First Resolution of a Free Secondary Phosphine Chiral at Phosphorus and Stereospecific Formation and Structural Characterization of a Homochiral Secondary Phosphine−Borane Complex

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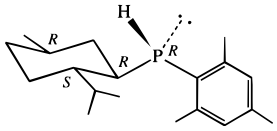
Received November 22, 1995[⊗]

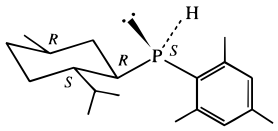
The R_P diastereomer of (−)-menthylmesitylphosphine, (R_P)-**1**, has been isolated with high configurational purity at phosphorus by fractional crystallization of an (R_P)-**1**/(S_P)-**1** = 43/57 mixture from acetonitrile containing a trace of sodium acetylacetonate as a proton scavenger or by deboranation of the corresponding borane complex (S_P)-**2** with diethylamine, thereby effecting the first resolution of a secondary phosphine chiral at phosphorus. The crystal and molecular structure of (S_P)-**2** has been determined. The ready isolation of (S_P)-**2** of 97% diastereomeric purity in 66% yield from an equilibrium (R_P)-**2**/(S_P)-**2** = 28/72 mixture in *n*-hexane by second-order asymmetric transformation and its quantitative and stereospecific conversion under mild conditions into (R_P)-**1** of similar purity augurs well for the future of the resolved secondary phosphines in stereoselective syntheses.

Introduction

Although the first resolution of a simple acyclic tertiary phosphine chiral at phosphorus was reported in 1961,[1] the resolution of a similar secondary phosphine does not appear to have been achieved hitherto, despite the observation by NMR spectroscopy of diastereomers of compounds due to slow inversion at a pyramidal secondary phosphine-*P* stereocenter.[2,3] The amphoteric nature of a secondary phosphine, in particular its basicity (protonation of a chiral secondary phosphine produces an achiral phosphonium ion),[4] is the chief reason for sensitivity to racemization of such compounds. Thus, when protected from protons by coordination to metal ions [M^{+}←PHR^1R^2],[5] chalcogens [X←PHR^1R^2, where X = O, S, or Se],[6] or borane [H_3B←PHR^1R^2],[7] secondary phosphines have been resolved, but recovery of the optically active secondary phosphines from the adducts has not been accomplished hitherto. In recent work we showed that isotopic exchange between (±)-PHMePh and (±)-PDEtPh was negligible in highly purified acetonitrile containing sodium acetylacetonate (Na[acac]) as proton scavenger and that the lower limit for the barrier to unimolecular inversion for (±)-PHPh*i*Pr was > 97.5 ± 0.5 kJ mol^{-1}.[8] In 1979 the synthesis of (−)-menthylphenylphosphine was reported but no attempts were made to separate the pair of diastereomers observed.[3] Here we report that the diastereomers of (−)-menthylmesityl-phosphine, (R_P/S_P)-**1**, can be separated by fractional crystallization of the mixture from acetonitrile containing Na[acac], thereby effecting the first resolution of a free secondary phosphine chiral at phosphorus. We also show that (R_P)-**1** of high configurational purity can be recovered from (S_P)-(−)-menthylmesitylphosphine−borane, (S_P)-**2**, by treatment with diethylamine under mild conditions. A preliminary account of part of this work has been published.[9]



(R_P)-**1**



(S_P)-**1**

Results and Discussion

(a) Synthesis and Separation of Diastereomers of (−)-Menthylmesitylphosphine ((R_P/S_P)-1). Treatment of dichloromesitylphosphine with (−)-menthylmagnesium chloride (1.14 equiv) in tetrahydrofuran at −78 °C affords chloromenthylmesitylphosphine in high yield as an equimolar mixture of the two diastereomers epimeric at phosphorus, according to the $^{31}P\{^1H\}$ NMR spectrum. Upon reduction with lithium aluminium hydride in diethyl ether, the chlorophosphine yields (−)-menthylmesitylphosphine, (R_P/S_P)-**1**, in 48% yield after seven recrystallizations from highly purified acetonitrile.[10] The moderately air-stable product crystallizes from hot acetonitrile as long needles having mp 79−88 °C, and is readily soluble in benzene, dichloromethane, diethyl ether, and *n*-hexane. In benzene-d_6, the $^{31}P\{^1H\}$ NMR spectrum of the phosphine

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1996.

