Chemoselective Benzoylations of 1,2-Diols. Reactivity Comparisons of Reagents. Triphenylphosphine–Benzoyl Peroxide and Triphenylphosphine–Diethyl Azodicarboxylate–Benzoic Acid

Anne M. Pautard and Slayton A. Evans, Jr.*

The William Rand Kenan, Jr., Laboratories of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27599-3290

Received September 4, 1987

The triphenylphosphine–benzoyl peroxide (TPP–BPO) reagent initiates stereospecific benzoylation of secondary carbinol stereocenters with essentially complete inversion of stereochemistry. Monobenzoylations of 1,2-propanediol and styrene glycol with TPP–BPO and triphenylphosphine–diethyl azodicarboxylate–benzoic acid reagents afford a predominance of the more sterically encumbered C-2 benzoate with complete inversion of stereochemistry. Formation of a quintessential 1,3,2λ^5-dioxaphospholane intermediate, followed by proton-assisted and highly stereoselective ring opening of the phospholanes to isomeric oxyphosphonium ions, allows for Arbusov displacement of triphenylphosphine oxide by benzoate anion. This rationale adequately accounts for both the high chemoselectivity and the stereochemistry of the reactions.

Introduction

The need for high levels of chemoselective discrimination and protection of polyfunctional organic substrates has been adequately documented in the recent literature.[1] The benzoyloxy functional group exhibits a number of desirable features[2] including a relatively high resistance to acid-catalyzed hydrolysis, and consequently numerous "benzoylation" reagents have emerged for effecting chemoselective and chemospecific N-[3] and O-benzoylations.[4] Benzoyl transfer agents based on phosphorus atom activation have been described and exhibit chemoselective behavior favoring primary benzoylation over secondary in unsymmetrical diols.[5] To our knowledge, there are no reagents capable of initiating site selectivity in a single step such that the thermodynamically *least* stable regioisomer can be stereospecifically accessed.[6] Herein, we address this issue by describing a highly chemoselective benzoylation procedure of 1,2-diols affording both the kinetically and thermodynamically *least* stable benzoate regioisomer.

Results and Discussion

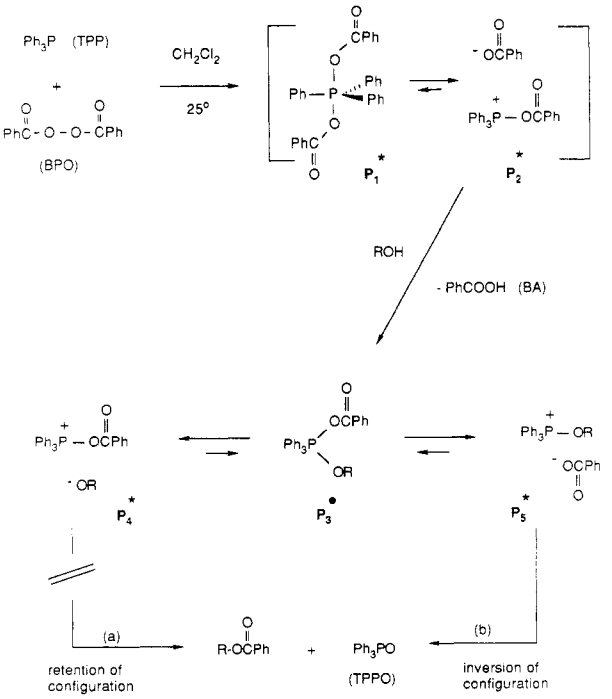
Benzoylation of Alcohols. The reaction of triphenylphosphine (TPP) and benzoyl peroxide (BPO) is exothermic at 30 °C, affording benzoic anhydride and triphenylphosphine oxide (TPPO).[7] In fact, ^{18}O-labeling of BPO coupled with competition experiments with other substituted benzoate anions formed the basis of a thorough mechanistic investigation of this reaction.[8] When alcohols

Table I. Benzoylation of Alcohols with TPP–BPO Reagent

alcohol, ROH	benzoate, ROC(O)Ph (%)[a]	alcohol, ROH	benzoate, ROC(O)Ph (%)[a]
n-butyl	81	isopropyl	72
sec-butyl	40	ethyl	67
benzyl	55	*n*-amyl	55
methyl	68	2-pentyl	40
n-propyl	64	cycloheptyl	37

[a] The general procedure required the combination of 2 mmol of TPP with 1 mmol of alcohol in 5 mL of CH_2Cl_2 at 25 °C. Dropwise addition of a solution of BPO (2 mmol) in 5 mL of CH_2Cl_2, followed by stirring overnight and removal of dichloromethane solvent, afforded the crude benzoate, whose yield was determined by ^{13}C NMR integration and/or HPLC analyses.

