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THE REGIOSELECTIVE AND STEREOSPECIFIC SUBSTITUTION OF UNSYMMETRICAL 1,2-DIOLS USING THE 1,3,2λ^5-DIOXAPHOSPHOLANE METHODOLOGY.

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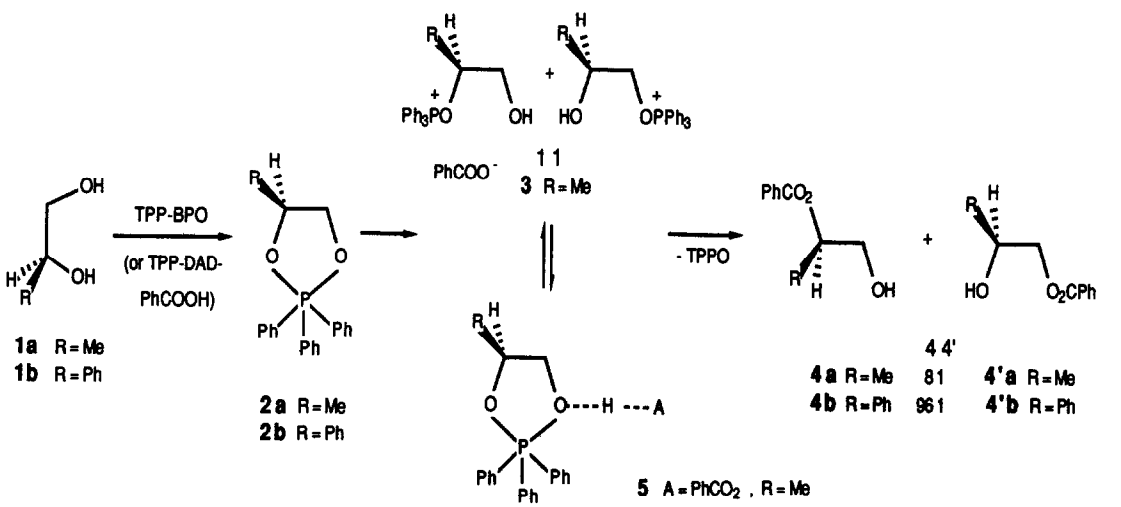
Abstract Stereospecific tosylate ($^-$OTs) or azide (N_3^-) substitution at the C-4 stereocenter of a monosubstituted 1,3,2λ^5-dioxaphospholane (the equivalent of the C-2 stereocenter in an unsymmetrical 1,2-diol) is readily achieved by treatment with either p-toluenesulfonic acid (p-TsOH) in tetrahydrofuran solvent or p-TsOH/sodium azide in acetonitrile solvent, respectively

Introduction

Monobenzoylation of unsymmetrical 1,2-diols **1** [i.e., 1,2-propanediol (**1a**) and 1-phenyl-1,2-ethanediol (**1b**)], affording both the kinetically and thermodynamically less stable C-2 benzoate[1], can be implemented by activating trivalent phosphorus in two ways Oxidative addition of triphenylphosphine (TPP) with benzoyl peroxide (BPO), or reaction of TPP with diethyl- or diisopropyl azodicarboxylate (DAD and DIAD, respectively) and benzoic acid (BA)[2] affords an organophosphorus intermediate which readily reacts with 1,2-diols The origin of the regio-selectivity favoring the C-2 benzoate is not completely resolved but it appears to result from an initial "complexation" (i.e., **2**·BA) between intermediate 1,3,2λ^5-dioxaphospholane **2** and the carboxylic acid [3] We earlier speculated that either displacement of triphenylphosphine oxide (TPPO) from oxyphosphonium ions **3** by benzoate anion or collapse of a "complexed" dioxaphospholane **5**[3] could provide access to benzoates **4** (Scheme 1)

Scheme 1. Reaction of 1,2-Diols with TPP-BPO or TPP-DAD-PhCOOH.



