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Absolute Configurations, Predominant Conformations and Tautomeric Structures of Enantiomeric *tert*-Butylphenylphosphine Oxides

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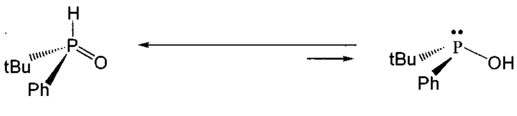
Enantiomeric *tert*-butylphenylphosphine oxides have been isolated via resolution of the racemate with mandelic acid and investigated by using vibrational circular dichroism (VCD). Vibrational absorption and circular dichroism spectra of dextrorotatory, levorotatory, and racemic mixture of *tert*-butylphenylphosphine oxide have been measured in $CDCl_3$ and $CHCl_3$ solutions in the 2000−900 cm^{-1} region. Experimental spectra are compared with the ab initio predictions of absorption and VCD spectra obtained with density functional theory using B3LYP/6-31G* basis set for different tautomeric structures and conformers of (*S*)-*tert*-butylphenylphosphine oxide. This comparison indicates that (−)-*tert*-butylphenylphosphine oxide is of the (*S*)-configuration and indicates only one tautomeric structure and one conformation predominant for *tert*-butylphenylphosphine oxide in $CDCl_3$ and $CHCl_3$ solutions.

Introduction

Chiral phosphine oxides are precursors of chiral phosphines, which in turn, serve as efficient ligands in homogeneous catalysis. Chiral phosphines are therefore extensively used in asymmetric and stereoselective synthesis.[1−2] For these reasons, synthesis and characterization of both chiral phosphine oxides and phosphines have attracted much attention in recent years. In a rich family of substrates for the synthesis of a variety of enantiomerically pure phosphine oxides and other related structures, the enantiomers of secondary *tert*-butylphenylphosphine oxide **1** can be considered among the most promising ones.[3] They are especially useful for the preparation of the enantiomeric *tert*-butylphenylphosphinothioic acids and their seleno analogues.[4−5] The enantiomeric *tert*-butylphenylphosphinothioic acids have recently been used as versatile chiral solvating agents for the NMR determination of the enatiomeric excesses of a large number of chiral organic and hetero-organic compounds.[6−8] We have also noted that *tert*-butylphenylphosphinoselenoic acid behaves similarly.[9]

(−)-*tert*-Butylphenylphosphine oxide (**1**) was assigned (*S*)-configuration by chemical correlation.[4,5,10] An independent verification of its absolute configuration and determination of its predominant conformation would be useful. We have used vibrational circular dichroism (VCD) method for this purpose.

tert-Butylphenylphosphine oxide (**1**), like other secondary phosphine oxides and phosphites,[11] can exist in an equilibrium between the pentavalent **1a** and trivalent tautomeric structures **1b**. However, the stability of the pentavalent and trivalent tautomeric forms of **1** has not been studied theoretically, and the equilibrium constant is unknown, although some theoretical studies on simple phosphine oxides, $P(OH)_3$ and $OPH(OH)_2$ have been reported.[12]



1a **1b**

Trivalent, tricoordinate organophosphorus compounds are prone to react with the formation of the corresponding pentavalent tetracoordinated derivatives. For example, secondary phosphine oxides and phosphites are easily converted into the corresponding acid chlorides by treatment with carbon tetrachloride/triethylamine or *N*-

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chlorosuccinimide.[5,13] Now we have observed that this conversion occurs easily in carbon tetrachloride alone.

