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Enantioselective Acylation Using a Second-Generation *P*-Aryl-2-phosphabicyclo[3.3.0]octane Catalyst

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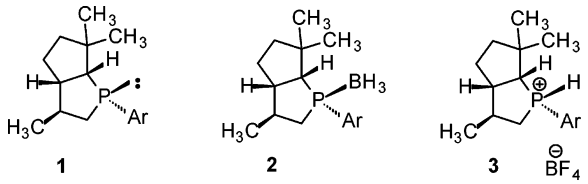
Received May 26, 2004

Abstract: The synthesis of *P*-aryl-2-phosphabicylco[3.3.0]-octane·HBF_4 salts **3a** and **3c** is described. Incorporation of the *P*-3,5-di-*tert*-butyl-4-methoxyphenyl group in **3c** allows use of a less expensive aryl bromide starting material. Deprotonation of the air-stable salts in situ with triethylamine releases the corresponding phosphines **1a** and **1c** for use in the kinetic resolution of representative secondary alcohols. The method is convenient for small-scale experiments and affords enantioselectivities *s* close to the values obtained using the free phosphines **1a** and **1b** in cases where *s* is ca. 40 or lower.

In 1993, a report from our laboratory demonstrated that tri-*n*-butylphosphine serves as a nucleophilic acylation catalyst,[1a] a discovery that eventually led to the development of the enantioselective *P*-aryl-2-phosphabicyclo[3.3.0]octane ("PBO") catalysts **1a**,**b**.[1b,c] The 3,5-di-*tert*-butylphenyl derivative **1b** was preferred for most applications because it is more effective for enantioselective acyl transfer compared to **1a**. However, the synthesis of **1b** starts from the expensive 3,5-di-*tert*-butyl-1-bromobenzene.[2] An analogue **1c** has now been prepared from the cheaper 2,6-di-*tert*-butyl-4-bromophenol and has been tested in acyl transfer reactions.

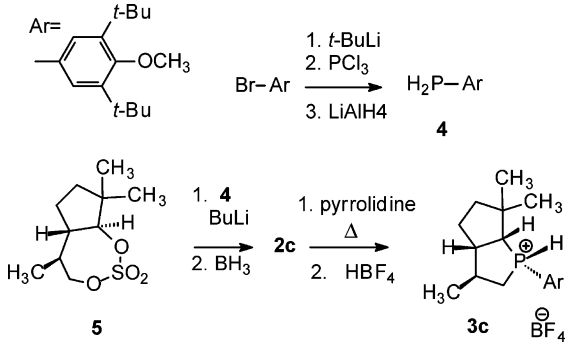
We have also reevaluated the methodology for preparing catalyst solutions containing **1a**,**b**. In the last step of our published route, phosphorus was protected by complexation with borane[3] to allow isolation and purification. The free phosphines **2a**,**b** were then released as needed by warming with pyrrolidine followed by filtration chromatography. This procedure was relatively simple, but attempts to quantify the amount of free phosphine or to transfer the material often resulted in partial oxidation, especially in small-scale experiments.[4] We were therefore interested in the recent report of Fu et al. where air-stable trialkylphosphonium tetrafluoroborate salts were used as versatile sources of air-sensitive trialkylphosphines.[5] We have compared this approach with the borane decomplexation technique in the case of catalysts **1a** and **1c**, generated in situ from **3a** and **3c** as described below.



1 **2** **3** BF_4^-

a Ar = Ph **b** Ar = 3,5-*t*-Bu_2Ph **c** Ar = 3,5-*t*-Bu_2-4-MeO-Ph

Our study began with the synthesis of **2c**. The starting arylphosphine **4** was prepared from 4-bromo-2,6-di-*tert*-butyl phenol by *O*-methylation[6] and the usual sequence of bromine−lithium exchange, reaction with PCl_3, and reduction with $LiAlH_4$.[1b,c] The conversion to the phosphine **1c** was then carried out by lithiating **4** and reacting the derived lithiophosphide with the cyclic sulfate **5**.[1b,c] Subsequent treatment with THF−borane gave the complex **2c** in 87% yield. Decomplexation of **2c** with pyrrolidine afforded the free phosphine **1c**, and protonation with aqueous HBF_4 produced the phosphonium tetrafluoroborate salt **3c** in 90% yield. Crystallization provided pure precatalyst **3c** as a moderately hygroscopic solid, but no decomposition was observed over 6 months for a sample that was stored in a vial and frequently opened to air.



