[Supporting Information]
Catalytic Meerwein-Pondorf-Verley Reduction by Simple Aluminum Complexes

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Supporting Information Available: General reaction procedures, quantitative analysis and relevant ^{1}H NMR spectra for titration experiments between $AlMe_3$ and $AlMe_2Cl$ (6 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

General Information and Materials. Toluene was distilled over sodium/benzophenone. ^{i}PrOH was distilled over $Mg(O^iPrO)_2$, C_6D_6, cyclohexanone, benzaldehyde, acetophenone, and 2-pentanone were dried over CaH_2. All solvents were distilled under nitrogen and saturated with nitrogen prior to use. All other reagents were purchased from the Aldrich Chemical Company and used without further purification, unless otherwise noted.

^{1}H NMR spectra were recorded on a Varian Mercury 300 FT-NMR spectrometer (300 MHz for ^{1}H NMR). ^{1}H chemical shifts are in ppm downfield from tetramethylsilane (TMS, δ scale) with the residual solvent resonances as internal standards.

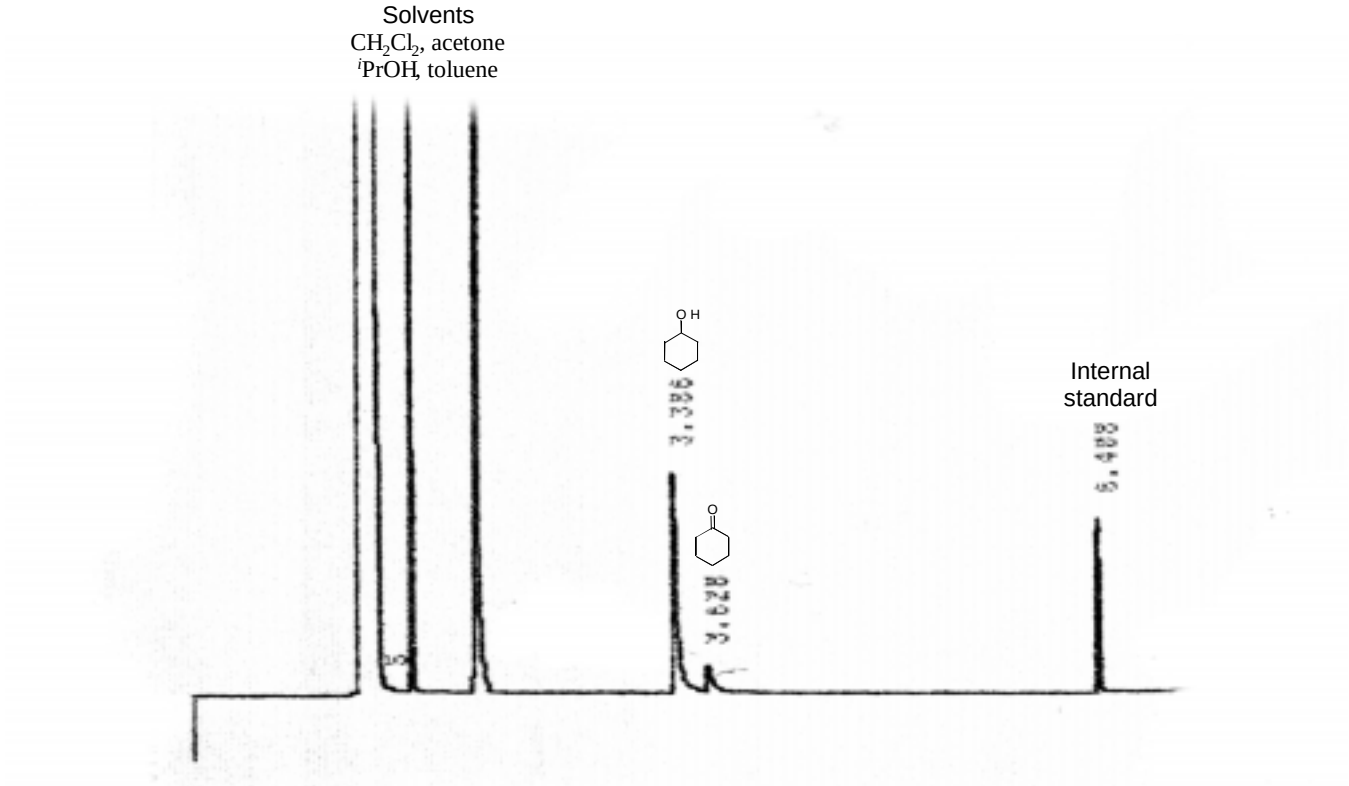
GC analyses of reaction mixtures were carried out on a Hewlett Packard 5890A equipped with an FID detector and an HP3396A integrator. The column used was a 30-m HP-5 capillary column with 0.32-mm inner diameter and 0.25-μm film thickness. Flow rate = 1.8 mL/min. GC yields were determined through integration of the product peak against 1,2,4,5-tetramethylbenzene (internal standard) using pre-established response factors. Chiral GC analysis was performed on a Varian 3700 equipped with an FID detector and an HP3390A integrator. The chiral column used was a 30-m Supelco β-Dex™ 225 fused silica capillary column with 0.25-mm inner diameter and 0.25-μm film thickness. Flow rate = 1.8 mL/min. Retention times for various components of the reaction mixture were assigned by the injection of a pure sample of each component in the reaction. Analysis of stereoselectivity of products in enantioselective reaction was assigned by comparing against known standards.