Scheme I. Mechanistic Rationale for Formation of Benzoate Esters from Reaction of Triphenylphosphine, Benzoyl Peroxide, and Alcohols



(1) (a) Mukaiyama, T.; Pai, F.-C.; Onaka, M.; Narasaka, K. *Chem. Lett.* **1980**, 563. (b) Posner, G. H.; Oda, M. *Tetrahedron Lett.* **1981**, *22*, 5003.

(2) (a) Loewenthal, H. J. E. *Tetrahedron* **1959**, *6*, 269. (b) Reese, C. B. In *Protective Groups in Organic Chemistry*; McOmie, J. F. W., Ed.; Plenum: New York, 1973; pp 109–118.

(3) Murahashi, S.-I.; Naota, T.; Nakajima, N. *Tetrahedron Lett.* **1985**, *26*, 925–928.

(4) (a) Kim, S.; Chang, H.; Kim, W. J. *J. Org. Chem.* **1985**, *50*, 1751–1752. (b) Carey, F. A.; Hodgson, K. O. *Carbohydr. Res.* **1970**, *12*, 463. (c) Stawinski, J.; Hozumi, T.; Narange, S. A. *J. Chem. Soc., Chem. Commun.* **1976**, 243–244. (d) Holy, A.; Soucek, M. *Tetrahedron Lett.* **1971**, 185–188. (e) Abbas, S. A.; Haines, A. H. *Carbohydr. Res.* **1975**, *39*, 358. (f) Abbas, S. A.; Haines, A. H.; Wells, A. G. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1351–1357. (g) Havel, M.; Valek, J.; Pospisek, J.; Soucek, M. *Collect. Czech. Chem. Commun.* **1979**, *44*, 2443. (h) Mukaiyama, T.; Pai, F.-C.; Onaka, M.; Narasaka, K. *Chem. Lett.* **1980**, 563–566.

(5) (a) Sekine, M.; Kume, A.; Hata, T. *Tetrahedron Lett.* **1981**, *22*, 3617–3620. (b) Kabachnik, M. I.; Rossiiskaya, P. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1945**, 594. (c) Terauchi, K.; Sakurai, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 883. (d) Pashinkin, A. P.; Gazizov, T. K.; Pudovik, A. N. *Zh. Obshch. Khim.* **1970**, *40*, 28.

(6) See, however: Ricci, A.; Roelens, S.; Vannucchi, A. *J. Chem. Soc., Chem. Commun.* **1985**, *21*, 1457–1458.

(7) Challenger, F.; Wilson, V. K. *J. Chem. Soc.* **1927**, 209.

0022-3263/88/1953-2300$01.50/0

Table II. Benzoylation of Diols in Dichloromethane at Ambient Temperature[a]

	benzoate (%)					
	TPP–BPO			TPP–DAD–BA		
diol	sec	prim	di-	sec	prim	di-
1,2-propanediol	79.1[b]	11.4[b]	9.5	79.7	12.0	8.3
styrene glycol	79.6[b,c]	3.8[b,c]	16.7[c]	80.9	3.1	16.0
				–	47[d]	5[d]
1,3-butanediol	t[e]	>90	t[e]	t[e]	>90	t[e]
					70[f]	7[f]
					80[g]	10[g]