4 **5** **3c** BF_4^-

The *P*-phenyl precatalyst **3a** was obtained by a similar approach. Thus, the free phosphine **1a** was generated by decomplexation of **2a** with warm pyrrolidine, and aqueous HBF_4 in CH_2Cl_2 was added. Removal of solvent afforded phosphonium tetrafluoroborate **3a** as a white powder that was contaminated with a small amount of unreacted phosphine borane, but crystallization gave pure **3a** in 86% yield. The crystalline salt was exposed

(1) (a) Vedejs, E.; Diver, S. T. *J. Am. Chem. Soc.* **1993**, *115*, 3358. (b) Vedejs, E.; Daugulis, O. *J. Am. Chem. Soc.* **1999**, *121*, 5813. (c) Vedejs, E.; Daugulis, O. *J. Am. Chem. Soc.* **2003**, *125*, 4166. (d) Vedejs, E.; MacKay, J. A. *Org. Lett.* **2001**, *3*, 535.

(2) 3,5-Di-*tert*-butylbromobenzene is commercially available from Aldrich for $130/5 g.

(3) For selected reviews on phosphine boranes, see: (a) Brunel, J. M.; Faure, B.; Maffei, M. *Coord. Chem. Rev.* **1998**, *180*, 665. (b) Ohff, M.; Holz, J.; Quirmbach, M.; Borner, A. *Synthesis* **1998**, 1391.

(4) The best procedure from the borane complex is to decomplex a substantial amount of the phosphine borane and to immediately divide it between several reactions. Alternatively, the phosphine can be stored in the solid state or in hydrocarbon solution, but both methods of storage require rigorous exclusion of air, and oxidation has been observed over extended periods of time. Solutions of PBO catalysts in deoxygenated toluene or benzene can be stored outside the glovebox in a flask under a good rubber septum for 1−2 months before the phosphine oxide is observable by ^{31}P NMR.

(5) Netherton, M. R.; Fu, G. C. *Org. Lett.* **2001**, *3*, 4295.

(6) Miller, B. *J. Org. Chem.* **1965**, *30*, 1964.

10.1021/jo049112p CCC: $27.50
Published on Web 09/04/2004

TABLE 1. Enantioselective Acylations Catalyzed by 3a[a]

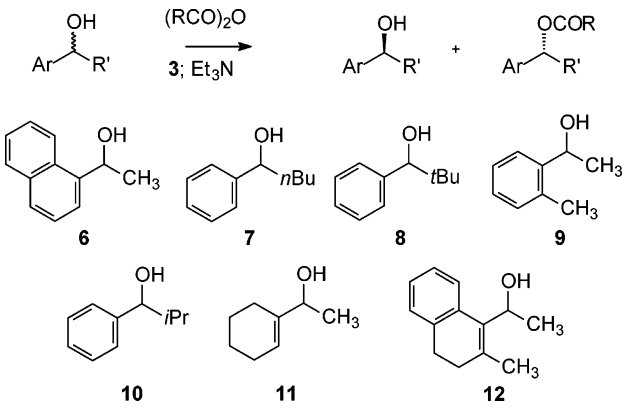
entry	alcohol	R	solvent	T (°C)	s (**3a**/Et_3N)	s (**1a**)
1	**6**	*i*-Pr	toluene	rt	21	(21)[b]
2	**7**	*i*-Pr	toluene	rt	13	(11)[b]
3	**8**	Ph	toluene	rt	24	(24)[b]
4	**6**	3-Py[c]	3:1 *t*-AmOH/DCM[d]	−25	23	(20)
5	**7**	3-Py[c]	3:1 *t*-AmOH/DCM[d]	−25	16	
6	**8**	3-Py[c]	3:1 *t*-AmOH/DCM[d]	−25	47	(57)
7	**9**	3-Py[c]	3:1 *t*-AmOH/DCM[d]	−25	16	(17)

