (Fisher A-22) was purified by distillation at 90 °C (15 mm) and stored over $CaSO_4$. The purity of all reagents was checked by GC and infrared spectrometric analyses. Solutions were concentrated by distillation with a rotary evaporator at 40 mmHg, unless otherwise noted.

GC Analysis. GC analyses were performed on a Hewlett-Packard 7620A instrument with a flame ionization detector and helium carrier gas. Injection port, detector, and heated collector temperatures were 220 °C. Oven temperature was programmed from 80 to 220 °C at 2 °C/min. Two columns were used: a 0.125 in. × 15 ft stainless steel analytical column packed with 5% Carbowax 20M on 70/80 mesh Anakrom ABS (Analabs, Inc., North Haven, Conn.), and a 0.25 in. × 9 ft stainless steel preparative column packed with 20% Carbowax 20M on 60/80 mesh Anakrom ABS. The carrier gas flow rates were 33 mL/min for the analytical and 220 mL/min for the preparative column. Peak areas were determined with a Hewlett-Packard 3380A integrator.

TLC and Column Chromatographic Analyses. Analtech silica gel GF plates of 250- or 500-μ thickness were used. The 250-μ (analytical) plates were sprayed with anisaldehyde–phosphomolybdic acid reagent[9] for detection of spots. The 500-μ (preparative) plates were sprayed with 0.1% Rhodamine B in isopropyl alcohol followed by irradiation from beneath the plate with 366-nm light for visualization of bands. They appeared as alternate light and dark zones, which were scraped off and eluted with ether or ethanol. Ether was the developing solvent, unless otherwise noted. For column chromatography, Fisher F-101 Florisil deactivated with water (6%) was used.

(+)-1-Hydroxycarvomenthol (1). A solution of 28 g (0.20 mol) of (+)-1-menthene, $[\alpha]^{25}_D$ +86° (neat), n^{27}_D 1.4528, bp 181–182 °C (763 mm), 300 mg (0.054 mol) of KOH, and 40 ml of H_2O in 160 mL of 2-propanol was cooled to 3 °C with an ice bath, then stirred vigorously while 64 g (0.41 mol) of $KMnO_4$ was added, portionwise, over a 2-h period. The reaction mixture was maintained at 3–5 °C during this period and then stirred for an additional 1 h at 3–5 °C. The product was filtered through a Celite pad, and the pad washed several times with a 1:1 mixture of ice-cold 2-propanol and water (total of 300 mL). The combined filtrates were diluted with 500 mL of water, saturated with Na_2SO_4, and extracted with 1 L of CH_2Cl_2. Removal of solvent at 30–50 °C left 22 g of low-melting solid. The product was recrystallized twice from hexane. After drying overnight in an evacuated desiccator over $CaSO_4$, the product weighed 7.9 g and had mp 77–78 °C; $[\alpha]^{29}_D$ +8.2 ± 0.6° (c 42.0, acetone); IR (Nujol mull) 3.02 (s), 6.95 (s), 7.32 (s), 7.53 (m), 8.60 (s), 9.38 (s), 9.97 (m), 10.64 (m), 10.78 (s), 13.60 μ (m) (lit.[11] $[\alpha]_D$ + 14°, mp 77.5 °C). Attempts to recover additional product 1 from the mother liquor by recrystallization or bisulfite washing were unsuccessful.