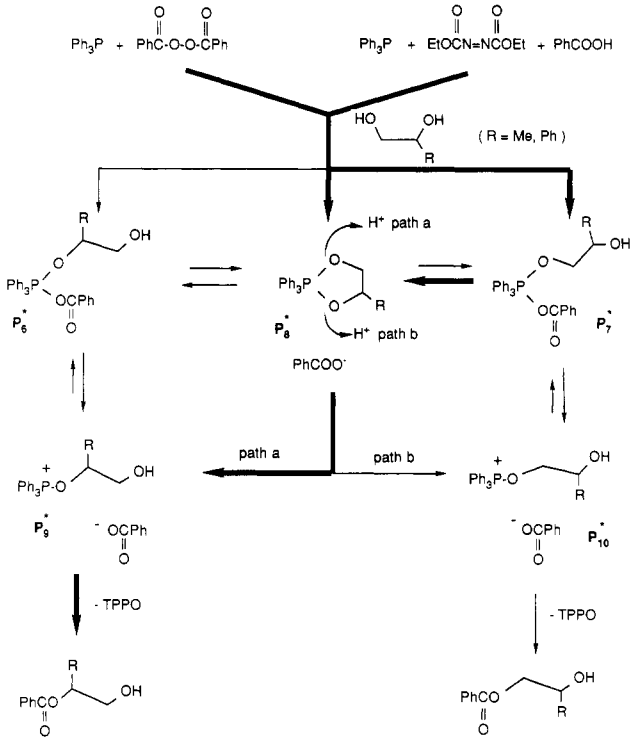
[a] The relative ratios of products were determined by HPLC analyses, and the identity of each component was ascertained by comparison of retention times with authentic materials. The structures of the components were confirmed by either (i) independent synthesis or (ii) comparison of physical properties reported elsewhere.[4a,6] [b] See ref 6 for ^{13}C NMR data. [c] See ref 4a for ^{1}H NMR data. [d] Apparently, the major product, the C-2 benzoate arising from reaction of TPP–DAD–BA with styrene glycol, was mistakenly assigned from ^{1}H NMR data as the primary C-1 benzoate. See: Mitsunobu, O.; Kimura, J.; Iiisuni, K.; Yanagida, N. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 510–513. [e] t = trace amounts. [f] 1.5 molar equiv of TPP and DAD. See footnote *b*. [g] 1.5 molar equiv of BA. See footnote *b*.

are added to the TPP–BPO medium during initiation of the "active organophosphorus reagent", benzoate esters are rapidly formed in moderate to good yields (Table I). The control experiment involving reaction between benzoic anhydride and a generic alcohol gave no measurable benzoylation under identical experimental conditions. This is understandable since the positive charge on P^{IV} phosphorus enhances both the electrophilicity of the carbonyl[9] and the propensity for benzoyl transfer[10] (vide infra). An analogous comparison exists between reactions of *N*-acetylpyridinium chlorides and benzoic anhydride with nucleophiles.[11] These facts suggest that the carboxylic ester probably arises from direct hydroxyl interception of the P^{IV} intermediate (presumably, P_2*), followed by equilibration of either oxyphosphonium ions P_4* or P_5* through (acyloxy)phosphorane P_3*[12] (Scheme I). A ^{31}P NMR examination at −78 °C of the TPP and BPO reaction in dichloromethane solvent reveals a resonance characteristic of oxyphosphonium ions[13] at δ 66.0, suggesting that if an equilibrium exists between (acyloxy)phosphonium ion P_2* and bis(acyloxy)phosphorane P_1*, P_2* is highly favored.

The consequences of reaction via P_4* or P_5* are easily distinguished by a stereochemical analysis involving a chiral or conformationally homogeneous alcohol with a defined carbinol stereocenter. Interception of P_4* (path a) with an alkoxide group would afford retention of stereochemistry at the carbinol carbon while reaction through P_5* (path b) clearly dictates inversion of stereochemistry at the carbinol stereocenter (Scheme I). A 75:25 trans–cis mixture of 4-*tert*-butylcyclohexanol was benzoylated with TPP–BPO to afford a 71:29 cis–trans mixture of 4-*tert*-butylcyclohexyl benzoates, demonstrating nearly complete inversion of stereochemistry at the carbinol stereocenter.

Benzoylation of 1,2-Diols. The chemoselectivity exhibited by the TPP–BPO reagent toward monobenzoylation of 1,2-diols is novel. While a relatively high level of chemoselectivity for benzoylation of 1,2-propanediol (1) was anticipated, the 7.3:1 ratio of C-2:C-1 benzoates was admittedly opposite of our expectations. Also, on the basis of the results in Table II, it is clearly

Scheme II. Mechanistic Rationale for Formation of C-1 and C-2 Benzoate Esters from 1,2-Diols



evident that the Mitsunobu procedure affords the same product ratios.[16] This certainly implies that the same quintessential intermediate in *both* reactions is responsible for the observed product distribution. Scheme II summarizes our mechanistic rationales employing both TPP–BPO and TPP–diethyl azodicarboxylate (DAD)–benzoic acid (BA) reagents with unsymmetrical 1,2-diols.