[a] All reactions used 0.1 M substrate in the given solvent with a ca. 1:2 ratio of precatalyst/Et_3N and 2.5 equiv of anhydride unless noted. [b] Reference 1c. [c] 0.5 equiv of anhydride and 1 equiv of Et_3N. [d] *t*-AmOH = *tert*-amyl alcohol; DCM = CH_2Cl_2.

to the air for 1 week and was found to be mildly hygroscopic, but no decomposition was observed.

PBO tetrafluoroborate salt **3a** was tested as a precatalyst in several acylation reactions via in situ deprotonation with Et_3N (Table 1). Alcohols **6** and **7** were initially chosen as representative substrates from the aryl alkyl carbinol series, and their isobutyroylations using the in situ **3a**/Et_3N method proceeded with selectivities similar to those observed for reactions catalyzed by preformed **1a** (from **2a** and pyrrolidine, entries 1 and 2). The benzoylation of **8** with **3a**/Et_3N also occurred with selectivity comparable to that of the preformed phosphine catalyst **1a**.

In addition, several other substrates were tested in nicotinoylation reactions with nicotinic anhydride.[7] This reagent was expected to mimic the steric effect of benzoic anhydride but to react faster due to the electron-withdrawing effect of pyridine nitrogen. Indeed, the reactions were considerably faster (ca. 5-fold) and were conveniently conducted using 0.5 equiv of the anhydride, in contrast to the benzoylations where 2.5 equiv of the anhydride was necessary. The nicotinoylations were performed in 3:1 *tert*-amyl alcohol/CH_2Cl_2 at −25 °C, entries 4−7, with CH_2Cl_2 added to prevent freezing of *tert*-amyl alcohol at low temperatures and to provide solubility for nicotinic anhydride. Aryl alkyl carbinols **6**−**9** all exhibited high selectivities, with a particularly high value of $s = 47$ obtained for the hindered substrate **8**, although this substrate exhibited even better selectivity with catalyst **1a** under the same conditions.



Next, the more highly substituted precatalyst **3c** was tested in acylation reactions with Et_3N added to release the catalyst **1c** in situ (Table 2). The isobutyroylation of **6** at rt worked well, and $s = 30$ was observed, marginally lower than the value of $s = 35$ obtained with the preformed catalyst **1b** (entry 1). In contrast, the results using nicotinic anhydride were relatively poor (entries 2 and 3), suggesting that this reagent is not well matched for use with catalyst **1b**. A similar drop in enantioselectivity has been observed in our earlier studies for reactions where benzoic anhydride was activated by catalyst **1b**, as also shown in the example of entry 8 vs entry 9. On the other hand, the benzoylation of the hindered alcohol **8** proceeded with similar, modest selectivity using either catalyst (entries 5 and 6). No further experiments were performed with nicotinic or benzoic anhydrides in this series.

TABLE 2. Enantioselective Acylations Catalyzed by 3c[a]

entry	alcohol	R	solvent	cat. (%)	time (h)	conv (%)	T (°C)	s (**3c**)	s (**1b**)[b]
1	**6**	*i*-Pr	toluene	6	1.5	35	rt	30	(35)
2	**6**	3-Py	toluene	1	0.17	58	rt	7	
3	**6**	3-Py[c]	toluene	2	4.5	28	−40	8.1	
4	**7**	*i*-Pr	heptane	2	9.5	52	−40	40	(55)
5	**8**	*i*-Pr	toluene	15	139	19	rt	13	(10)
6	**8**	Ph	toluene	9	3.5	49	rt	10.2	(10)
7	**9**	*i*-Pr	heptane	1	16	48	−40	65	(145)
8	**10**	Ph	toluene	4	1	57	rt	5.2	(6.9)
9	**10**	*i*-Pr	heptane	2	45.5	46	−40	82	(99)
10	**11**	*i*-Pr	heptane	5	13	52	−40	34	(52)
11	**12**	*i*-Pr	heptane	7	64	55	−40	49	(82)

[a] Reactions used 0.1 M substrate and ca. 1:2 **3c**/Et_3N and 2.5 equiv of anhydride unless noted. [b] Reference 1c. [c] 1 equiv of anhydride.