General Reaction Procedure. All reactions were carried out under a dry nitrogen atmosphere unless otherwise noted. A stock solution of the internal standard (1,2,4,5-$Me_4C_6H_2$ (2 mM in ^{i}PrOH)) is

prepared in the drybox and used as the stock hydride source for MPV reduction involving ^{i}PrOH. For reactions utilizing chiral 2^{o} alcohol, the internal standard was added to the reaction mixture as a solid.

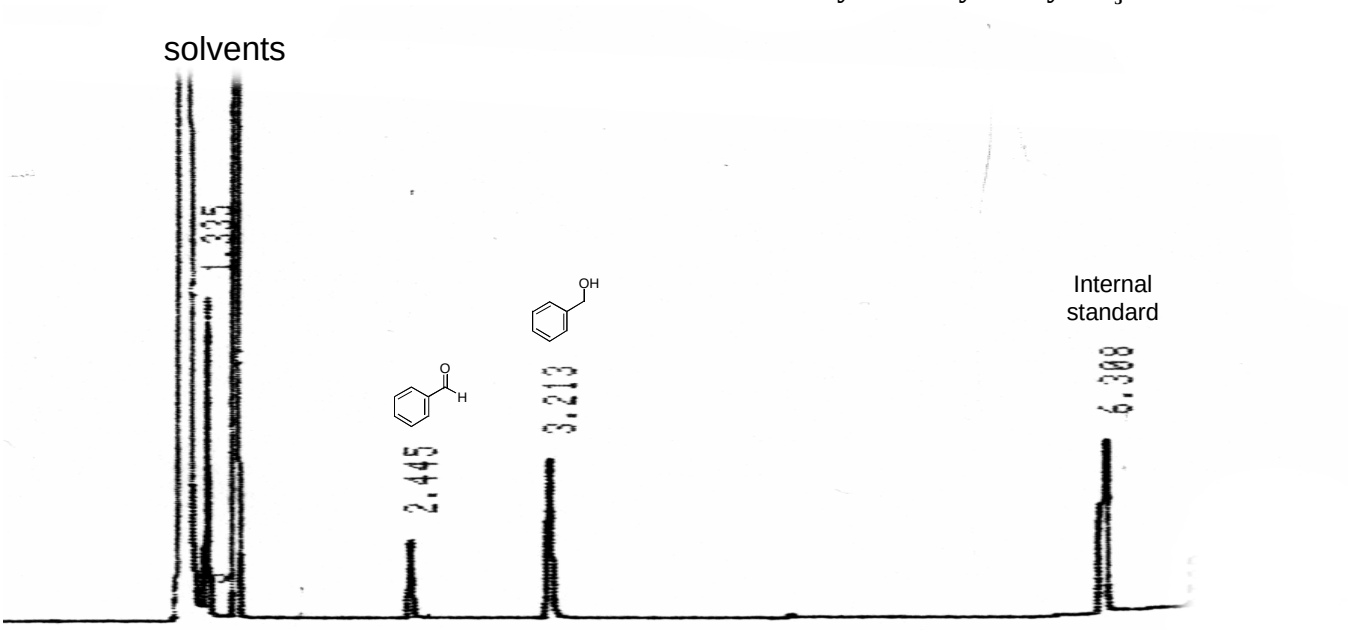
Into a 4-mL vial equipped with a magnetic stir bar was added toluene (1 mL) and the aluminum reagent (21 μmol). The hydride source (2^{o} alcohol, 10 or 40 equiv) and the carbonyl substrate (10 equiv) were added and the vial was sealed with a Teflon-lined silicone septa. The reaction was stirred at room temperature (*reactions utilizing chiral 2^{o} alcohol were carried out at 0 ^{o}C*) under nitrogen (3-16 hours). Aliquots were passed through a plug of neutral aluminum oxide [activated, ~150 mesh] and analyzed on GC versus internal standard to determine selectivity and conversion data. Flash column chromatography using 230-400 mesh silica gel (purchased from Merck, column dimensions = 2.5 cm x 12 cm) and CH_2Cl_2 eluent, was carried out on all reactions utilizing chiral hydride sources. GC traces of the MPV reduction of cyclohexanone, benzaldehyde, and α-chloroacetophenone as well as the chiral GC traces of racemic α-chloroacetophenol and the two reactions utilizing chiral hydrides are provided on the following pages.