(+)-1-Hydroxyneoisocarvomenthol (2). Compound **2** was obtained from Newhall[6] as a mixture with **3** (TLC showed green spots with R_f 0.3 for **2** and 0.6 for **3**). A 430-mg sample of the mixture was chromatographed on a 2.5 × 57 cm column (40 g) of Florisil packed in benzene and eluted with CH_2Cl_2 and CH_2Cl_2–EtOH. Elution with 1% EtOH in CH_2Cl_2 afforded 260 mg of **2**, $[\alpha]^{29}_D$ +1.49 ± 0.4° (c 20.2, acetone) (lit.[10,11] $[\alpha]_D$ + 2°). A sample of **2** isolated by preparative GC of the mixture (retention times 67 and 68 min for **3** and **2**, respectively, 40% of **3** and 60% of **2** by peak areas) after crystallization from hexane afforded colorless needles: mp 85–87 °C (lit.[10,11] 85–86 °C); IR (Nujol mull) 3.04 (s), 7.48, 8.66 (s), 8.91 (s), 9.31 (s), 9.81, 9.98, 10.44 (m), 10.81, 11.87, 12.00, 13.75 μ.

(+)-1-Hydroxyneocarvomenthol (3). Compound **3**[6] obtained from Newhall had mp 87–89 °C; $[\alpha]^{29}_D$ +41.4 ± 1.2° (lit.[10,11] mp 90 °C, $[\alpha]_D$ 48°); IR (Nujol mull) 2.96 (s), 7.73, 8.53 (m), 9.06, 9.70 (s), 10.40, 10.96, 11.65, 13.80 μ; TLC R_f 0.6 (dark green) and GC t_R 67 min (>99% of total peak area).

Hydration of (+)-Limonene to (+)-α-Terpineol. The solvomercuration–demercuration procedure of Brown et al.[12] was applied to the hydration of 42 g (0.31 mol) of (+)-limonene (Glidden P and F grade, $[\alpha]^{25}_D$ +100°). After saturation of the aqueous layer with K_2CO_3 and separation of the upper layer, the lower layer was extracted with 150 mL of THF. The upper layer combined with the THF extract of the lower layer was filtered (Whatman no. 1 filter paper, then phase separating paper), and the filtrate dried over Na_2SO_4, filtered, and concentrated by distillation to about 300 mL to afford a mixture of two liquid phases and a white solid. The mixture of lower layer and white solid was extracted with ether, and the extract was dried over Na_2SO_4, filtered, and concentrated at 30–50 °C to give 39 g of liquid. The crude product was distilled at 8–10 mmHg to give three fractions of the following boiling points and weights (g): 63–95 °C, 6 (fraction 1); 95–103 °C, 25 (fraction 2); 95–103 °C, 2 (fraction 3). The pot residue weighed 2.5 g. The second and third fractions had IR spectra identical with that of α-terpineol. The second fraction was a colorless liquid, $[\alpha]^{27}_D$ +96.0° (neat) (lit. $[\alpha]_D$ +95°[16]), and the third fraction was a yellow liquid, $[\alpha]^{27}_D$ +82°. Yield, based on the second fraction, was 53%.

Permanganate Oxidation of α-Terpineol to 4. A mixture of 16 g (0.104 mol) of (+)-α-terpineol (fraction 2 above), 95 mL of 2-propanol, 20 mL of water, and 130 mg (0.0023 mol) of KOH was cooled in an ice bath under nitrogen to 1–4 °C and stirred rapidly while 15 g (0.095 mol) of $KMnO_4$ was added, in portions, over a period of 0.5 h. The mixture was stirred under nitrogen at 1–6 °C for an additional 2 h. The product was filtered through a Celite pad and the pad washed with 150 mL of CH_2Cl_2. The lower layer of the filtrate was extracted with 300 mL of water in a separatory funnel, and the aqueous (upper) layer, with two 150-mL portions of ether. The combined aqueous material contained most the desired product and was neutralized to pH 6.8 with HCl. Distillation at 30 °C (15 mmHg) gave 4.2 g of glassy liquid; TLC with 16% ethanol in ether showed a large purple spot at R_4 0.5 and a smaller purple spot at R_f 0.4. A 1.3-g sample of the crude product was crystallized from ether, then recrystallized from ethanol–ether to afford 0.3 g of **4**, mp 80–81 °C, and 0.3 g, mp 79–81 °C, from the mother liquor on standing in a refrigerator, TLC R_f 0.5 (purple spot), $[\alpha]^{27}_D$ +16.6 ± 0.8° (*c* 19.1). The IR spectrum (Nujol mull) had bands at 3.03 (s), 7.37 (s), 8.60 (m), 9.39 (s), 9.49 (m), 10.92 (s), 12.30, 12.91, 13.70 μ. Anal. Calcd for $C_{10}H_{20}O_3$: C, 63.79; H, 10.71. Found: C, 63.64; H, 10.90. A sample was dissolved in ethanol and a glassy film deposited on an NaCl IR plate: IR 3.00 (s), 6.10, 6.93, 7.35 (m), 8.48 (m), 8.97 (m), 9.56 (s), 10.25, 10.60, 11.03 (s), 11.40, 11.50, 12.29 (m), 12.99, 13.70 μ.