The determination of absolute configuration by chemical methods is based on the assumption of the steric course of a given reaction. VCD is an independent spectroscopic method without dependency on such assumptions to determine the absolute configuration and predominant conformations in solution phase. Recent developments in the application of density functional theory[14−16] and improvements in VCD instrumentation make it possible to use VCD for a confident determination of the absolute configurations and/or conformations in solution phases.[17−18] Successful determinations of both the absolute configurations and predominant conformations of 1,2,2,2-tetrafluoroethylmethyl ether,[17a] desflurane,[17b] epichlorohydrin,[17c] 3-butyn-2-ol,[17d] Troger's base,[18a] and phenyloxirane[18b] in solution phase are some recent examples that reflect the reliability of VCD method. In addition, the combination of ab initio and experimental methods can be used to study chemical reactions and elucidate their equilibrium.[19−20]

P-chiral phosphines have not been studied before using VCD. Also the quantum mechanical predictions of vibrational properties of *tert*-butylphenylphosphine oxide have not been undertaken before. Therefore we have measured the VCD of (−)-, (+)-, and (±)-*tert*-butylphenylphosphine oxide and undertaken the state-of-the-art ab initio theoretical VCD investigations using B3LYP/6-31G* basis set. These results are used to elucidate the absolute configuration, predominant conformation, and tautomeric structures of *tert*-butylphenylphosphine oxide.

Results and Discussion

The geometries were optimized with B3LYP/6-31G* basis set using the standard dihedral angles of 0°, 60°, 120°, 180°, 240°, or 300° for the $Ct-P-C_1-C_2$ segment (where Ct is the central carbon atom of *tert*-butyl group, see Figure 1) for the two tautomeric structures of (*S*)-*tert*-butylphenylphosphine oxide. These starting geometries converged to two conformations for each of the two tautomeric forms, differing in the dihedral angles for $Ct-P-C_1-C_2$ segment (**a** and **a′** for pentavalent form; **b** and **b′** for trivalent form), as summarized in Table 1 and shown in Figure 1. Keeping the $Ct-P-C_1-C_2$ segment in gauche plus (labeled as **b**) conformation, the geometries of the resulting three conformations based on the difference in the dihedral angle $H-O-P-Ct$ of trivalent form were studied (**b1**, **b2** and **b3** in Figure 1). Only two stable conformations (**b1** and **b2**) are obtained, and **b3** conformation converged to **b1** (possibly due to the interaction between hydroxyl hydrogen atom and benzene ring). The converged $Ct-P-C_1-C_2$ and $H-O-P-Ct$ dihedral angles, optimized electronic energies, Gibbs energies, and relative populations are listed in Table 1. Because of the symmetry of benzene ring, the two different conformations for each tautomeric structure have the same energies and they cannot be distinguished. The pentavalent form has a much lower energy than the trivalent form, and thus is expected to be the predominant conformation for isolated (*S*)-*tert*-butylphenylphosphine oxide. This result is in agreement with those obtained for simple phosphine oxide tautomers,[12] where the pentavalent form $OPH(OH)_2$ was predicted to have a lower energy than the trivalent form $P(OH)_3$. Although the trivalent PH_2OH tautomers[12] are slightly more stable than the pentavalent form OPH_3, the oxide form is stabilized significantly in aqueous environment. On the basis of the relative populations, the equilibrium constant is predicted to be 2.7×10^{-5} for the equilibrium between pentavalent and trivalent structures of (*S*)-*tert*-butylphenylphosphine oxide. The transition state for conversion from pentavalent to trivalent form has also been determined using B3LYP/6-31G* basis set (see Table 1). In the transition state, H atom moves from P toward O, so that P−H bond length increases from 1.43 Å in pentavalent form to 1.48 Å in transition state; O−H bond length decreases from 2.48 Å in pentavalent form to 1.45