Since the intermediacy of (acyloxy)phosphonium ion P_2* is essential for phosphoranylation of an alcohol (i.e., P_2* → P_3*), phosphoranylation of a diol should also require initial formation of a phosphorane similar to P_3* as the focal intermediate. The kinetic initiative to form (acyloxy)phosphorane P_3* from an unsymmetrical 1,2-diol [i.e., where R = $CH_2CH(OH)CH_3$] through phosphoranylation of the primary hydroxyl group has been previously explored.[17]

(8) (a) Greenbaum, M. A.; Denney, D. B.; Hoffman, K. *J. Am. Chem. Soc.* **1956**, *78*, 2563. (b) Denney, D. B.; Greenbaum, M. A. *J. Am. Chem. Soc.* **1957**, *79*, 979.
(9) Fersht, A. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1970**, *92*, 5432.
(10) Hofle, G.; Steglich, W.; Vorbruggen, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 569–583.
(11) Fersht, A. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1970**, *92*, 5442.
(12) See also: Achmatowicz, O., Jr.; Grynkiewicz, G. *Tetrahedron Lett.* **1977**, 3179–3182.
(13) The ^{31}P NMR shift assigned to P_2* seems reasonable since it is similar to shifts exhibited by ethoxytriphenylphosphonium tetrafluoroborate (Ph_3P^+OEt,BF_4^-; δ 62)[14] and (neopentyloxy)triphenylphosphonium bromide [$Ph_3P^+OCH_2C(CH_3)_3,Br^-$; δ 61.7].[15]
(14) Denney, D. B.; Denney, D. Z.; Wilson, L. A. *Tetrahedron Lett.* **1968**, 85–89.
(15) Kelly, J. W.; Evans, S. A., Jr. *J. Org. Chem.* **1986**, *51*, 5490.
(16) Mitsunobu, O.; Kimura, J.; Iiizuni, K.; Yanagida, N. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 510–513.

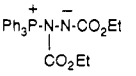
When a 1,2-diol is used, initial capture of P_2* is expected to give isomeric (acyloxy)phosphoranes P_6* and P_7*. We were unable to obtain ^{31}P NMR evidence for either of these two species;[18] nevertheless, both can ionize to the respective oxyphosphonium ions P_9* and P_{10}*. It is probably reasonable to expect that the alkoxyphosphonium ion would be more stable than the (acyloxy)phosphonium ion. Stabilization through backbonding between the electrons on the ethereal oxygen and the d orbitals on phosphorus should increase the stability of the alkoxyphosphonium ion. Assuming that primary phosphoranylation is favored (i.e., P_7*)[13] and direct equilibration of P_9* and P_{10}* is energetically prohibitive, then benzoylation by Arbusov displacement of triphenylphosphine oxide (TPPO) should favor formation of primary benzoate.

However, since the C-2 benzoate is the major product by a substantial amount, we envision the intermediacy of 1,3,2λ^5-dioxaphospholane P_8* as the key to explaining the large C-2:C-1 benzoate product ratios. We believe that 1,3,2λ^5-dioxaphospholane P_8* is formed in both reactions (e.g., TPP–BPO–diol and TPP–DAD–BA–diol) and undergoes a highly chemoselective ring opening initiated by hydrogen bonding and ultimately proton transfer involving benzoic acid to give the regioisomeric oxyphosphonium ions P_9* and P_{10}*. Apparently, proton association transpires at the least hindered ring oxygen to effect ring opening to mainly P_9*.[21] Once formed, reversibility to P_8* through P_6* and P_7* is negligible between 0 and −78 °C. Consequently, Arbusov displacement of TPPO by benzoate anion from both oxyphosphonium ions P_9* and P_{10}* occurs without difficulty.

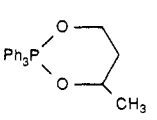
We have independently prepared 1,3,2λ^5-dioxaphospholane P_8* (R = CH_3).[22] Treatment with benzoic acid in CH_2Cl_2 solvent at −78 °C gives a 6.7:1 ratio of C-2:C-1 benzoates. Employing (*S*)-(+)-1,2-propanediol, we have demonstrated that the C-2 benzoate is formed with complete inversion of stereochemistry at the secondary carbinol stereocenter.[21]

We have also obtained direct evidence supporting the presence of both oxyphosphonium ions P_9* and P_{10}*. One equivalent of TPP and BPO initiates monophosphoranylation of 1,2-propanediol in CH_2Cl_2 at −78 °C and exhibits two ^{31}P NMR resonances at δ 62.0 and 63.5. These resonances occur in the region expected for oxyphosphonium ions, and their identity was conclusively confirmed by examining a known mixture (89:11) of 1-methoxy-2-propanol and 2-methoxy-1-propanol in TPP–BPO at −78 °C. ^{31}P NMR examination of the expected mixture of oxyphosphonium ions indicated resonances at δ 62.0 (92%) and 63.5 (8%). We conclude that the upfield resonance is attributable to the 1-methoxy-2-oxa phosphonium ion, and consequently, the ^{31}P resonance of oxyphosphonium ion P_9* should be assigned as δ 62.0.

