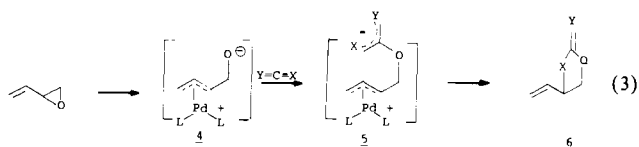
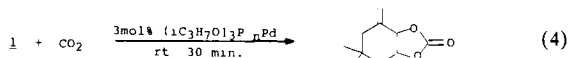


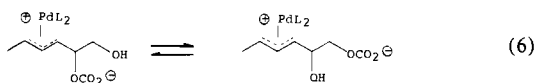
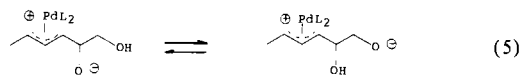
anion be a reasonable enough nucleophile to subsequently cyclize to constitute a useful approach (eq 3). The choice of the proper



catalyst proved to be critical in the realization of such a scheme. With a goal of *cis*-diol formation, pilot experiments used CO₂ and (Ph₃P)₄Pd. Reactions led to little to no reaction and fairly rapid deposition of a black solid, presumably Pd black. Anticipating that the basicity of the Ph₃P leads to its being stripped from the Pd by preferential coordination to CO₂, switching to a less basic phosphorus ligand may overcome destruction of the active catalyst. Indeed, generating a Pd(0) complex in situ using triisopropyl phosphite as the ligand with **1** as the substrate leads to an excellent yield of the carbonate as exemplified in eq 4 and generalized in Table I. The mildness of the reaction conditions, room temperature and 40 psi of pressure, is especially noteworthy.



Considering the high reactivity of vinyl carbonates as substrates for Pd(0),⁸ the excellent yields demonstrate the much higher reactivity of the vinyl epoxides which we believe, in part, stems from carbon dioxide serving as a co-catalyst. Entry 7 lends some credence to this suggestion. Equilibration of either the initial alkoxide or carbonate as in eq 5 or 6 might have led to six-

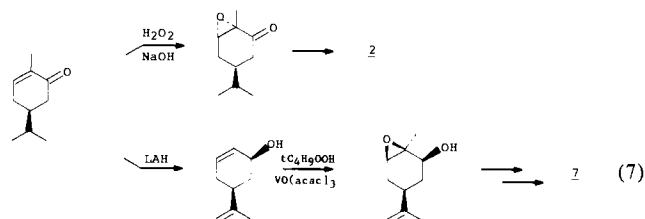


membered rings. None form. Such high chemoselectivity even in the presence of a potential neighboring group enhances the applicability of this approach. Thus, these reactions proceed rapidly at room temperature in contrast to other Pd-catalyzed reactions of vinyl epoxides. It does require a slightly elevated CO₂ pressure (40 psi) for satisfactory results. While formation of the carbonate is rapid (i.e., 4 → 5, eq 3), the second stage, cyclization of **5** to product **6**, is slow enough that a *cis* olefin completely isomerizes to a *trans* olefin prior to cyclization (Table I, entry 5) but fast enough that equilibration of the carbonate as in eq 6 does not occur.

The reaction exhibits high chemo-, regio-, and diastereoselectivity in both cyclic and acyclic cases. The effectiveness of this approach is illustrated by the efficiency of the *cis* carbonate formation with **2** in contrast to the failure of any trapping with a carboxylic acid (eq 2). Entry 6 is quite interesting since it contains a vinyl epoxide and a butenolide, both of which can be envisioned to be activated by Pd(0). The unfavorable geometry of the latter leaving group may account for its failure to react. Entries 3 and 4 nicely highlight the stereochemical control available in this equivalent of a *cis* hydroxylation. Vinyl epoxide **2** derives from the direct epoxidation of carvone followed by olefination, whereas the hydroxyl directed epoxidation establishes the stereochemistry of the vinyl epoxide **7** (eq 7). Having each diastereomeric epoxide translates into having either *cis*-diol.