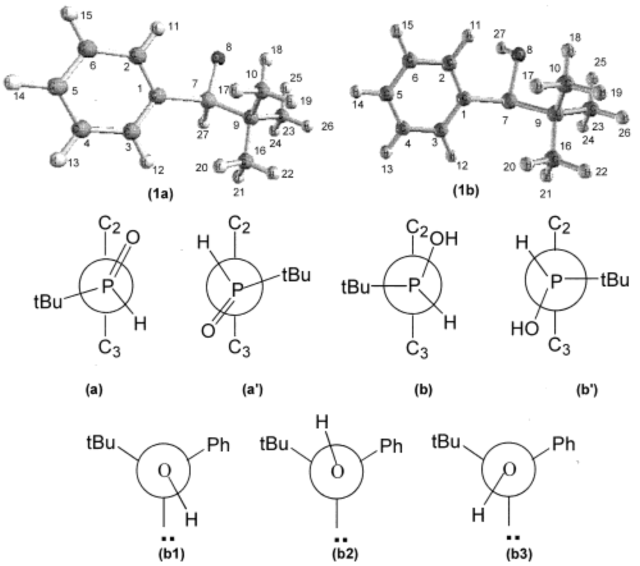

Figure 1. Tautomeric structures and different conformations of (*S*)-*tert*-butylphenylphosphine oxide. Structure **1a** is pentavalent form and **1b** is trivalent form; **a** and **a′** are conformations around C_2-C_1-P-Ct dihedral segment for pentavalent form; **b** and **b′** are conformations around C_2-C_1-P-Ct dihedral segment, and **b1**, **b2**, and **b3** are conformations around $Ct-P-O-H$ dihedral segment for trivalent form.

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Table 1. Conformations and Energies of (*S*)-*tert*-Butylphenylphosphine Oxide

tautomeric structure[a]	starting geom.[b] C_2C_1PCt	C_2C_1PO	C_2C_1PH/-CtPOH	converged geom.[b] C_2C_1PCt	C_2C_1PO	C_2C_1PH/-CtPOH	label[c]	energy[d] electronic	Gibbs	ΔE[e]	Pop.[f] (%)
pentavalent	0	−120	120	100.7	−27.3	−152.8	a	−806.695498	−806.506557	0	100
	60	−60	180	100.7	−27.3	−152.8	a	−806.695498	−806.506557	0	
	120	0	−120	100.7	−27.3	−152.8	a	−806.695498	−806.506557	0	
	180	60	−60	−80.7	151.2	25.8	a′	−806.695498	−806.506557	0	
	−120	120	0	−80.7	151.2	25.8	a′	−806.695498	−806.506557	0	
	−60	180	60	−80.7	151.2	25.8	a′	−806.695498	−806.506557	0	
trivalent	90	−10	180	91.3	−9.37	140.2	b1	−806.686430	−806.496627	6.23	0
	90	−10	−60	100.2	−4.3	−46.6	b2	−806.683758	−806.493629	8.11	
	90	−10	60	91.3	−9.37	140.2	b1	−806.686430	−806.496627	6.23	
	−90	160	140	−92.0	167.4	140.2	b′	−806.686430	−806.496627	6.23	
transition state				107.6	−9.8	−70.6		−806.596043	−806.411054	59.9	

[a] The bond lengths in pentavalent, transition state, and trivalent form respectively, are as follows: P−O bond length 1.50, 1.62, 1.69 Å; P−H bond length 1.43, 1.48, 2.20 Å; O−H bond length 2.48, 1.45, 0.97 Å. [b] Dihedral angle; among C_2C_1PH and CtPOH angles, C_2C_1PH is for pentavalent form and transition state, and CtPOH is for trivalent form. [c] See Figure 1 for the labels. [d] In Hartrees. [e] Relative energy difference, in kcal/mol. [f] Percent population based on Gibbs energies.

Å in transition state; P−O bond length increases from 1.50 Å in pentavalent form to 1.62 Å in transition state. From the calculated energies, the transition state is found to be ~60 kcal/mol higher in energy over the pentavalent form, so the activation barrier for conversion from pentavalent to trivalent form is quite high for isolated molecules. Furthermore, the structure of transition state indicates that one would not expect racemization to take place during conversion from pentavalent to trivalent form.