A number of isobutyroylations were studied (entries 4, 5−7, and 9−11) and afforded selectivities comparable to those obtained with the previously optimized catalyst **1b** at room temperature. However, differences between **3c**/Et_3N and **1b** became apparent at lower temperatures. Three isobutyroylation reactions of benzylic alcohols were conducted in heptane at −40 °C (entries 4, 7, and 9), the optimized conditions for catalyst **1b**. All three examples gave high selectivities with **3c**/Et_3N, but the *s* values were diminished compared to those using **1b**. Two additional substrates **11** and **12** were isobutyroylated with precatalyst **3c** in heptane at −40 °C to represent the allylic alcohol category as previously reported.[1b,c] Alcohol **11** reacted with $s = 34$ (compare to $s = 52$ using catalyst **1b**)[1b−d] and **12** gave $s = 49$ (compare to $s = 82$ using catalyst **1b**).[1d]

Clearly, the in situ generation of phosphine **1c** from **3c** /Et_3N serves as an effective source of the acylation catalyst **1c** for the kinetic resolution of aryl alkyl carbinols and allylic alcohols for those reactions where *s* is below ca. 40. Somewhat lower *s* values observed with precatalyst **3c** compared to preformed catalyst **1b** are probably due to intrinsic differences between the two aryl groups. Interference by the Et_3N and the derived $Et_3N{\cdot}HBF_4$ may be a factor in some of the most highly selective low-temperature reactions, but the findings of Table 1 suggest that the in situ procedure does not cause substantial deterioration of enantioselectivities compared to the use of preformed catalyst when enantioselctivites *s* are in the range of 10−40.

In summary, we have prepared air-stable PBO tetrafluoroborate salts (**3a** and **3c**) as precursors to PBO

(7) Badgett, C. O. *J. Am. Chem. Soc.* **1947**, *69*, 2231.

catalysts. In accord with the Fu precedent,[5] these salts are trivial to handle, even on a small scale, and serve as convenient precatalysts for PBO-catalyzed kinetic resolutions. The stability of the salts allows accurate quantification of the precatalyst in air, and in situ deprotonation with Et_3N releases the free phosphines in typical acylation experiments. Precatalyst **3a** usually gives products with enantioselectivities comparable to those with **1a**. Precatalyst **3c** affords similar room-temperature enantioselectivity compared to the optimized PBO catalyst **1b**, but the beneficial effect of lower reaction temperatures is more pronounced for **1b**. Overall, the in situ generation of **1a** and **1c** is competitive with many of the recently described alternatives for nonenzymatic kinetic resolution of unsaturated alcohol substrates.[8]