For confirmation of the identity of **4**, a sample of the racemic compound was synthesized by permanganate oxidation of (±)-α-terpineol.[13] The racemate had mp 99–102 °C (lit.[13] mp 120.5 °C), and analytical TLC under the above conditions revealed a single spot at R_f 0.5. Films deposited from ethanolic (±)-**4** and (+)-**4** gave identical IR spectra. The IR spectrum of (±)-**4** (Nujol mull) had bands at 3.00 (s), 7.50 (s), 8.39 (s), 8.48 (s), 9.40 (s), 9.50 (s), 10.26 (s), 11.05 (s), 12.30 (s), 13.00 (m), 13.67 μ (s). The substantial differences between (+)-**4** and (±)-**4** in melting point and IR of their crystalline mulls were attributed to differences in crystalline form.

[1*S*-(1α,2β,3β,5α)]-2,6,6-Trimethylbicyclo[3.1.1.]heptane-2,3-diol (5) and [1*S*-(1α,2β,3α,5α)]-2,6,6-Trimethylbicyclo-[3.1.1]heptane-2,3-diol (6). The cis and trans glycols **5** and **6** were synthesized according to published procedures.[4,14] The melting point of **5** was 55–57 °C, $[\alpha]^{27}_D$ +2.4 ± 0.4° (*c* 39.0). Compound **6** had mp 161–162 °C, $[\alpha]^{30}_D$ +42.8 ± 2° (*c* 5.70). The literature values[4,14] for **5** were mp 55–56 °C, $[\alpha]^{25}_D$ −0.71° (*c* 2, $CHCl_3$). For **6** the values were mp 169–170 °C, $[\alpha]^{20}_D$ 49°. The TLC R_fs (purple spots) and GC retention times were 0.6 and 67 min for **5**, and 0.3 and 71 min for **6**.

2,10-Pinanediol (7). By a published procedure,[15] 28 g of (−)-β-pinene (Aldrich Chemical, $[\alpha]^{30}_D$-20°) was oxidized in 2-propanol–water with 30 g of $KMnO_4$. The product (10.5 g) was a low-melting solid. Recrystallization from hexane twice gave 6.0 g, mp 60–65 °C. Analytical GC produced a peak pattern indicative of instability. Analytical TLC showed a major blue-purple spot at R_f 0.4 and two minor spots at R_f 0.7. The product was further purified by column chromatography. An 800-mg sample was separated on a 1.9 × 20 cm column (43 g) of adsorbent packed in hexane and eluted with mixtures of hexane, methylene chloride, and ether. The desired product **7**[15] was eluted in the ether fractions, wt 500 mg, mp 82–84 °C, $[\alpha]^{27}_D$ −29 ± 3° (*c* 4.45) (lit.[15] mp 83.5 °C). Analytical TLC showed a single blue-purple spot at R_f 0.4.