The converged pentavalent and trivalent forms were found to have potential energy minima (i.e., all vibrational frequencies are real) at the B3LYP/6-31G* level. The absorption and VCD intensities were calculated for the **a**, **b1**, and **b2** conformations at the B3LYP/6-31G* level. The predicted absorption and VCD spectra were simulated with 5 cm^{-1} half widths and Lorentzian band shapes (shown in Figures 2−3). The theoretical spectra for the predominant conformation **a** can be compared to the experimental spectra in Figures 4 and 5.

The experimental absorption spectra of enantiomeric **1** obtained for 0.2 M $CDCl_3$ and $CHCl_3$ solutions are shown in Figure 4, where the absorption spectrum of the solvent has been subtracted. Two different solvents are used because $CHCl_3$ has interfering solvent absorption in the 1300−1150 cm^{-1} region and $CDCl_3$ has interfering absorption below 950 cm^{-1}. The absorption bands in the predicted spectrum show one-to-one correspondence with the absorption bands in experimental spectrum. The notable differences are the following: (a) the two well-separated experimental bands (nos. 16 and 17) at 1236 and 1214 cm^{-1} correspond to closely spaced bands at 1205 and 1199 cm^{-1} in the predicted spectrum; (b) the relative intensities of the two experimental absorption bands (nos. 34 and 35) at 931 and 918 cm^{-1} are about equal, while the corresponding intensities in the simulated spectrum are not; (c) the predicted bands (nos. 4−6 and 7−8) at 1475 and 1461 cm^{-1} are not resolved in the experimental spectra; and (d) the relative intensity of the 1439 cm^{-1} band (no. 10) observed in experimental spectrum is larger than that in the simulated spectrum. Except for these differences the experimental spectra in $CDCl_3$ and $CHCl_3$ solutions are considered to be in good agreement with the predicted absorption spectrum for pentavalent form **a**. In addition, since the experimental absorption spectra (Figure 4) do not show a band corresponding to the predicted strong band at 1043 cm^{-1} for trivalent form **b1** and at 1024 cm^{-1} for trivalent form **b2** (Figure 2), it is concluded that the trivalent form cannot have a significant population in $CDCl_3$ and $CHCl_3$ solutions. This experimental observation is also in agreement with the calculated results (Table 1).

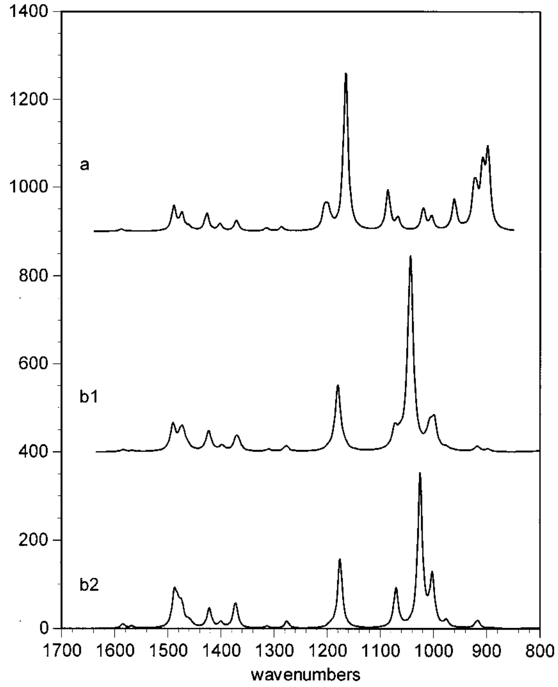


Figure 2. Ab initio vibrational absorption spectra for three conformers of (*S*)-*tert*-butylphenylphosphine oxide obtained with B3LYP/6-31G* basis set. The labels on the traces are the conformation labels (Figure 1).