Experimental Section

(1*R*,2*R*,4*S*,5*S*)-4,8,8-Trimethyl-2-phenylphosphabicyclo-[3.3.0]octane·HBF$_4$ (3a). Phosphine borane **2a**[1c] (79 mg, 0.30 mmol) was added to a round-bottom flask equipped with a magnetic stir bar and reflux condenser. The flask was flushed with N_2 for 30 min, and then pyrrolidine (8 mL, distilled from CaH_2) was added. The resulting solution was heated at 50 °C in an oil bath for 100 min. Pyrrolidine was evaporated (N_2 stream), and the residue was filtered through a 10 × 1.2 cm pad of silica gel (the flask and the column containing silica gel were purged with N_2 for 1 h) in benzene under N_2, collecting 50 mL. The solvent was evaporated (N_2 stream) and taken up in CH_2Cl_2 (3 mL, degassed). Aqueous HBF_4 (50 wt %%, 0.3 mL, 2.12 mmol) was added via syringe, and the resulting mixture was stirred for 15 min. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL). The organic layers were combined, dried ($MgSO_4$), and filtered. Removal of solvent (aspirator) provided a white powder. Pure material (87 mg, 86% yield) was obtained by dual chamber crystallization from ether/CH_2Cl_2: mp 136−137 °C; HRMS calcd for $C_{16}H_{24}P^+$ 247.16160, found *m*/*z* 247.1607, error = 4 ppm; IR (neat, cm^{-1}) 1033, PH; 500 MHz NMR ($CDCl_3$, ppm) δ 7.91−7.84 (2 H, m) 7.79−7.74 (1 H, m) 7.65 (2 H, ddd, J = 7.8, 7.8, 3.4 Hz) 7.57 (1 H, d, J = 21.0 Hz) 3.57 (1 H, ddd, J = 9.8, 9.8, 6.2 Hz) 2.95−2.79 (3 H, m) 2.42−2.32 (1 H, m) 2.20−2.12 (1 H, m) 1.72−1.53 (3 H, m) 1.33 (3 H, d, J = 6.2 Hz) 1.12 (3 H, s) 0.65 (3 H, s); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 135.1 (d, J = 4.6 Hz), 133.3 (d, J = 10.7 Hz), 130.4 (d, J = 13.7 Hz), 115.6 (d, J = 73.2 Hz), 54.5 (d, J = 7.6 Hz), 50.3 (d, J = 42.7 Hz), 44.2 (d, J = 7.6 Hz), 44.1 (d, J = 3.1 Hz), 42.4 (d, J = 9.2 Hz), 30.1 (d, J = 6.1 Hz), 29.2, 29.0 (d, J = 58.0 Hz), 25.4 (d, J = 6.1 Hz), 19.9 (d, J = 13.7 Hz); ^{31}P NMR (162 MHz {H}, $CDCl_3$, ppm) δ 20.3; ^{19}F NMR (376 MHz, $CDCl_3$, ppm) δ −151.4.

3,5-Di-*tert*-butyl-4-methoxyphenylphosphine (4). A solution of 3,5-di-*tert*-butyl-4-methoxybromobenze[6] (10.2 g, 34.2 mmol) in THF (150 mL) was slowly added via cannula to a solution of *t*-BuLi (45 mL, 1.66 M solution in pentane) at −78 °C. The solution immediately turned yellow and cloudy. After the solution was stirred for 10 min, a solution of $ZnCl_2$ (fused under vacuum and diluted to ca. 1 M solution in THF; 50 mL) was added dropwise via cannula (ca. 10 min) and stirred at −78 °C for 15 min. The cooling bath was removed, and the mixture was allowed to warm to room temperature and stirred for 30 min. Next, the mixture was transferred via cannula onto a solution of freshly distilled PCl_3 (4.5 mL, 51.3 mmol) in THF (85 mL) at −78 °C over ca. 70 min. After being stirred for 30 min at −78 °C, the mixture was warmed to room temperature and was stirred for 1.5 h. Assay by ^{31}P NMR (unlocked, crude reaction mixture) showed the presence of $ArPCl_2$ (δ_P = 166.1 ppm). The crude solution of $ArPCl_2$ was added dropwise to a stirred suspension of $LiAlH_4$ (7.7 g, 202.8 mmol) in ether (150 mL) at −78 °C via cannula over 1 h. After addition, the suspension was warmed to room temperature (1 h) and then carefully quenched at 0 °C with degassed (N_2 purge, 1 h) NH_4Cl solution in water (ca. 70 mL of 1:1 saturated solution/H_2O). The supernatant liquid was transferred via cannula onto $MgSO_4$ in an N_2-purged flask; the Al salt residue was shaken with ether (2 × 100 mL; all transfers with cannula under N_2 pressure); and all the organic layers were combined over $MgSO_4$. The liquid was decanted away from $MgSO_4$ (cannula), and the precipitate was washed with ether (50 mL). Solvents were evaporated (N_2 stream), and the residue was distilled in vacuo through a 10-cm Vigreaux column (STENCH!). The first fraction was collected at 60−64 °C/0.1 mm, 650 mg and was impure; the second fraction was collected at 64−68 °C/ 0.1 mm, 3.3 g and was ca. 85% pure **4** (contaminated with the arene from replacement of Br by H). This product was used in the subsequent step without additional purification: 500 MHz NMR (C_6D_6, ppm) δ 7.54 (2 H, d, J = 8.1 Hz) 3.84 (2 H, d, J = 97.8 Hz) 3.38 (3 H, s) 1.43 (18 H, s); ^{31}P NMR (161.9 MHz {H}, C_6D_6, ppm) δ −122.6.