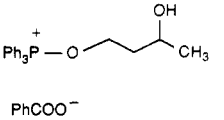
Combining TPP and DAD in THF solvent at 0 °C gave betaine P_{11}* (^{31}P NMR δ 44.9), and addition of 1,2-propanediol gave 1,3,2λ^5-dioxaphospholane P_8* (R = CH_3; ^{31}P NMR δ −37.5). Addition of benzoic acid gives a single substance whose ^{31}P NMR shift is entirely consistent with P_9* (^{31}P NMR δ 62.0).



P_{11}*

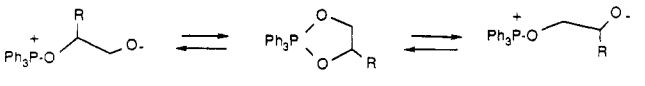


P_{12}•



P_{13}*

1,3-Butanediol gives largely the primary benzoate isomer in the presence of TPP–BPO, and this implies that the 1,3,2λ^5-dioxaphosphorinane intermediate P_{12}* does not form. Consequently, primary phosphoranylation of 1,3-butanediol affords only oxyphosphonium salt P_{13}*, which undergoes simple Arbusov expulsion of TPPO by benzoate anion.



P_{14}* P_8* (R=CH_3) P_{15}•

Finally, the importance of 1,3,2λ^5-dioxaphospholane P_8* (R = CH_3) and the accompanying oxyphosphonium ion P_9* and P_{10}* is demonstrated from the product ratio dependence on solvent polarity. In acetonitrile (ε 36.5), the C-2:C-1 benzoate ratio diminishes to 4:1 compared to that in dichloromethane solvent (ε 3.7). Apparently, the higher polarity solvent is effective in promoting ionization of 1,3,2λ^5-dioxaphospholane P_8* to the corresponding betaines (P_{14}* and P_{15}*) prior to proton-assisted ring opening. As a consequence, betaine P_{15}* should be thermodynamically favored and proton capture from benzoic acid leads directly to P_{10}* and ultimately to the C-1 benzoate.

Experiments are currently under way to develop the full scope of this reaction as a synthetic method for stereoselective entry of various nucleophiles at hindered carbinol sites.

Experimental Section[23]

Diethyl azodicarboxylate is commercially available. Triphenylphosphine was recrystallized from a solution of methanol and petroleum ether, and benzoyl peroxide was purified by recrystallization from chloroform and petroleum ether.

General Procedure for TPP–BPO Benzoylation of Diols. Benzoyl peroxide (242 mg, 1.0 mmol) was added slowly to a flask containing a solution of triphenylphosphine (264 mg, 1.0 mmol) and diol (1.5 mmol) in dichloromethane solvent (20 mL) under an argon atmosphere. The solution was stirred for 1 h at ambient temperature, then washed with a saturated solution of sodium bicarbonate (2 × 10 mL), followed by a washing with water (10 mL), and finally dried ($MgSO_4$). The solvent was removed (rotary evaporator), and the products were isolated by "rapid" chromatographic techniques employing silica gel and 25% ethyl acetate–75% hexanes as eluents.

(17) Kelly, J. W.; Evans, S. A., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 7681.

(18) The ^{31}P NMR shifts for P_3*, P_6*, and P_7* were expected in the range of δ −55 to −60 in accord with other dioxyphosphoranes existing in the trigonal bipyramidal conformation with two apical oxo ligands. For example: $Ph_3P(OEt)_2$[19] (δ −55.1); $Ph_3P(OCH_2CF_3)_2$[20] (δ −70.3); $Ph_3P(OC_6H_{13})_2$[15] (δ −56.2); $Ph_3P(OCH_2CMe_3)$[15] (δ −58.3).