The experimental VCD spectra of enantiomeric **1** obtained for 0.2 M $CDCl_3$ and $CHCl_3$ solutions are shown in Figure 5, where the VCD spectrum of the solvent has been subtracted. The VCD for racemic **1** which should be zero is also shown in Figure 5 to provide an indication of noise level in the VCD spectra of (+)- and (−)-**1**. The significant VCD bands in the observed (−)-*tert*-butylphenylphosphine oxide spectra are a positive−negative couplet with positive maximum at 1214 cm^{-1} (no. 16, 17) and negative maximum at 1172 cm^{-1} (no. 20), a negative−positive couplet with negative maximum at 1027 cm^{-1} (no. 24) and positive maximum at 1014 cm^{-1} (no. 26), and a negative−positive−negative triplet with peak maxima at 965 (no. 31), 946 (no. 32), and 931 cm^{-1} (nos. 33−35). The same features are seen in the predicted VCD

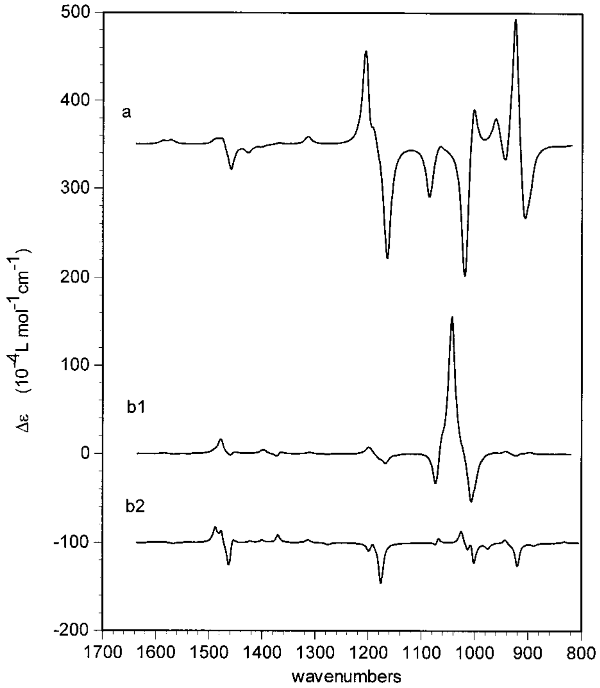


Figure 3. Ab initio VCD spectra for three conformers of (*S*)-*tert*-butylphenylphosphine oxide obtained with B3LYP/6-31G* basis set. The labels on the traces are the conformation labels (Figure 1).

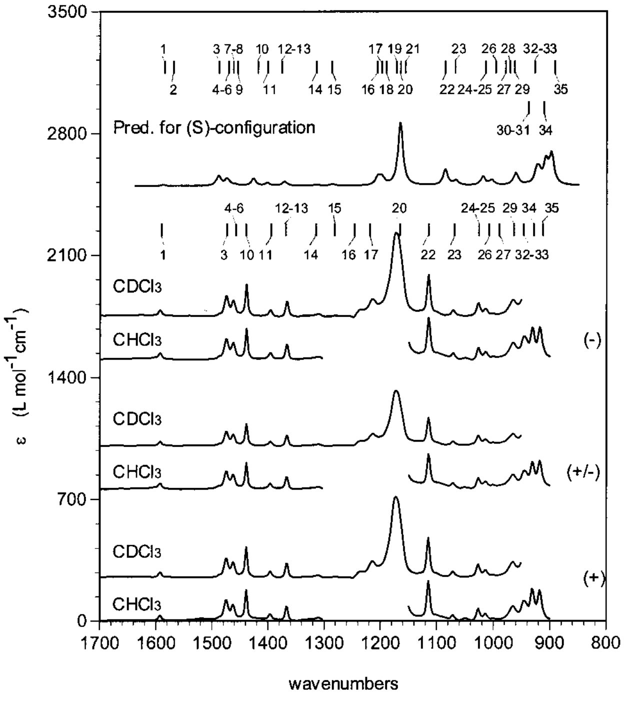


Figure 4. Comparison of the experimental absorption spectra of enantiomeric *tert*-butylphenylphosphine oxide at 0.2 M in $CDCl_3$ and $CHCl_3$ solutions (only ranges without interference of the solvent are shown) with the predicted absorption spectrum (top trace) for (*S*)-configuration of pentavalent form (structure **a** in Figure 1) obtained with B3LYP/6-31G* basis set.