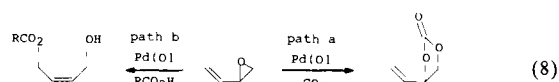
A typical experimental procedure follows. A mixture of 6.4 mg (0.029 mmol, 3 mol %) of palladium acetate and 49 μL (0.20 mmol) of triisopropyl phosphite in 1.5 mL of THF was stirred 10 min at room temperature. A solution of *n*-butyllithium (38

(8) Trost, B. M. In "New Synthetic Methodology and Biologically Active Substrates"; Yoshida, Z., Ed.; Kodansha Ltd.: Tokyo, 1981; p 78. Trost, B. M.; Runge, T. A. *J. Am. Chem. Soc.* **1981**, *103*, 7550. Also see: Tsuji, J.; Shimizu, I.; Minami, I.; Ohashi, Y. *Tetrahedron Lett.* **1982**, *23*, 4809.



μL of 1.5 M hexane solution, 0.057 mmol) was added. After 30 min, the resultant catalyst solution was added to a stirring solution of 156.5 mg (0.954 mmol) of **7** in 1.5 mL of THF in a Griffin-Worden pressure bottle (Kontes) under a CO₂ atmosphere and then pressurized to 40 psi with CO₂. After 4 h, the solution was concentrated in vacuo and the residue chromatographed to give 188.6 mg (95%) of cyclic carbonate.

The current reaction effects a regio- and diastereoselective synthesis of *cis*-1,2-diols from vinyl epoxides (path a, eq 8); whereas, with use of carboxylic acids as partners for Pd-mediated condensation with vinyl epoxides, a *cis*-1,4-diol synthesis results (path b, eq 8). From a single substrate, palladium templates,



which enforce substitution with retention of configuration, also allow control of regioselectivity by converting an intermolecular into an intramolecular delivery of a nucleophile—a flexibility that should prove useful in the synthesis of polyoxygenated natural and unnatural products.⁹

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health for their generous support of our programs.

(9) After the submission of this paper, the single reaction of butadiene monoepoxide with CO₂ mediated by (Ph₃P)₄Pd has been described: Fujinami, T.; Suzuki, T.; Kamiya, M. *Chem. Lett.* **1985**, 199. We had found that the reaction of entry 6 with use of (Ph₃P)₄Pd as catalyst failed—depositing only Pd black. Further attempts using this catalyst for entry 1 have also failed in our hands.

Isolation of Oxo-Centered Cobalt(III) Clusters and Their Role in the Cobalt Bromide Catalyzed Autoxidation of Aromatic Hydrocarbons

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Oxo-centered transition-metal cluster complexes¹⁻⁶ of the formula [M₃O(OAc)₆L₃]X, where M = Fe, Mn, Cr, Rh, and Ir and L = pyridine, β-picoline, H₂O, and methanol, and other heteronuclear clusters²⁻⁵ have recently been the subject of many spectroscopic studies. These types of complexes are of interest because they may be catalysts or catalyst intermediates in the oxidation of many organic substrates.⁷⁻⁹ Of particular interest

(1) Johnson, M. K.; Powel, D. B.; Cannon, R. D. *Spectrochim. Acta, Part A* **1981**, *37A*, 995.

(2) Blake, A. B.; Yavaci, A., *J. Chem. Soc., Chem. Commun.* **1982**, 1247.

(3) Johnson, M. K.; Cannon, R. D.; Powell, D. B. *Spectrochim. Acta, Part A* **1982**, *38A*, 307.

(4) Baikie, A. R. E.; Hursthouse, M. B.; New, D. B.; Thornton, P. *J. Chem. Soc., Chem. Commun.* **1978**, 62.

(5) Blake, A. B.; Yavaci, A.; Kubicki, H., *J. Chem. Soc., Chem. Commun.* **1981**, 796.

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(8) Barton, D. H. R.; Gastizer, M. J.; Motherwell, W. B. *J. Chem. Soc., Chem. Commun.* **1983**, 731.

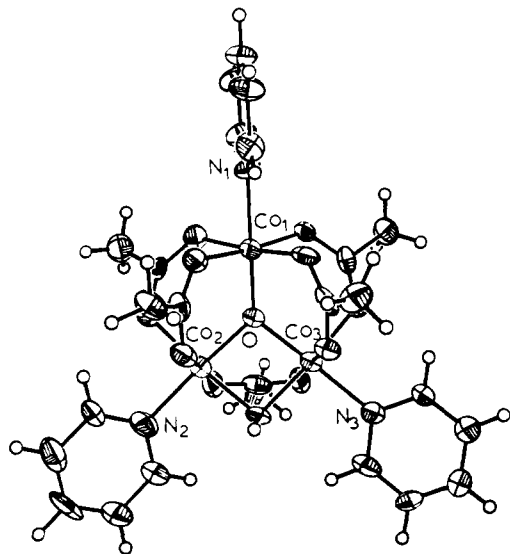
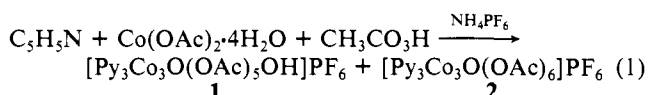