(19) Robinson, P. L.; Barry, C. N.; Kelly, J. W.; Evans, S. A., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 5210.

(20) Kubota, T.; Miyashita, S. ; Kitazume, T.; Ishikawa, N. *J. Org. Chem.* **1980**, *45*, 5052–5057.

(21) Brandstetter, H.; Zbiral, E. *Helv. Chim. Acta* **1978**, *61*, 1831.

(22) The bisphosphoranylation of 1,2-propanediol is easily initiated with diethoxytriphenylphosphorane in toluene solvent. Ethanol and toluene are removed in vacuo to afford largely 1,3,2λ^5-dioxaphospholane P_8*. See ref 15 for experimental details.

(23) All melting points were determined on a Mel-Temp apparatus, and they are uncorrected. HPLC analyses were performed on the LDC Milton-Roy Series 3000 analytical HPLC instrument with hexanes and tetrahydrofuran as eluents. All ^1H, ^{13}C, and ^{31}P NMR data were collected on the Bruker-IBM AC200 NMR spectrometer with tetramethylsilane (Me_4Si) and 85% H_3PO_4 as internal and external standards, respectively. Confirmation of assignment of the C-1 and C-2 benzoates was accomplished by using DEPT NMR techniques.[24]

1-Methoxy-2-propanol and 2-Methoxy-1-propanol. Propylene oxide (38.5 mL, 3.19 g, 0.55 mol) was added to a refluxing solution containing sodium hydroxide (500 mg, 12.5 mmol) and methanol (112 mL, 88.9 g, 2.775 mol). The solution was stirred at reflux for 12 h, allowed to cool to ambient temperature, and then neutralized with a dilute solution of sulfuric acid. The resulting solution was concentrated to dryness (rotary evaporator) to afford an oil. Fractional distillation [bp 35 °C (15 mmHg)][21] gave a mixture containing 88.7% 1-methoxy-2-propanol and 11.3% 2-methoxy-1-propanol as determined by ^{13}C NMR ($CDCl_3$). 1-Methoxy-2-propanol: ^{13}C NMR δ 20.5 (CH_3), 60.1 (OCH_3), 67.4 (CH), and 79.9 (CH_2). 2-Methoxy-1-propanol: ^{13}C NMR δ 17.0 (CH_3), 57.6 (OCH_3), 67.0 (CH_2), and 79.2 (CH).

(*S*)-(+)-1,2-Propanediol. A solution of (*S*)-ethyl lactate (23.6 g, 22.7 mL, 0.2 mol) in 50 mL of tetrahydrofuran was added dropwise (2 h, 0 °C) to a solution of lithium aluminum hydride (5.34 g, 0.141 mol) in anhydrous tetrahydrofuran (300 mL). The resulting mixture was stirred at ambient temperature for 9 h. The mixture was hydrolyzed by addition of water (6.2 mL), 15% aqueous sodium hydroxide (6.2 mL), and more water (18.8 mL). This mixture was refluxed for 1 h, cooled at ambient temperature, and filtered. The tetrahydrofuran filtrate was dried (K_2CO_3), filtered, and evaporated to dryness (rotary evaporator) to afford an oil. Distillation at reduced pressure (2–7 mmHg) gave (*S*)-(+)-1,2-propanediol (10.7 g, 70%): bp 35–40 °C [lit.[22] bp 82–83 °C (10 mmHg)]; ^1H NMR ($CDCl_3$) δ 1.13 (d, 3 H, J = 6.5 Hz, CH_3), 3.3 (m, 2 H, CH_2), 3.7 (m, 1 H, CH), and 4.54 (s, 2 H, OH); ^{13}C NMR ($CDCl_3$) δ 18.7 (CH_3), 67.7 (CH_2), and 68.2 (CH).