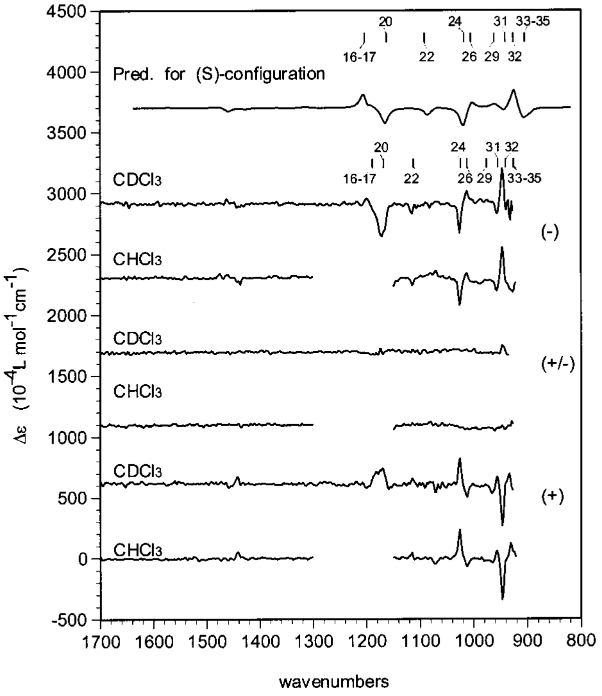
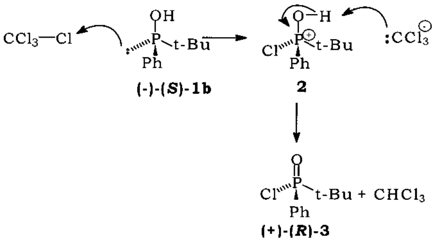


Figure 5. Comparison of the experimental VCD spectra of enantiomeric *tert*-butylphenylphosphine oxide at 0.2 M in $CDCl_3$ and $CHCl_3$ solutions (only ranges without interference of the solvent are shown) with the predicted VCD spectrum (top trace) for (*S*)-configuration of pentavalent form (structure **a** in Figure 1) obtained with B3LYP/6-31G* basis set.

spectrum for the pentavalent form of (*S*)-*tert*-butylphenylphosphine oxide except that the relative intensity for the negative band (no. 20) at 1165 cm^{-1} is somewhat lower than that seen in the experimental VCD spectrum. The major VCD features observed for (−)-*tert*-butylphenylphosphine oxide are reproduced in the predicted VCD spectrum for the pentavalent form of (*S*)-*tert*-butylphenylphosphine oxide. For the most stable trivalent form **b1**, a sharp positive VCD band is expected (see Figure 3) at 1043 cm^{-1}. A corresponding positive VCD band is not present in the experimental VCD spectrum of (−)-*tert*-butylphenylphosphine oxide (Figure 5). This observation indicates that the population of the trivalent form is insignificant in $CHCl_3$ and $CDCl_3$ solutions. In CCl_4 solvent, however, evidence for the presence of trivalent form is obtained by the occurrence of a reaction between *tert*-butylphenylphosphine oxide and the solvent. This reaction is explained by the following scheme.