Figure 1. Perspective ORTEP drawing of the $[\text{Py}_3\text{Co}_3\text{O}(\text{OAc})_5\text{OH}]^+$ cation in crystalline $[\text{Py}_3\text{Co}_3\text{O}(\text{OAc})_5\text{OH}][\text{PyCoBr}_3]$. Nonhydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density; hydrogen atoms are represented by arbitrarily small spheres which are in no way representative of their true thermal motion.

are clusters where $M = \text{Co}$ because these clusters may be involved in the cobalt-catalyzed autoxidation of *p*-xylene to terephthalic acid. We wish to report the synthesis, characterization, and reactivity of the first fully characterized oxo-centered cobalt clusters, $[\text{Py}_3\text{Co}_3\text{O}(\text{OAc})_5\text{OR}]^+ \text{X}^-$ (Py = pyridine; R = H, CH_3CO ; X = PyCoBr_3 , OAc, PF_6),^{6,10} and present evidence that they are possible catalyst intermediates in cobalt-catalyzed autoxidation of aromatic hydrocarbons.

Treatment of an acetic acid solution of cobaltous acetate, pyridine, and NH_4PF_6 with one molar equivalent of peracetic acid (35%) at room temperature resulted in the immediate formation of a brown crystalline solid. This solid was identified as a mixture of **1** and **2** (eq 1), and the isolated yield was 87%.



The cations of **1** and **2** can also be prepared as their $[\text{PyCoBr}_3]^-$ salts by the peracetic acid oxidation of cobalt bromide in the presence of pyridine. The clusters **1** and **2** are interconvertible¹¹ in acetic acid, and can be separated by fractional crystallization from CH_2Cl_2 /hexane. ^1H NMR experiments have shown that **1** and **2** are initially formed as their acetate salts and are the only pyridine complexes present. Both compounds have been characterized spectroscopically,¹² and the $[\text{PyCoBr}_3]^-$ salt of **1** was

(9) Fristod, W. E.; Peterson, J. R. *Tetrahedron Lett.* **1983**, *24*, 4547.

(10) Ziolkowski, J. J.; Pruchnik, F.; Szymanska-Buzar, T. *Inorg. Chim. Acta* **1973**, *7*, 473.

(11) The relative concentrations of **1** and **2** in acetic acid depend upon the amount of water present in solution. No attempt has been made to distinguish between the reactivities of **1** and **2**.

(12) The ^1H NMR (400 MHz) spectrum of **1** (CD_2Cl_2 ; δ) displayed signals at 9.2 (d, 2 H), 8.8 (d, 4 H), 8.3, (t, 1 H), 8.1 (t, 2 H), 7.9 (t, 2 H), and 7.7 (t, 4 H) arising from two equivalent and one unique pyridine ligands and signals at 2.2 (s, 3 H), 2.1 (s, 6 H), and 2.0 (s, 6 H) arising from two sets of two equivalent acetate ligands and one unique acetate ligand. The spectrum of **2** consists simply of signals at 8.9 (d, 2 H), 8.1 (t, 1 H), and 7.7 (t, 2 H) for the three equivalent pyridine ligands and a sharp singlet at 2.1 (6 H) for six equivalent acetate ligands. The fast atom bombardment (FAB) mass spectrum of **1** consisted of a parent ion at m/z 742 and fragment ions corresponding to loss of pyridine and acetate ligands. The FAB/MS of **2** was similar except the parent ion was observed at 784. Anal. Calcd for $\text{C}_{30}\text{H}_{36}\text{Br}_3\text{Co}_4\text{N}_4\text{O}_{12}$ (1, PyCoBr_3 salt): C, 32.14; H, 3.21; N, 5.00; Br, 21.43; Co, 21.07. Found: C, 32.59; H, 3.21; N, 4.76; Br, 21.03; Co, 20.59. Anal. Calcd for $\text{C}_{27}\text{H}_{33}\text{Co}_3\text{F}_6\text{N}_3\text{O}_{13}\text{P}$: C, 34.88; H, 3.55; N, 4.52; Co 19.05; F, 12.27. Found: C, 34.15; H, 3.56; N, 4.87; F, 13.08; Co, 18.25.