Determination of Optical Purity. (i) (*S*)-1-(*tert*-Butyldimethylsiloxy)-2-propanol. A solution of *tert*-butyldimethylsilyl chloride (301 mg, 2.0 mmol), triethylamine (0.3 mL), and a catalytic quantity of (dimethylamino)pyridine (50 mg) in dichloromethane solvent (2 mL) was slowly added to a solution of (*S*)-(+)-1,2-propanediol (0.3 mL, 304 mg, 4.0 mmol) in dichloromethane (3 mL). The solution was stirred overnight (14 h) under a nitrogen atmosphere and washed with water (10 mL), followed by a saturated ammonium chloride solution (10 mL). The solution was dried over Na_2SO_4 and then evaporated to dryness (rotary evaporator) to give (*S*)-1-(*tert*-butyldimethylsiloxy)-2-propanol: ^1H NMR ($CDCl_3$) δ 0.03 (s, 6 H, CH_3), 0.86 (s, 9 H, CH_3), 1.08 (d, 3 H, J = 6.7 Hz, CH_3), 2.55 (s, 1 H, OH), 3.25–3.60 (m, 2 H, CH_2), and 3.75 (m, 1 H, CH); ^{13}C NMR ($CDCl_3$) δ –5.2 ($SiCH_3$), 19.8 ($SiCCH_3$), 18.2 (CH_3), 25.8 ($SiCCH_3$), 67.8 (CH), and 68.5 (CH_2).

(ii) (*S*)-1-(*tert*-Butyldimethylsiloxy)-2-(benzoyloxy)-propane. (*S*)-1-(*tert*-Butyldimethylsiloxy)-2-propanol from above was allowed to react with benzoyl chloride (0.4 mL, 564 mg, 4.0 mmol) in pyridine solvent (4.0 mL) at 25 °C for 48 h. The solution was heated to reflux for 1 min, cooled, and poured into water (10 mL) with stirring. The resulting suspension was extracted with dichloromethane (2 × 10 mL), and the combined extracts were washed with 5% Na_2CO_3 (10 mL) and water (2 × 10 mL), dried ($MgSO_4$), and evaporated to dryness (rotary evaporator). A sample of the residue was examined by NMR: ^1H NMR ($CDCl_3$) δ –0.072 (s, 3 H, CH_3), –0.086 (s, 3 H, CH_3), 0.75 (s, 9 H, CH_3), 1.2 (d, 3 H, J = 6.7 Hz, CH_3), 3.6 (m, 2 H, CH_2), 5.1 (m, 1 H, CH), and 7.8–8.0 (m, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ –5.9 ($SiCH_3$), 16.0 (CH_3), 25.3 ($SiCCH_3$), 65.1 (CH_2), 69.3 (CH), 161.8 (C=O), and 127.6–134.6 (C_6H_5).

(iii) (*S*)-2-(Benzoyloxy)-1-propanol. A 1 M solution of tetra-*n*-butylammonium fluoride (4.0 mL, 4.0 mmol) in tetrahydrofuran was added to (*S*)-1-(*tert*-butyldimethylsiloxy)-2-(benzoyloxy)propane from above in tetrahydrofuran (5 mL) at 0 °C for 5 min. The solution was allowed to come to ambient temperature (3 h) with stirring. Water (5 mL) was added to the solution and stirring continued overnight. Most of the tetrahydrofuran was removed during rotary evaporation, and the remaining aqueous solution was extracted with dichloromethane. The CH_2Cl_2 solution was dried ($MgSO_4$) and evaporated to dryness (rotary evaporator) to afford a residue, which was purified by "rapid" chromatography employing silica gel and 30% ethyl acetate–75% hexanes as eluents: ^1H NMR ($CDCl_3$) δ 1.28 (d, 3 H, J = 6.8 Hz, CH_3), 2.25 (s, 1 H, OH), 3.7 (m, 2 H, CH_2), 5.1 (m, 1 H, CH), and 7.2–8.0 (m, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 16.3 (CH_3), 66.0 (CH_2), 72.9 (CH), 128.3, 128.4, 129.6, 130.1, 133.0, 133.6 (C_6H_5), and 166.6 (C=O). ^1H NMR analyses of the product, 2-(benzoyloxy)-1-propanol, with Eu(hfc)$_3$ indicated a 91.4% ee attributable to (*S*)-(+)-1,2-propanediol. When (*S*)-(+)-1,2-propanediol reacts with TPP–BPO reagent, the 2-(benzoyloxy)-1-propanol obtained from this reaction corresponds to the (*R*)-(–)-2-(benzoyloxy)-1-propanol (92.8% ee) as determined by ^1H NMR–Eu(hfc)$_3$ experiments.