(-)-(*S*)-**1b**

2

(+)-(*R*)-**3**

A similar mechanism has been postulated earlier in the acid-catalyzed exchange of the active hydrogens of dialkyl phosphonates,[21] and it seems possible that actual species reacting with halogen is the phosphite, trivalent tautomer.[22]

Conclusion

The comparison of experimental and ab initio predicted absorption and VCD spectra indicates that (a) (−)-*tert*-

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butylphenylphosphine oxide is of (*S*)-configuration, in agreement with the known absolute configuration;[4,5,10] (b) only one tautomeric structure and one conformation is predominant for (−)-*tert*-butylphenylphosphine oxide in $CHCl_3$ and $CDCl_3$ solutions; and (c) P-chiral phosphines can be studied using a combination of experimental and ab initio VCD investigations since such molecules do show significant VCD signals.

Experimental Section

General. NMR spectra were recorded at 200 MHz. All optical rotation measurements were done on a photopolarimeter. During our attempts to obtain both enantiomers of *tert*-butylphenylphosphine oxide according to the reported procedure,[3] we have noted that the efficiency of resolution is strongly influenced by the presence of moisture in the racemic phosphine oxide and the absolute configuration of optically active mandelic acid. Therefore, separate procedures for the isolation of (+)-*tert*-butylphenylphosphine oxide ($[\alpha]_{589} = +38.1$, $c = 1.84$, MeOH, ee = 93.1%) and (−)-*tert*-butylphenylphosphine oxide ($[\alpha]_{589} = -29.1$, $c = 1.09$, $CHCl_3$, ee = 78.5%) are given below. The ee values were calculated on the basis of the value $[\alpha]_{589} = -40.45$ (MeOH) and $[\alpha]_{589} = -36.6$ ($CHCl_3$) given in ref 3.

Resolution of Wet Racemic *tert*-Butylphenylposphine Oxide with Enantiomerically Pure (+)-(*S*)-Mandelic Acid. Slightly wet racemic *tert*-butylphenylphosphine oxide (3.68 g, 0.02 mol) was dissolved in ethyl ether. (+)-(*S*)-Mandelic acid (3.04 g, 0.02 mol) was added slowly to this solution. After addition of each portion, the solid acid disappeared rapidly and the solution became cloudy. The reaction mixture was left at room temperature for 10 days. During this period crystals of the complex did not appear. After that time anhydrous $MgSO_4$ was added to the solution which became immediately transparent. The reaction mixture was left again at room temperature for a few days. After 48 h colorless crystals of the complex formed were filtered off (0.725 g). To isolate optically active *tert*-butylphenylphosphine oxide, the isolated complex was dissolved in 5% aqueous solution of K_2CO_3 and the water phase was extracted with $CHCl_3$. The combined chloroform extracts were dried over anhydrous magnesium sulfate. Evaporation of the solvent gave the chemically pure *tert*-butylphenylphosphine oxide (0.300 g, 9%) with $[\alpha]_{589} = -29.1$ ($c = 1.09$, $CHCl_3$, ee = 78%). The spectral and analytical data were in full agreement with those reported.[3]

Resolution of Freshly Distilled, Dry Racemic *tert*-Butylphenylphosphine Oxide with (−)-(*R*)-Mandelic Acid. Freshly distilled and dry racemic *tert*-butylphenylphosphine oxide (3.68 g, 0.02 mol) was dissolved in ethyl ether. (−)-(*R*)-Mandelic acid (3.04 g, 0.02 mol) was added slowly to this solution. After keeping for 20 h at room temperature, the homogeneous reaction mixture was left at −18 °C for 7 h. After this time the complex formed was filtered off rapidly at room temperature (2.9 g). It was dissolved in 5% aqueous K_2CO_3, and the water phase was extracted with $CHCl_3$. The combined organic extracts were washed with 5% aqueous solution of K_2CO_3 and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave the pure *tert*-butylphenylphosphine oxide (1.350 g, 0.0074 mol) which had $[\alpha]_{589} = +20.9$ ($c = 1.11$, MeOH, ee = 52%). This sample of optically active phosphine oxide was dissolved in ethyl ether and (−)-(*R*)-mandelic acid (1.29 g, 0.0085 mol) was added slowly to this solution. After addition of each portion the solid acid disappeared rapidly. Just after addition of the last portion of the acid the colorless crystals of the complex started to appear. The reaction mixture was left at room temperature for 16 h. The complex formed was filtered off (1.312 g, 0.0039 mol). It had $[\alpha]_{589} = -64.8$ ($c = 1.03$, $CHCl_3$). To isolate optically active phosphine oxide, the isolated complex (1 g) was dissolved in 5% aqueous solution of K_2CO_3. The water phase was extracted with $CHCl_3$. The combined chloroform extracts were dried over anhydrous magnesium sulfate. Evaporation of the solvent gave the virtually pure dextrorotatory *tert*-butylphenylphosphine oxide (0.474 g, 16.9%) with $[\alpha]_{589} = +38.1$ ($c = 1.84$, MeOH, ee = 93.1%). The spectral (^1H and ^{31}P NMR) fully supported its structure.