The GC trace for the MPV reduction of cyclohexanone catalyzed by Me_3Al



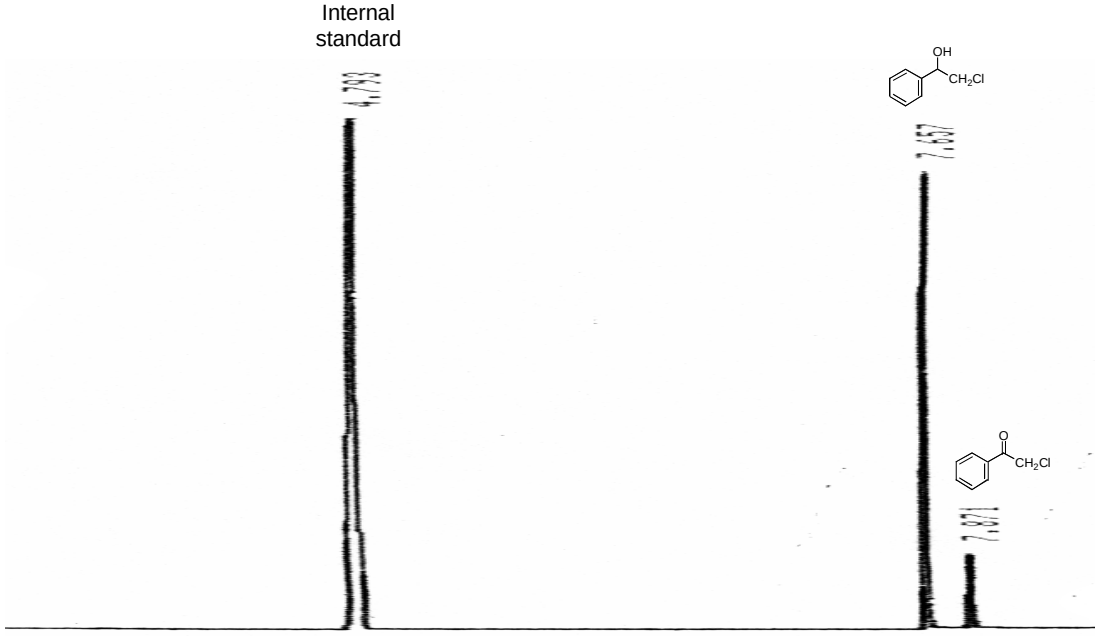
Temp. Program: initial temp. = 60 ^{o}C, initial time = 4 min., ramp = 40 ^{o}C/min., final temp = 250 ^{o}C, final time = 10 min.