***cis*-4-*tert*-Butylcyclohexyl benzoate**: lit.[25] mp 117–118 °C); ^1H NMR ($CDCl_3$) δ 0.9 (s, 9 H, CH_3), 1.11 (tt, J = 11.4, 3.4 Hz, 1 H, H_4 ax.), 1.44 (dq, J = 12.2, 3.2 Hz, 2 H, $H_{3,5}$ ax.), 1.57 (tt, 2 H, $H_{2,6}$ ax.), 1.66 (br d, J = 12.1 Hz, 2 H, $H_{3,5}$ eq), 2.09 (br d, J = 13.6 Hz, 2 H, $H_{2,6}$ eq), 5.3 (s, 1 H, H_1), 7.4–8.1 (m, 5 H, aromatic hydrogens); ^{13}C NMR ($CDCl_3$) δ 20.6 ($C_{3,5}$), 26.4 (CH_3), 29.6 ($C_{2,6}$), 31.4 (C), 46.4 (C_4), 68.8 (C_1), 127.2–131.7 (aromatic carbons), and 165.5 (C=O). Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 76.70; H, 9.17. (^1H NMR chemical shift assignments were made by using 2D NMR techniques; tt = triplet of triplets; dq = doublet of quartets.) Chromatographic purification of this substance gave an oil, which did not crystallize.

***trans*-4-*tert*-Butylcyclohexyl benzoate**: mp 84–86 °C; ^1H NMR ($CDCl_3$) δ 0.85 (s, 9 H, CH_3), 1.06 (tt, J = 12.3, 3.2 Hz, 1 H, H_4 ax.), 1.18 (dq, J = 13, 3.4 Hz, 2 H, $H_{3,5}$ ax.), 1.46 (dq, J = 12.5, 3 Hz, 2 H, $H_{2,6}$ ax.), 1.86 (br d, J = 13.4 Hz, 2 H, $H_{3,5}$ eq), 2.15 (br d, J = 12.8 Hz, 2 H, $H_{2,6}$ eq.), 4.88 (t, 1 H, H_1), 7.35–8.1 (m, 5 H, aromatic hydrogens); ^{13}C NMR ($CDCl_3$) δ 24.5 ($C_{3,5}$), 26.6 (CH_3), 31.2 ($C_{2,6}$), 31.4 (C), 46.0 (C_4), 73.1 (C_1), 127.3–131.6 (aromatic carbons), and 164.8 (C=O). Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.51; H, 9.19.

Acknowledgment is made to the Department of Energy, the Ford Foundation–National Research Council, the National Science Foundation (CHE-8720270), and the University of North Carolina Research Council for support of this research. We are grateful to Dr. Jeffery W. Kelly and William Murray for their valuable insight, assistance, and suggestions.

Registry No. TPP, 603-35-0; BPO, 94-36-0; DAD, 1972-28-7; BA, 65-85-0; *n*-butyl alcohol, 71-36-3; *sec*-butyl alcohol, 78-92-2; benzyl alcohol, 100-51-6; methyl alcohol, 67-56-1; *n*-propyl alcohol, 71-23-8; isopropyl alcohol, 67-63-0; ethyl alcohol, 64-17-5; *n*-amyl alcohol, 71-41-0; 2-pentyl alcohol, 6032-29-7; cycloheptyl alcohol, 502-41-0; 1,2-propanediol, 57-55-6; styrene glycol, 93-56-1; 1,3-butanediol, 107-88-0; 2-(benzoyloxy)-1-propanol, 51591-52-7; 1-(benzoyloxy)-2-propanol, 37086-84-3; 1,2-bis(benzoyloxy)propane, 19224-26-1; styrene glycol α-benzoate, 53574-78-0; styrene glycol β-benzoate, 10335-95-2; styrene glycol α,β-dibenzoate, 7717-61-5; 1-(benzoyloxy)-3-butanol, 59694-08-5; propylene oxide, 75-56-9; 1-methoxy-2-propanol, 107-98-2; 2-methoxy-1-propanol, 1589-47-5; (*S*)-ethyl lactate, 687-47-8; (*S*)-(+)-1,2-propanediol, 4254-15-3; (*S*)-1-(*tert*-butyldimethylsiloxy)-2-propanol, 113534-13-7; (*S*)-1-(*tert*-butyldimethylsiloxy)-2-(benzoyloxy)propane, 113534-14-8; (*S*)-2-(benzoyloxy)-1-propanol, 113566-73-7; (*R*)-2-(benzoyloxy)-1-propanol, 113566-74-8.

(24) Rahman, A.-u. *Magnetic Resonance: Basic Principles*; Springer-Verlag: New York, 1986; pp 227–233.

(25) Foster, A. B.; Jefferis, R.; Webber, J. M. *Carbohydr. Res.* **1967**, *4*, 352.