Reaction of (−)-(*S*)-*tert*-Butylphenylphosphine Oxide 1 with Carbon Tetrachloride. (−)-(*S*)-*tert*-Butylphenylphosphine oxide **1** (0.0325 g, 0.178 mmol, $[\alpha]_{589} = -23.1$ ($c = 1.11$, MeOH); ee = 56.5%) was dissolved in carbon tetrachloride. The specific rotation of this solution was found to change during 72 h from, $[\alpha]_{589} = -0.167$ to 0.372. The ^{31}P spectrum measured after that time indicated more than 90% conversion of the starting phosphine oxide **1** into the corresponding phosphinoyl chloride **3**. To isolate the optically active chloride **3**, the reaction mixture was diluted with chloroform and the organic solvents were washed with 5% aqueous solution of K_2CO_3 and water. The organic solution was dried over anhydrous magnesium sulfate. Evaporation of the solvents gave the crude chloride **3** which was purified by the preparative TLC affording the spectrally pure (+)-(*R*)-**3** (0.0135 g, 45%) with $[\alpha]_{589} = 18.9$ ($c = 0.75$, benzene). The ^1H NMR spectrum of this sample recorded in the presence of (+)-(*R*)-*tert*-butylphenylphosphinothioic acid as a chiral solvating agent[6−8] indicated that the phosphinoyl chloride **3** obtained has ee = 42% [by integration of the doublets at $\delta = 1.239$ ppm (for major diastereomer) and $\delta = 1.196$ ppm (for minor diastereomer)].

Measurements. The infrared and VCD spectra were recorded on a commercial Fourier transform VCD spectrometer.[17] The VCD spectra were recorded with 3 h data collection time at 4 cm^{-1} resolution. Spectra were measured in $CDCl_3$ and $CHCl_3$ solvents at 0.2 M and at path length of 120 μm. The sample was held in a variable path length cell with BaF_2 windows. In the presented absorption spectra, the solvent absorption was subtracted out. In the presented VCD spectra the raw VCD spectrum of the solvent was subtracted.

Calculations. The ab initio vibrational frequencies, absorption and VCD intensities for (*S*)-*tert*-butylphenylphosphine oxide were calculated using Gaussian 98 program[16] on a Pentium II 300 MHz PC. The calculations used the density functional theory with B3LYP functional[14] and 6-31G* basis set.[20] The procedure for calculating the VCD intensities using DFT theory is due to Cheeseman et al.[15] as implemented in Gaussian 98 program.[16] The theoretical absorption and VCD spectra were simulated with Lorentzian band shapes and 5 cm^{-1} full width at half-height. Since the ab initio predicted band positions are higher than the experimental values, the ab initio frequencies were scaled with 0.9613.

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Supporting Information Available: Cartesian coordinates for the optimized structures of pentavalent form, trivalent form and transition state of (*S*)-*tert*-butylphenylphosphine oxide are given. This material is available free of charge via the Internet at http://pubs.acs.org.

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