Procedure for Acetophenone Reduction. A. General Procedure. A mixture of 80 mg (2.1 mmol) of $LiAlH_4$ (PCR Inc., Gainesville, Fla.) and 8 mL of ether was stirred under nitrogen and cooled to 20 °C with an ice water bath. A solution of 360 mg of glycol (2.1 mmol) in 3 mL of ether was added over a period of 15 min, while the temperature was maintained at 20 °C. A solution of 230 mg (1.9 mmol) of acetophenone in 1 mL of ether was added to the resultant mixture over a 2-min period. The temperature was allowed to rise to 25 °C and the mixture was stirred under nitrogen at 25 °C for 1 h. Since a precipitate was present from undissolved impurities in the hydride, it was not possible to determine whether the reaction was homogeneous or not. For decomposition of excess hydride, the mixture was cooled in an ice bath, and a solution of 75 mg (4.2 mmol) of H_2O dissolved in 1 mL of THF was added with vigorous stirring. Hydrogen evolution was measured by water displacement for both reagent preparation and reaction steps. The above reactant ratios were varied, and THF was substituted for ether in some runs. The temperature of either reagent preparation or reaction steps was also varied (see Tables I and II). Reaction time was decreased for those runs carried out at 66 °C: 2 min for runs F, H, and I: 5 min for run L; and 15 min for run M.

In the workup, the reaction mixture was filtered with a Celite pad, and the pad washed with ether. One to four filtrations were required. The filtrate was concentrated at 30–50 °C, placed in a volumetric flask, and diluted to 25 mL with ether. A 2-μL aliquot was analyzed by GC. Peak areas were compared to those of a standard sample of acetophenone and α-methylbenzyl alcohol at known concentrations (retention times 40 and 48 min, respectively).

The ether solution was concentrated to 1–2 mL at 30–50 °C, and the residue was transferred to a distilling bulb and distilled at 25–60 °C (0.3–1 mmHg). The distillate was diluted with CH_2Cl_2 to 200–500 μL. The diluted sample was injected into a preparative GC column, and the α-methylbenzyl alcohol collected. Optical rotations were measured at 26–29 °C. Precision of measurement was ±0.06°.

The extent of racemization during workup was evaluated. A 230-mg sample of (+)-α-methylbenzyl alcohol (K & K Chemicals, Plainview, N.Y., $[\alpha]^{27}_D$ +41.4°) was added to the distillation residue from one of the runs, and the sample subjected to the normal workup procedure. The rotation of the α-methylbenzyl alcohol sample collected, $[\alpha]^{28}_D$ +39.3°, indicated that over 98% of the original optical activity was retained.

B. Procedure with Added Alcohol. The general procedure (A) was followed, except that after glycol addition, a solution of the alcohol in 1 mL of ether or THF was added over 2 min, and the mixture was stirred for 10 min at 20 °C.

Hydrogen evolution for both steps was measured for runs H, M, and P and runs with glycols **3** (ratio 0.5) through **7** (Table II). For run O and runs with glycols **2** and **3** (ratios 1.1 and 1.7, Table II), hydrogen evolved from the reagent preparation step only was measured. Hydrogen evolution was not measured for the remaining runs. The ratio of actual to theoretical hydrogen evolved was 1.04 ± 0.13 std dev for the reagent preparation and 0.87 ± 0.11 for the total.

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Registry No.—**1**, 5729-92-0; 1 hydride complex, 62006-55-7; **2**, 20688-46-4; **2** hydride complex, 62057-38-9; **3**, 4031-57-6; **3** hydride complex, 62057-39-0; **4**, 62014-81-7; **4** hydride complex, 62006-56-8; **5**, 18680-27-8; **5** hydride complex, 62006-57-9; **6**, 21803-49-6; **6** hydride complex, 62057-40-3; **7**, 62015-66-1; **7** hydride complex, 62006-58-0; (+)-1-menthene, 1195-31-9; (+)-limonene, 5989-27-5; (+)-α-terpineol, 7785-53-7; (+)-α-pinene, 7785-70-8; (−)-β-pinene, 127-91-3; acetophenone, 98-86-2; $LiAlH_4$, 16853-85-3.

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