In an effort to enhance our mechanistic understanding of this unique transforma-tion, we have examined the reactions of dioxaphospholane **2** with nucleophiles· azide (N_3^-) and tosylate (OTs^-). We have also identified an equilibration between oxyphosphonium ions **3** and dioxaphospholane **2** which serves to clarify an important tenent of the mechanism.[4] These findings are reported herein

Results and Discussion

I. Stereochemistry

When either (S)-(-)-1,2-propanediol [(S)-**1a**][1a,5] or 2-phenyl-1,2-ethanediol (**1b**)[6] are treated with TPP/DIAD or diethoxytriphenylphosphorane (DTPP)[7] reagents in tetrahydrofuran (THF) solvent (0-5°C, ice bath), the prerequisite 1,3,2λ^5-dioxaphospholanes **2** were obtained The reaction of 1,3,2λ^5-dioxaphospholane **2a** (R = Me)[6] with p-toluenesulfonic acid (p-TsOH) in the presence of sparingly-soluble, sodium azide (NaN_3) gave initially the regioisomeric oxyphosphonium ions **3**[8] in nearly equal quantities.[9]

The isomeric oxyphosphonium ions **3a** are in dynamic equilibrium[4] with 1,3,2λ^5-dioxaphospholane **2a** as shown by the temperature dependence (-78° → 17° → -78°C) of their ^{31}P NMR spectra (See Figure 1) in THF solvent (vide infra) However, at ambient temperature (ca. 25°C) the sulfonate anion (p-TsO^-) rapidly displaces TPPO affording >95% yield of (R)-2(4-methylbenzenesulfonyloxy)-1-propanol [(R)-**6a**] with high stereospecificity (>92%ee) at the C-2 carbinol center Surprisingly, none of the regioisomeric C-1 tosylate was observed by ^{13}C NMR analysis

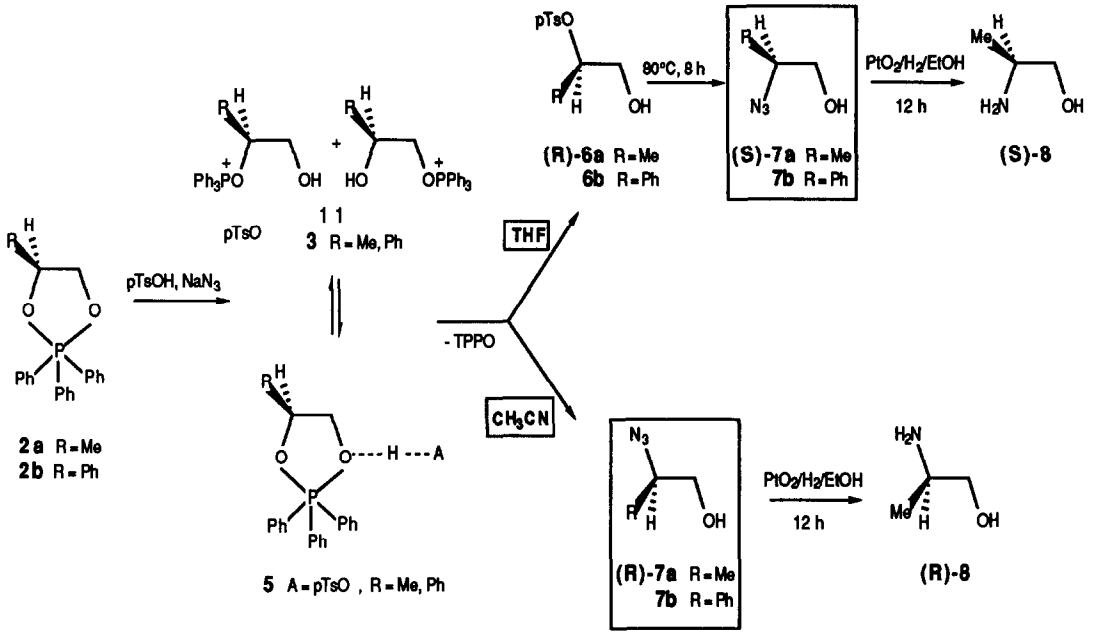
Subsequent heating of the reaction mixture (80°C, 8 h) containing (R)-**6a** and NaN_3 in THF solvent[10] afforded (S)-2-azidopropanol [(S)-**7a**] in 87%ee and 88% yield The configurational identity of (S)-(+)-**7a** was confirmed by comparing the sign and magnitude of its optical rotation with that of the (R)-(-)-**7a** antipode [12] These findings, coupled with knowledge of the absolute configuration of (S)-**1a**, require that tosylate **6a** form with nearly complete inversion of configuration from **2a** (Scheme 2)