(1*R*,2*R*,4*S*,5*S*)-4,8,8-Trimethyl-2-(3′,5′-di-*tert*-butyl-4′-methoxyphenyl)phosphabicyclo[3.3.0]octane Borane Complex (2c). The compound was prepared by modification of a literature procedure.[1c] To a solution of 3,5-di-*tert*-butyl-4-methoxyphenylphosphine **4** (252 mg, 0.84 mmol) in THF (6 mL) was added *n*-BuLi (0.53 mL of a 1.65 M solution in hexanes, 0.88 mmol, Acros) at 0 °C. The resulting yellow solution was cooled to −78 °C after being stirred for 10 min. Next, a solution of cyclic sulfate **5**[1c] (164 mg, 0.70 mmol, 99.7%ee) in THF (3 mL) was added over 4 min via cannula. The yellow solution was stirred at −78 °C for 10 min. The cooling bath was removed, and the solution was allowed to warm to room temperature (ca. 30 min). Stirring was continued at room temperature for 1 h, during which time the solution went colorless. The solution was recooled to −78 °C, and additional *n*-BuLi (0.53 mL of a 1.65 M solution in hexanes, 0.88 mmol) was added. The solution turned orange-yellow and was stirred at −78 °C for 10 min. The solution was then warmed to room temperature (ca. 30 min) and stirred for 2 h. Assay by ^{31}P NMR (unlocked, crude reaction mixture) showed the formation of the desired phosphine (−3.1 ppm) as a single diastereomer along with unidentified secondary phosphines (−60.3 ppm). After addition of borane−THF (2.5 mL of a 1 M solution in THF), the solution became colorless and was stirred for 30 min. The solvent was evaporated (N_2 stream), HCl (5 mL of a 5% solution in water) and CH_2Cl_2 (5 mL) were added, and the mixture was extracted with CH_2Cl_2 (3 × 15 mL). The extracts were combined, dried ($MgSO_4$), and filtered. After removal of solvent (aspirator), the residue was purified by flash chromatography (15 × 3 cm), hexanes/toluene 2:1 eluent. Elution of 375 mL of solvent was followed byproduct in the next 430 mL. Evaporation (aspirator) yielded 245 mg (87%) of **2c**. Analytical TLC, 2:1 hexane/toluene, R_f = 0.15. Pure material was obtained by crystallization from hexane: mp 83−85 °C; α_D = +10.6 (c = 0.58, EtOAc); HRMS calcd for $C_{25}H_{44}BNaOP$ 425.31210, found *m*/*z* 425.3118, error = 1 ppm; IR (neat, cm^{-1}) 2265, BH; 400 MHz NMR ($CDCl_3$, ppm) δ 7.60 (2 H, d, J = 11.0 Hz) 3.68 (3 H, s) 2.63−2.41 (3 H, m) 2.29−2.16 (1 H, m) 2.06−1.94 (1 H, m) 1.87 (1 H, ddd, J = 15.4, 11.7, 4.0 Hz) 1.55−1.34 (3 H, m) 1.5−0.3 (3 H, br m) 1.43 (18 H, s) 1.20 (3 H, d, J = 5.9 Hz) 0.98 (3 H, s) 0.46 (3 H, s); ^{13}C NMR (125.7 MHz, $CDCl_3$, ppm) δ 162.3, 144.1 (d, J = 10.1 Hz), 131.5 (d, J = 10.1 Hz), 121.1 (d, J = 44.9 Hz), 64.5, 56.6 (d, J = 31.1 Hz), 54.8 (d, J = 2.7 Hz), 44.2, 44.1, 43.2, 36.0 (d, J = 38.5 Hz), 36.0, 31.9, 30.7 (d, J = 4.6 Hz), 29.3 (d, J = 4.6 Hz), 24.1 (d, J = 4.6 Hz), 20.9 (d, J = 10.1 Hz); ^{31}P NMR (161.9 MHz, {H}, $CDCl_3$, ppm) δ 31.0, br m.