characterized by a single-crystal X-ray diffraction study.¹³ As shown in the ORTEP drawing, Figure 1, the cation of **1** is an oxo-centered cobalt cluster with slightly distorted octahedral metal cores. Two of the metal-metal distances are similar [3.182 (2) and 3.178 (2) Å], whereas the remaining metal-metal distance [2.758 (2) Å] is contracted owing to the presence of the hydroxy bridge. The central oxygen in this cluster is equidistant [1.803 (7) Å] from the three cobalt ions and only slightly out of plane with them. Other oxo-centered metal trimers such as $\text{Py}_3\text{Mn}_3\text{O}(\text{OAc})_6$ and $[(\text{MeOH})_3\text{Fe}_3\text{O}(\text{pivalate})_6]^+$ have similar bridging acetate ligands.^{4,14} The ^1H NMR and FAB/MS spectra of **1** and **2** in solution are consistent with the oxo-centered, solid-state structure.¹²

The clusters **1** and **2** have been found to be oxidizing agents and can be used as catalyst precursors for the autoxidation of aromatic hydrocarbons. For example, warming a solution containing a mixture of **1** and **2**, toluene, and LiBr in acetic acid produces benzyl bromide (93% of theoretical) and HBr. At 80 °C and with 2 equiv of LiBr per cobalt atom, the half-life of this reaction is approximately 2 min. If the reaction is carried out in the presence of O_2 , then the product is benzoic acid and the oxidation becomes autocatalytic.¹⁵ In the absence of bromide and O_2 , the toluene is converted to benzyl acetate in a much slower reaction requiring 3 h at reflux. Hronec reported¹⁵ that the addition of pyridine to the cobalt bromide catalyzed autoxidation of *p*-xylene dramatically increases the rate. It is conceivable that the formation of the cations of **1** and **2** is responsible for the rate-enhancement. In fact, large quantities (32% yield) of **1** and **2** can be prepared without the addition of peracetic acid by bubbling air through a warm (70 °C) acetic acid solution of cobalt acetate, pyridine, *p*-xylene, and NH_4PF_6 which contains a small amount of HBr. In this preparation, *p*-tolualdehyde and *p*-toluic acid are formed along with **1** and **2**.

The autoxidation of aromatic hydrocarbons presumably proceeds by the following mechanism.¹⁶ First, Br^- is oxidized by **1** or **2** to give Br^\cdot ¹⁷ which is the chain initiator and abstracts a hydrogen atom from toluene to give a benzylic radical. The benzylic radical reacts with O_2 to give an organic peroxide, leading to oxidation products,¹⁸ or, in the absence of O_2 , combines with Br^- to give benzyl bromide. The fact that **1** and **2** and LiBr react with a mixture of toluene and ethylbenzene with the same selectivity as Br_2 under the same conditions is consistent with this scheme. Treatment of a toluene/ethylbenzene solution in acetic acid at 80 °C with LiBr and **1** and **2** produced α -methylbenzyl bromide and benzyl bromide in a ratio of 14:1, respectively. Under similar conditions, the same product ratio was observed by using Br_2 as the brominating reagent.

The oxo-centered cobalt clusters described here represent the first such trinuclear cobalt clusters to be completely characterized. The isolation of these clusters from actual metal-catalyzed autoxidation reactions suggests that they are possible catalyst intermediates. The results of stoichiometric reactions involving these clusters imply that a major role of cobalt in the cobalt-catalyzed autoxidation of *p*-xylene is to oxidize bromide ion to bromine radical. The chemistry of these oxo-centered clusters and other derivatives will be described in more detail in the future.

(13) $[\text{Py}_3\text{Co}_3\text{O}(\text{OAc})_5\text{OH}][\text{PyCoBr}_3]$ crystallizes in the space group $P2_1C$ with $a = 15.643$ (4) Å, $b = 14.413$ (4) Å, $c = 18.337$ (6) Å, $\beta = 99.96^\circ$, $V = 4072$ (2) Å³, $Z = 4$, $R = 0.052$, and $R_w = 0.041$. The structural determination was carried out at Crystalalytics Company, Lincoln, NE.