When the same reaction was performed in acetonitrile (MeCN) solvent rather than THF, sulfonate ester **6** was not formed Instead, azide (R)-**7a** was formed directly in 93% yield with essentially complete inversion of configuration at C-2 (90%ee) The configurational identity at the C-2 stereocenter was confirmed by catalytic hydrogenation of azide (R)-**7a** to the known (R)-2-amino-1-propanol [(R)-**8**] [13]

Several interesting points require comment. First, it seems apparent that formation of tosylate **6a** from the ion pairs, oxyphosphonium ions **3** OTs^- or intermediate **5** HOTs requires displacement of TPPO by p-TsO^- through essentially an S_N2 mode with the accompanying inversion of configuration at C-2 Increased solubility of NaN_3 in THF solvent (ε 7 32)[14] at 80°C promotes a facile displacement of p-TsO^- by N_3^- with nearly complete inversion of configuration In fact, in THF solvent the overall 87%ee for the conversion of **2a** to (S)-**7a** translates to net retention of configuration at the C-2 stereocenter from diol **1a**!

In a high dielectric medium (i e , MeCN solvent, ε 36 5),[14] the solubilized NaN_3 affords a highly nucleophilic N_3^- ion which captures oxyphosphonium ion **3** or intermediate **5** with minimal competition from p-TsO^- affording (R)-2-azido-1-propanol with 90%ee and nearly complete inversion of configuration at C-2

Scheme 2. Reactions of 1,3,2λ^5-Dioxaphospholanes with p-TsOH and NaN_3 in Tetrahydrofuran and Acetonitrile Solvents



The same basic sequence of reactions characterizes the chemistry of dioxaphospholane **2b** [prepared by transoxaphosphoranylation of 2-phenyl-1,2-ethanediol (**1b**) with DTPP or TPP/DAD]. At 0°C in the presence of p-TsOH and NaN_3 in THF solvent, dioxaphospholane **2b** gives exclusively (>95% by ^{13}C NMR) 2-phenyl-2-tosyl-1,2-ethanediol (**6b**) then under higher reaction temperatures (110°C; 12 h) in DMF solvent, 2-azido-2-phenyl-1-ethanol (**7b**) is formed in 92% overall yield On the other hand, the reaction of **2b** at 0°C in MeCN solvent with p-TsOH and NaN_3 gave **7b** in 79% These results emphasize the role and importance of solvent polarity in dictating the course of the substitution reaction It is apparent that in the more polar MeCN solvent the soluble NaN_3 affords a highly nucleophilic N_3^- ion which reacts with oxyphosphonium ion **3** or intermediate **5b**·HOTs to afford **7b** without the intermediacy of **6b**

II. Mechanistic Implications of the Equilibrium Between the 1,3,2λ^5-Dioxaphospholane and the Oxyphosphonium Ions

The low temperature ^{31}P NMR spectrum of 1,3,2λ^5-dioxaphospholane **2a** in THF (-78°C) displays a sharp singlet at δ -37 5 ppm (Figure 1) When an equivalent of benzoic acid is added to the THF solution containing dioxaphospholane **2a**, two singlets are observed (-78°C) at δ 61 0 and 62 5 ppm corresponding to the C-2 and C-1 oxyphosphonium ions **3**, respectively, as well as a small quantity of TPPO (δ 32 ppm) When the temperature is raised to 17°C, these resonances coalesce to a broad singlet centered at δ 22 ppm The process is entirely reversible in that a lowering of the temperature to -78°C reestablishes the resonances for ions **3** along with that for