The GC trace for the MPV reduction of benzaldehyde catalyzed by Me_3Al



Temp. Program: initial temp. = 90 °C, initial time = 4 min., ramp = 40 °C/min., final temp = 250 °C, final time = 10 min.

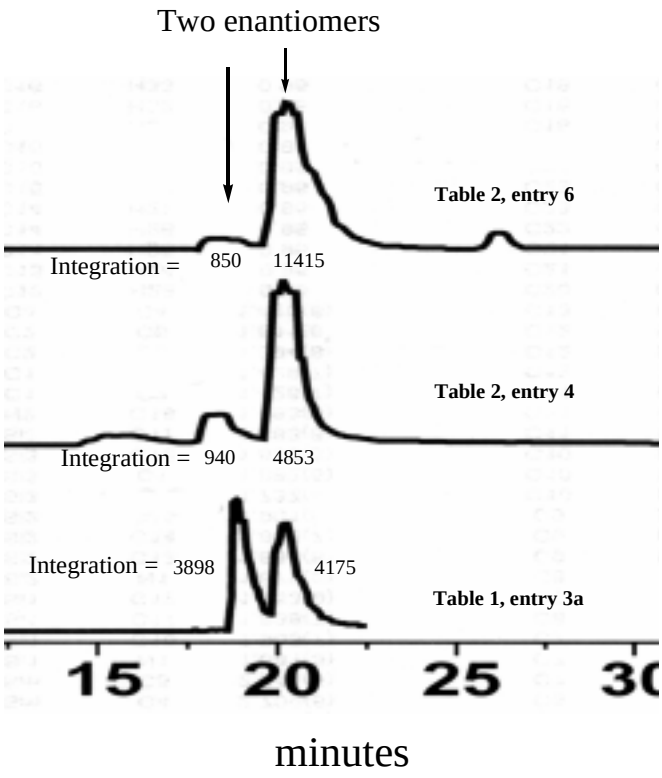
The GC trace for the MPV reduction of α-chloroacetophenone catalyzed by Me_3Al



Temp. Program: initial temp. = 110 °C, initial time = 4 min., ramp = 40 °C/min., final temp = 250 °C, final time = 10 min.

The Chiral GC traces for the chiral MPV reduction of α-chloroacetophenone catalyzed by Me_3Al and Me_2AlCl

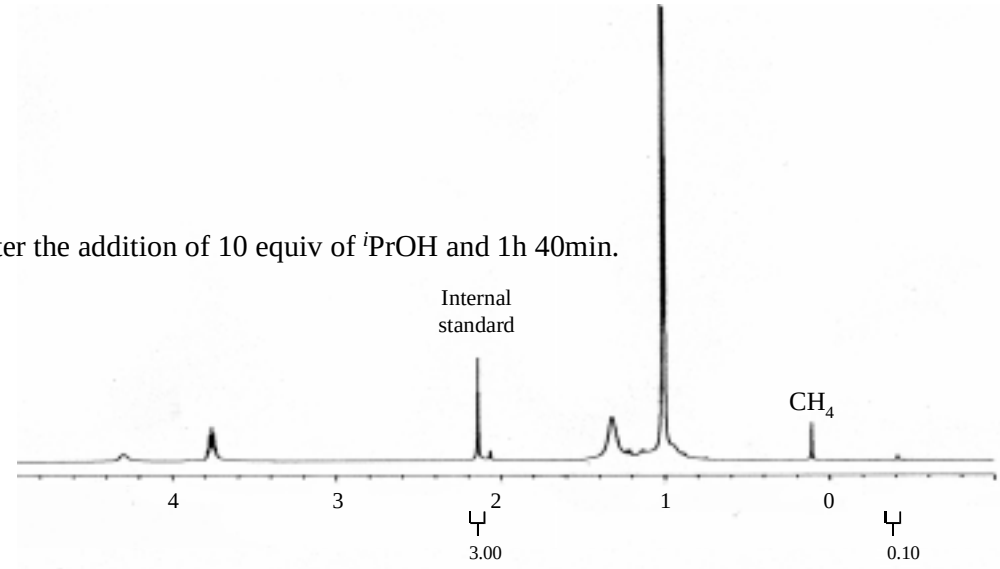
Included are the chiral GC traces for the MPV reductions of α-chloroacetophenone using ^{i}PrOH and the two chiral 2º alcohols as hydride sources with peak integration. The major peak on the right hand side of the top two traces corresponds to (R)-(-)-2-chloro-1-phenylethanol. The traces were digitized using PhotoPaint (v. 9) with UnScanIt and graphed in Origin Pro (v. 6.1).