(14) Blake, A. B.; Fraser, L. R. *J. Chem. Soc., Dalton Trans.* **1975**, 193.

(15) (a) For example, at 100 °C, this catalyst system for the oxidation of xylene resulted in 65 equiv of product per hour per cobalt while the use of CoBr_2 results in only 23 equiv of product per hour per cobalt (1 equiv represents 2 mol of oxygen consumed). (b) Hronec, M.; Ilavsky, J. *Oxid. Commun.* **1983**, *3*, 303 and references cited therein.

(16) (a) Kamiya, Y. *J. Catal.* **1974**, *33*, 480. (b) Jones, G. H. *J. Chem. Res., Miniprint* **1981**, 2801.

(17) In the absence of hydrocarbon, molecular bromine is produced in 70% yield in refluxing chlorobenzene solution by the reaction of **1** and **2** with LiBr.

(18) The Co(III) clusters are presumably regenerated by reaction of organic peroxides with Co(II). (a) Hendriks, C. F.; van Beck, H. C. A.; Heertjes, P. M. *Ind. Eng. Chem. Prod. Res. Dev.* **1979**, *18*, 38. (b) Scott, E. J. *J. Phys. Chem.* **1970**, *74*, 1174.

Supplementary Material Available: A crystal structure analysis report from *Crystalitics* which includes atomic coordinates for all atoms and anisotropic thermal parameters for non-hydrogen atoms (14 pages). Ordering information is given on any current masthead page.

The Quest for Free Metaphosphate in Solution: Racemization at Phosphorus in the Transfer of the Phospho Group from Phenyl Phosphate to *tert*-Butyl Alcohol in Acetonitrile

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Received April 22, 1985

Since 1955,^{1,2} much evidence has been accumulated to suggest that many nucleophilic displacement reactions of phosphoric monoesters follow a dissociative pathway involving monomeric metaphosphate as an intermediate.³ Yet recently, when we investigated the stereochemical course of the methanolysis of phenyl [¹⁶O,¹⁷O,¹⁸O]phosphate monoanion and of 2,4-dinitrophenyl [¹⁶O,¹⁷O,¹⁸O]phosphate dianion in aqueous methanol, the product methyl phosphate showed complete *inversion* at phosphorus.⁴ Even the methanolysis of an *N*-phosphoguanidine, which is among "the most reactive precursors of metaphosphate",⁵ was found to proceed with inversion.⁴ To reconcile these findings with the earlier mechanistic results, we suggested that phospho group transfers in protic media occur either by a preassociative pathway⁶ in which the metaphosphate-like species is never free or by an "exploded" associative transition state.⁴ We have carried the search for free metaphosphate further, and we report here the first case of *racemization at phosphorus during the solvolysis of a phosphoric monoester*.

All the experimental results from studies of nucleophilic reactions of labile phosphoric monoesters indicate almost complete bond breaking between the phospho moiety and the leaving group at the transition state, yet the consistent observation of stereochemical inversion at phosphorus demands that these reactions are either preassociative stepwise (involving a metaphosphate intermediate of extremely short lifetime) or concerted (with a loose S_N2-like transition state).⁴ Even when a Conant-Swan fragmentation is used to generate a metaphosphate-like species in protic media, stereochemical inversion is the outcome.⁷ For reactions of alcohols in *aprotic* solvents, however, Ramirez and his collaborators have observed phospho group transfer from aryl phosphate monoesters to hindered acceptors such as *tert*-butyl alcohol⁸ and have suggested that the formation of *tert*-butyl phosphate is a criterion for the intermediacy of monomeric metaphosphate.⁸ We have evaluated the stereochemical course