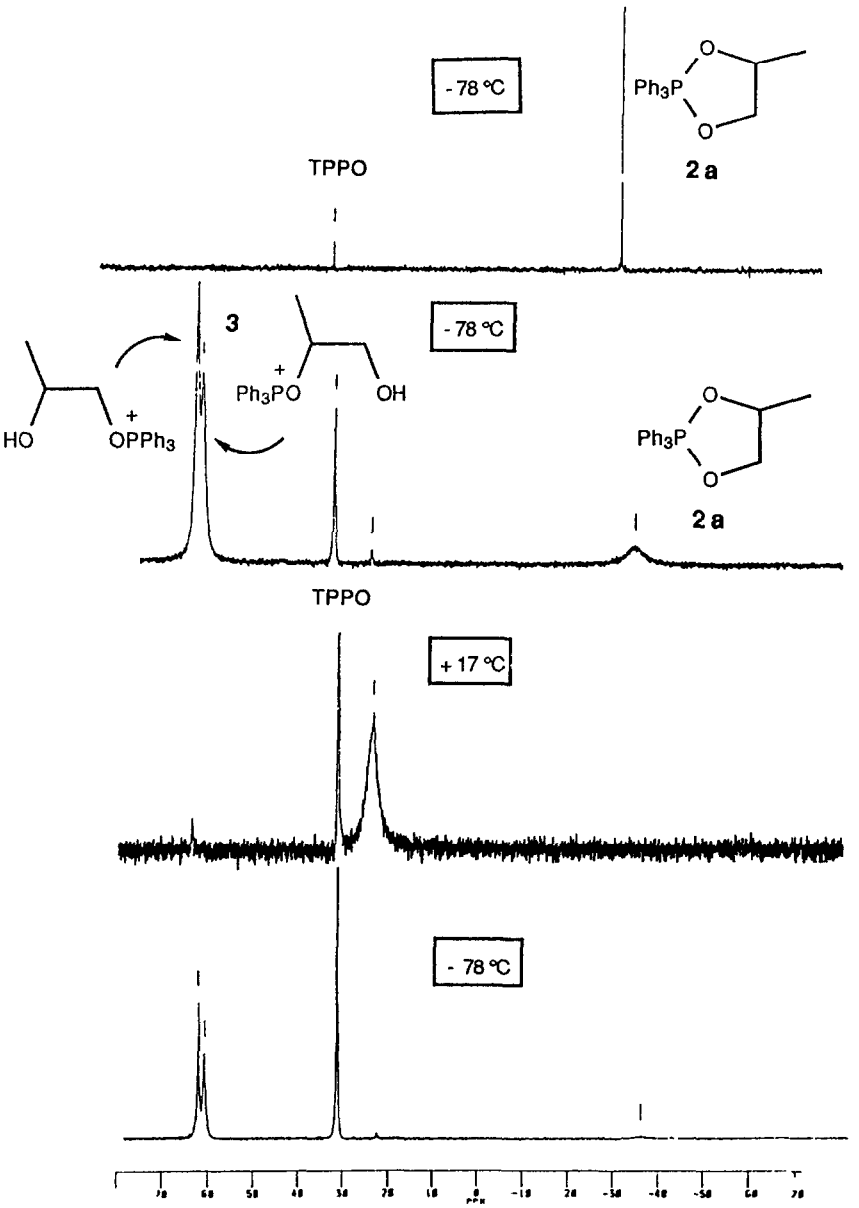


Figure 1. Variable ^{31}P NMR Spectra of 1,3,2λ^5-Dioxaphospholane 2a and the Isomeric Oxyphosphonium Ions 3.

dioxaphospholane **2a**. During the course of this equilibration, the intensity of the ^{31}P NMR resonance for TPPO also increases, indicating that the displacement of TPPO by benzoate anion is also a sluggish competitor

It seems clear that rapid interconversion of oxyphosphonium ions **3** is facilitated through the intermediacy of oxaphospholane **2a** in the presence of benzoic acid. Certainly, if the rate of equilibration is faster than the rate of displacement of TPPO from the oxyphosphonium ions **3** by benzoate anion, it is anticipated that the C-1 benzoate should emerge as the predominant isomer The fact that the C-2 isomer is favored reflects selective capture of an intermediate similar in structural constitution to **2** with benzoate (and exclusively with tosylate and azide in this study)

A tentative rationale might involve an initial coordination between dioxaphosphorane **2** and benzoic acid or p-TsOH at the least sterically hindered P-O-C oxygen This "complexed" oxygen should increasingly prefer the apical array considering the high apicophilicity of highly electronegative substituents [15] Through pπ-dπ back-bonding between the equatorial or basal oxygen and the phosphorus atom, the adjacent carbon should experience electron deficiency resulting in a net enhancement of the electrophilicity of the equatorial carbon.[16] In this way, selective complexation via hydrogen bonding to the least hindered oxygen serves to activate the secondary or C-2 carbon for associative S_N2 displacement.