(1*R*,2*R*,4*S*,5*S*)-4,8,8-Trimethyl-2-(3′,5′-di-*tert*-butyl-4′-methoxyphenyl)phosphabicyclo[3.3.0]octane·HBF$_4$ (3c).

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Phosphine borane **2c** (320 mg, 0.79 mmol) was added to a round-bottom flask equipped with a magnetic stir bar and reflux condenser. The flask was flushed with N_2 for 30 min, and pyrrolidine (25 mL, distilled from CaH_2) was then added. The resulting solution was heated at 50 °C in an oil bath for 100 min. Pyrrolidine was evaporated with an N_2 stream, and the residue was filtered through a 10 × 1.2 cm pad of silica gel (the flask and the column containing silica gel were purged with N_2 for 1 h) in toluene under N_2, collecting 50 mL. The solvent was evaporated (N_2 stream) and taken up in CH_2Cl_2 (12 mL, degassed). Aqueous HBF_4 (50 wt %%, 0.8 mL, 5.53 mmol) was added via syringe, and the resulting mixture was stirred for 15 min. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL). The organic layers were combined, dried ($MgSO_4$), and filtered. Removal of solvent (aspirator) provided a 9:1 mixture of the desired phosphonium salt and phosphine borane **2c** by NMR assay. The phosphine borane was removed (recovered 28 mg of **2c**, 9%) by trituration with hexanes providing 339 mg (90%) of a white powder. Pure material was obtained by crystallization from ether: mp 142−148 °C; HRMS calcd for $C_{25}H_{42}OP^+$ 389.29740, found *m*/*z* 389.2976, error = 1 ppm; IR (neat, cm^{-1}) 1060, PH; 400 MHz NMR ($CDCl_3$, ppm) δ 7.6 (2 H, d, J = 15.4 Hz) 7.49 (1 H, d, J = 17.1 Hz) 3.69 (3 H, s) 3.49−3.40 (1 H, m) 2.92−2.76 (2 H, m) 2.73−2.61 (1 H, m) 2.33−2.18 (1 H, m) 2.18−2.05 (1 H, m) 1.68−1.42 (3 H, m) 1.4 (18 H, s) 1.29 (3 H, d, J = 6.6 Hz) 1.05 (3 H, s) 0.58 (3 H, s); ^{13}C NMR (100.57 MHz, $CDCl_3$, ppm) δ 166.0, 147.6 (d, J = 12.2), 132.0 (d, J = 13.7 Hz), 108.3 (d, J = 76.3 Hz), 65.2, 54.5 (d, J = 9.1 Hz), 50.3 (d, J = 44.2 Hz), 44.3 (d, J = 6.1 Hz), 44.1 (d, J = 3.1 Hz), 42.7 (d, J = 7.6 Hz), 36.5, 31.9, 30.3 (d, J = 6.1 Hz), 29.5 (d, J = 6.1 Hz), 29.4 (d, J = 48.8 Hz), 25.0 (d, J = 6.1 Hz), 20.2 (d, J = 12.2 Hz); ^{31}P NMR (161.91 MHz, {H}, $CDCl_3$, ppm) δ 19.5; ^{19}F NMR (376.3 MHz, $CDCl_3$, ppm) δ −151.6.

Acknowledgment. This work was supported by the National Science Foundation. We also thank Mr. S. A. Shaw and Ms. N. Tuttle for preparation of cyclic sulfate **4**.

Supporting Information Available: Characterization data and kinetic resolution procedures, general procedure for benzoylations and nicotinoylations, and NMR spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JO049112P