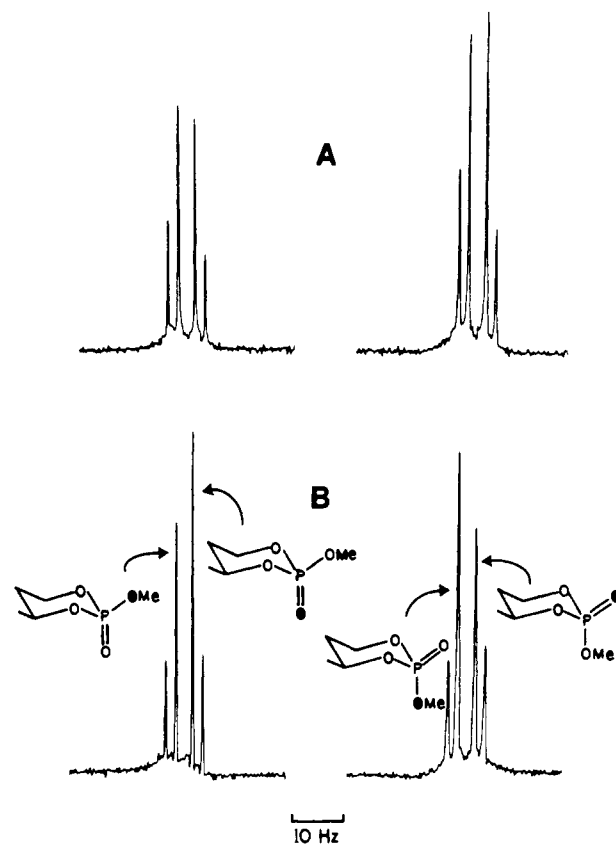


Figure 1. ³¹P NMR spectra of the products from the "in-line" ring closure and methylation⁴ of (A) 3-[¹⁶O,¹⁷O,¹⁸O]phospho-(*S*)-butane-1,3-diol obtained by phospho group transfer by wheat germ acid phosphatase from the sample of *tert*-butyl phosphate deriving from the *tert*-butanolysis of phenyl (*S*)-[¹⁶O,¹⁷O,¹⁸O]phosphate and (B) 1-[¹⁶O,¹⁷O,¹⁸O]phospho-(*S*)-butane-1,3-diol obtained by phospho group transfer by *E. coli* alkaline phosphatase from the reisolated reactant, phenyl (*S*)-[¹⁶O,¹⁷O,¹⁸O]phosphate. The spectra were taken on a Bruker WM-300 WB instrument at 121.5 MHz. Gaussian multiplication with Gaussian broadening, 0.12 Hz, and line broadening, -0.30 Hz. The natural line width at half-height is 0.9 ± 0.05 Hz. The downfield multiplet (syn isomers) is centered around -4.85 ppm and the upfield multiplet (anti isomers) around -5.85 ppm. The isotopically labeled species that provide stereochemical information are illustrated. The downfield signal in each quartet is from the unlabeled triester, and the upfield signal in each quartet is from the ¹⁸O₂ triester.

Table I. Predicted and Observed ³¹P Signal Intensities^a

	predicted ^b			obsd ^c
	if inversion	if retention	if racemization	
peak 2 ^d	39	61	50	51
peak 3 ^d	61	39	50	49

^a For the sample of 3-[¹⁶O,¹⁷O,¹⁸O]phospho-(*S*)-butane-1,3-diol derived from the *tert*-butanolysis of phenyl (*S*)-[¹⁶O,¹⁷O,¹⁸O]phosphate in acetonitrile. Peak heights for the stereochemically informative resonances (the middle pair of each quartet) are normalized to 100%. A least-squares curve-fitting program gave results within 1% of those obtained by direct measurement. ^b On the basis of the known isotopic composition of the recovered phenyl [¹⁶O,¹⁷O,¹⁸O]phosphate substrate. ^c See Figure 1A. ^d For the downfield quartet. Peaks are numbered from downfield up.

of such a reaction, by studying the phospho group transfer from the dianion of phenyl (*R*)-[¹⁶O,¹⁷O,¹⁸O]phosphate⁹ to *tert*-butyl alcohol in acetonitrile.¹⁰ The *tert*-butyl phosphate was isolated,¹¹

(9) The bis(triethylammonium) salt of phenyl (*R*)-[¹⁶O,¹⁷O,¹⁸O]phosphate⁴ was converted into the bis(tetra-*n*-butylammonium) salt according to ref 8.

(10) Phenyl (*R*)-[¹⁶O,¹⁷O,¹⁸O]phosphate (4.99 mmol, 0.5 M) in acetonitrile-*d*₃ containing *tert*-butyl alcohol (1 M), 70 °C, 6 h.

(11) By anion exchange chromatography on AG1-X8 (HCO₃⁻ form, from BioRad).

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