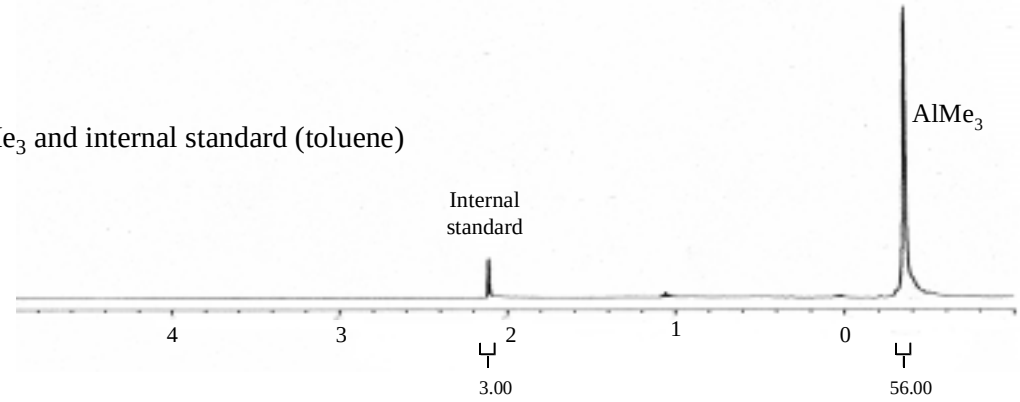
Temp. Program: initial temp. = 100 °C, initial time = 0 min., ramp = 2 °C/min., final temp = 180 °C, final time = 10 min.

The ^{1}H NMR(C_6D_6) spectra of the reaction of $AlMe_3$ with ^{i}PrOH

B) A, after the addition of 10 equiv of ^{i}PrOH and 1h 40min.

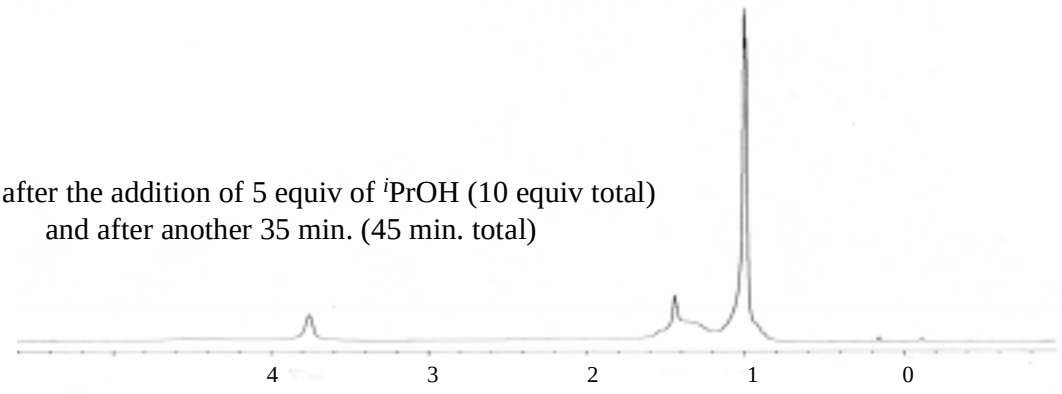


A) $AlMe_3$ and internal standard (toluene)



The ^{1}H NMR(C_6D_6) spectra of the reaction of $AlMe_2Cl$ with ^{i}PrOH

B) A, after the addition of 5 equiv of ^{i}PrOH (10 equiv total) and after another 35 min. (45 min. total)



A) $AlMe_2Cl$, 10 min. after the addition of 5 equiv of ^{i}PrOH