While this is not the final word, the stereochemical overview resulting from "protection" of a chiral monosubstituted 1,2-diol as a 1,3,2λ^5-dioxaphospholane, followed by "acid-promoted" nucleophilic displacement translates to (i) inversion of configuration at the C-2 stereocenter in polar solvents and (ii) double inversion or net retention of configuration at the C-2 stereocenter in nonpolar solvents

Experimental Section

All melting points are uncorrected All ^{1}H, ^{13}C, and ^{31}P NMR data were obtained on the Bruker-IBM AC 200 NMR spectrometer with tetramethylsilane (Me_4Si) and 85% H_3PO_4 as internal and external references, respectively. The commercially-available diols were purified and dried by distillation or heating at 40°C for 12 h under high vacuum p-Toluenesulfonic acid (p-TsOH) was recrystallized from a solution of ethanol and water and ultimately dehydrated (90°C, 12 h) under high vacuum The preparations of DTPP[7] and (S)-(+)-1,2-propanediol[1a,5] have been reported elsewhere

4-Methyl-, and 4-Phenyl-2,2,2-triphenyl-1,3,2λ^5-Dioxaphospholanes (2a,b). The preparations of 1,3,2λ^5-dioxaphospholanes **2a,b** are essentially identical and the following procedure is representative Under anhydrous conditions (argon atmosphere), 1 25 mL of 0 8 M DTPP in THF (1 0 mmol) was added to the diol (1 0 mmol) in anhydrous THF (3 mL) The solution was stirred at ambient temperature for 1 h The solvent and residual ethanol were removed in vacuo, to afford an extremely hygroscopic, oily residue which could not isolated nor purified by conventional methods **2a** ^{13}C NMR (toluene) δ 19 1 ($^3J_{P-C}$ = 7 0 Hz, CH_3), 65 4 (CH_2), 68 1 (CH), 126-133 (C_6H_5), and 146 ppm (ipso carbon, $^1J_{PC}$ = 117 5 Hz), ^{31}P NMR (toluene) δ -37 2 ppm **2b** ^{13}C NMR (toluene) δ 66 8 (CH_2), 72 7 (CH), 126-132 (C_6H_5), and 145 7 ppm (ipso carbon, $^1J_{PC}$ = 115 7 Hz, ^{31}P NMR (toluene) δ -36 8 ppm

Reaction of 1,3,2λ^5-Dioxaphospholanes 2a,b with p-TsOH and NaN_3 in THF Solvent.

Anhydrous THF (5 mL) was added to the 1,3,2λ^5-dioxaphospholane (1 0 mmol) and stirred for 0 5 h The solution was cooled to 0°C (ice bath) To the cooled solution, 0 72 mL of p-TsOH in THF (1 54 M, 1 1 mmol) was added followed by the addition of 70 mg of NaN_3 (1 1 mmol) The solution was kept at 0°C (ice bath) for 1 h and allowed to warm to ambient temperature with stirring for 12 h to afford tosylates **6a,b**

(i) (R)-2-(4-Methylbenzenesulfonyloxy)-1-propanol [(R)-6a] was isolated by removal of residual NaN_3 (filtration) followed by removal of the THF solvent (rotary evaporator) from the above solution to afford an oily residue (>95% by ^{13}C NMR). Tosylate **6a** was subsequently purified by flash chromatography employing silica gel and 70% ethyl acetate-30% hexanes as eluents to afford homogeneous (R)-**6a**[17] (TLC) as a syrupy residue that did not crystallize ^1H NMR ($CDCl_3$) δ 1 2 (d, 3 H, J = 6.6 Hz, CH_3), 2.1 (br s, 1 H, OH), 2 45 (s,3 H, H_3C-C_6H_4), 3 6 (d, 2 H, J = 6 0 Hz, CH_2), 4 67 (m, 1 H, J = 6 0 Hz, CH) and 7.3-7 9 ppm (m, 4 H, C_6H_4), ^{13}C NMR ($CDCl_3$) δ 16 9 (CH_3), 21 6 (H_3C-C_6H_4), 65.5 (CH_2), 80 0 (CH), and 127 7-129.8 ppm (C_6H_4). A chiral shift ^1H NMR study using Eu(hfc)$_3$ indicated a 92% ee. The R configuration was assigned after azide displacement of the tosylate gave (S)-(+)-2-azido-1-propanol, (S)-**7a**.

(ii) 1-(4-Methylbenzenesulfonyloxy)-1-phenyl-2-ethanol (6b) was isolated by first removal of residual NaN_3 by filtration, followed by removal of the THF solvent (rotary evaporator) from the above solution to afford a solid residue (>95% by ^{13}C NMR) Tosylate **6b** was subsequently purified by flash chromatography employing silica gel and 50% ethyl acetate-50% hexanes as eluents to afford homogeneous **6b**. mp 96-98°C (lit.,[18] 70°C), ^1H NMR ($CDCl_3$) δ 2 41 (s, 3 H, CH_3-C_6H_4), 3 62 (br s, 1 H, OH), 3 75 (dd, 1 H, ^2J = 12 Hz, ^3J = 3 8 Hz, CHHOH), 3 92 (dd, 1 H, ^2J = 12 Hz, ^3J = 7 8 Hz, CHHOH), 5 51 (dd, 1 H, ^3J = 3 75 Hz, ^3J = 7 7 Hz, CH), and 7 1-7 7 ppm (m, 9 H, C_6H_5 and C_6H_4), ^{13}C NMR ($CDCl_3$) δ 20 5 (H_3C-C_6H_4), 64 3 (CH_2), 84 2 (CH), and 126-136 ppm (C_6H_5 and C_6H_4)

(S)-(+)-2-Azido-1-propanol [(S)-7a]. In a separate experiment, the THF solution containing (R)-2(4-methylbenzenesulfonyloxy)-1-propanol, (R)-**6a**, and NaN_3 was evaporated to dryness (in vacuo), the solid residue was dissolved in anhydrous N,N-dimethylformamide (DMF, 3 mL) solvent and the resulting solution was stirred at 110°C (12 h) Removal of sodium tosylate by filtration followed by evaporation of the solvent to dryness (vacuum pump) gave an oily residue (88%) Purification by flash chromatography employing silica gel and 25% ethyl acetate-75% hexanes as eluents gave a noncrystallizing syrupy residue[21] ^1H NMR ($CDCl_3$) δ 1 2 (d, 3 H, J = 6 15 Hz, CH_3), 1 8 (br s, 1 H, OH), and 3 6 ppm (m, 3 H, CH and CH_2), ^{13}C NMR ($CDCl_3$) δ 15 4 (CH_3), 58 8 (CH), and 65 6 ppm (CH_2), IR (thin film, NaCl plates) 2100 cm^{-1} (N_3) A chiral shift ^1H NMR study with Eu(hfc)$_3$ indicated a 87%ee The (S)-(+) configuration was confirmed by comparing the optical rotation of this sample with that of the (R)-(-) antipode, (R)-**7a**, which in turn was further substantiated by catalytic hydrogenation[11] of azide (R)-**7a** to the known (R)-(-)-2-amino-1-propanol, [(R)-**8**] [12]

2-Azido-2-phenyl-1-ethanol (7b). In a separate experiment, a THF solution containing 2-phenyl-2-(4-methylbenzenesulfonyloxy)-1-ethanol (**6b**) and NaN_3 was concentrated to dryness (in vacuo) The residue was dissolved in anhydrous DMF (3 mL) and the resulting solution was heated at 110°C (12 h) Removal of sodium tosylate by filtration followed by evaporation of the DMF solvent (high vacuum) gave an oily residue (92%) which was further purified by flash chromatography employing silica gel and 15% ethyl acetate-85% hexanes as eluents to afford azido alcohol **7b** as a viscous oil ^1H NMR ($CDCl_3$)[20] δ 2 94 (br s, 1 H, OH), 3 75 (d, 2 H, J = 6 3 Hz, CH_2), 4 75(t, 1 H, J = 7 2 Hz, CH), and 7 3-7 5 ppm (m, 5 H, C_6H_5), ^{13}C NMR ($CDCl_3$) δ 66 2 (CH_2), 67 6 (CH), and 127-136 ppm (C_6H_5), IR (thin film, NaCl plates) 2100 cm^{-1} (N_3)

Reaction of 1,3,2λ^5-Dioxaphospholanes 2a,b with p-TsOH and NaN_3 in Acetonitrile Solvent.

In separate experiments, anhydrous CH_3CN (5 mL) was added to 1,3,2λ^5-dioxaphospholanes, **2a,b** (1.0 mmol) and stirred for 0 5 h The solution was cooled to 0°C (ice bath), then 70 mg of NaN_3 (1 1 mmol) was added followed by 0 72 mL of p-TsOH in THF (0 8 M, 1 1 mmol) The solution was stirred at 0-5°C (ice bath) for 1 h and then allowed to warm to 25°C with stirring over a 12 h period Removal of sodium tosylate (by filtration) followed by evaporation of CH_3CN (rotary evaporator) gave the azido alcohols **7a** (93%) and **7b** (79%) A chiral shift ^1H NMR study of (R)-(-)-2-azido-1-propanol [(R)-**7a**] from above with Eu(hfc)$_3$ indicated a 90%ee and the

(R) configuration was assigned after catalytic hydrogenation (48 PSI of H_2 gas)[11] with platinum oxide in ethanol to give the (R)-(-)-2-amino-1-propanol, (R)-**8**: {$[\alpha]^{25}_D$ -16° (0 093 g in 1 mL EtOH) lit.,[12] $[\alpha]^{25}_D$ -21 8° (0 275 g in 10 mL EtOH)}, ^{1}H NMR ($CDCl_3$)[12] δ 1.2 (d, 3 H, J = 5 6 Hz, CH_3), 3 05 (dd, 1 H, ^{2}J = 9 9 Hz, ^{3}J = 7 0 Hz, CHH'OH), 3 3 (dd, 1 H, ^{2}J = 9 9 Hz, ^{3}J = 3 4 Hz, CHH'OH), and 3 45 ppm (m, 1 H, CH), ^{13}C NMR ($CDCl_3$) δ 18 8 (CH_3), 48 0 (CH), and 67.3 ppm (CH_2)

Reaction of Propylene Oxide with p-TsOH. To examine the possibility of epoxides as transient intermediates in the conversion of **2a,b** to C-1 and C-2 derivatives as described in the above reactions, the ring opening of propylene oxide was examined under similar reaction conditions Under anhydrous conditions, 0 07 mL of propylene oxide (1 0 mmol) was added to 0 33 mL of p-TsOH in THF (3 M, 1 0 mmol), 278 mg of triphenylphosphine oxide (1 0 mmol) and 65 mg of NaN_3 (1 0 mmol) in hydroxy tosylates Finally, an additional control reaction has shown that propylene oxide does not react with benzoic acid in toluene or THF solvents at ambient temperature

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(8) Oxyphosphonium ions **3** 3-C-1 ion ^{13}C NMR (C_6D_6) δ 18 6 (CH_3), 65 7 (d, J = 7 2 Hz, CH), 76 5 (d, J = 8 9 Hz, CH_2) and 127-137 ppm (C_6H_5), ^{31}P NMR (C_6D_6) δ 62 5 ppm 3-C-2 ion ^{13}C NMR (C_6D_6) δ 17 6 (d, J = 2 7 Hz, CH_3), 65 4 (d, J = 4 2 Hz, CH_2), 84 4 (d, J = 10 Hz, CH), and 127-137 ppm (C_6H_5), ^{31}P NMR (C_6D_6) δ 60 7 ppm

(9) The same oxyphosphonium ions are also formed in a 1 1 ratio in CH_3CN solvent in the absence of NaN_3

(10) Replacement of THF solvent (in vacuo) with DMF after formation of (R)-6a) followed by stirring at 110°C (12 h) affords an excellent yield of (S)-**7a** Azide displacements of tosyl groups in DMF solvent are well-documented and are characterized by predominant inversion of configuration at the requisite stereocenter [11]

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