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S0020-1669(95)01494-7 CCC: $12.00

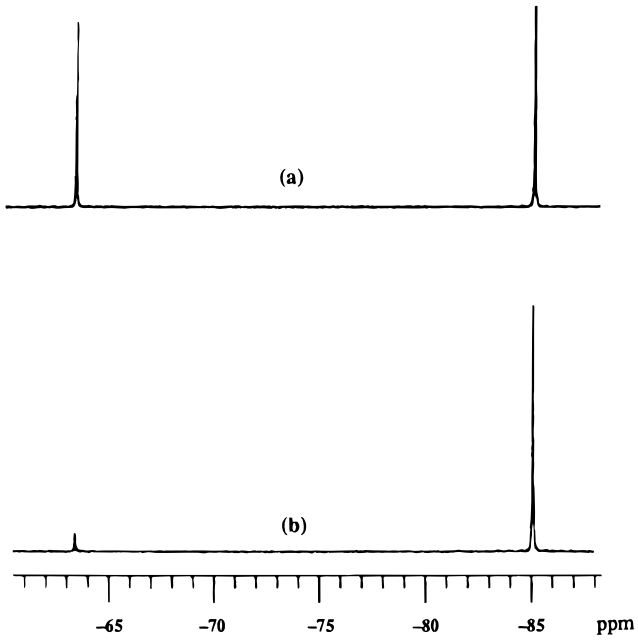


Figure 1. (a) $^{31}P\{^1H\}$ NMR spectrum of (R_P/S_P)-**1** in CD_3CN (equilibrium mixture). (b); similar spectrum of secondary phosphine in CD_3CN/Na[acac] showing 94% enrichment of (R_P)-**1**.

consists of two singlets for the pair of diastereomers at δ −62.62 ppm (55%) and δ −84.24 ppm (45%). In acetonitrile-d_3, the signals for the diastereomers appear at δ −63.47 ppm (43%) and δ −85.16 ppm (57%) (Figure 1a). Attempted fractional crystallization of the mixture from neat acetonitrile met with no success. When repeated in acetonitrile containing Na[acac] (0.04% w/v) over the temperature range 60−35 °C however, the fractional crystallization of the mixture (20 g l^{-1}) afforded ca. 50% of the material enriched in the diastereomer having δ −85.16 ppm, while the mother liquor was correspondingly enriched in the diastereomer having δ −63.47 ppm. The progress of the separation was monitored by recording the $^{31}P\{^1H\}$ NMR spectra of the various fractions in acetonitrile containing 0.04% Na[acac]. Six consecutive recrystallizations of the less soluble component of the mixture from the solvent containing base gave the diastereomer having δ −85.16 ppm in 94% purity, as indicated in Figure 1b. Dissolution of the enriched diastereomer in highly purified acetonitrile in the absence of the base led to immediate epimerization at phosphorus and the establishment of the equilibrium 43:57 mixture of diastereomers within the time of recording the NMR spectrum (ca. 5 min).

(b) Synthesis and Separation of Diastereomers of (−)-Menthylmesitylphosphine−Borane ((R_P/S_P)-2). Treatment of (R_P/S_P)-**1** (54:46) in benzene with 0.976 equiv of borane−dimethyl thioether complex at room temperature affords (R_P/S_P)-**2** in high yield, initially as a 54:46 mixture of diastereomers as indicated by the intensities of the two broad singlets for the phosphorus nuclei in the $^{31}P\{^1H\}$ NMR spectrum. The chemical shifts and intensities of the resonances for the diastereomers of **1** at δ_P −62.62 and −84.24 ppm correlated closely with the resonances for the diastereomers of **2** at −4.56 and −20.15 ppm, respectively. The boranation of the secondary phosphine is therefore stereospecific, with retention of configuration at phosphorus. At room temperature, the intensity of the resonance at δ_P −20.15 ppm increased to 72% over 18 h, whereupon it remained constant. At −28 °C, however, the rate of establishment of the equilibrium was slow. Consistent with the former observation, removal of solvent, followed by dissolution of the residue in *n*-hexane and subsequent filtration to remove a small quantity of solid impurity, gave a colorless solution from which the diastereomer having δ_P −20.15 ppm crystallized in overall 66% yield with 97% diastereomeric purity in a second-order asymmetric transformation.[11] The final mother liquor, when stored at room temperature for 1 d, contained both diastereomers in the equilibrium ratio (28:72). The less soluble borane adduct of 97% diastereomeric purity melts at 110 °C with partial epimerization at phosphorus, but when sublimed at 100 °C (0.5 mmHg) the ratio of diastereomers remained unchanged. The product was identified as (S_P)-**2** by X-ray crystallography (see below). Accordingly, the (R_P) configuration was assigned to the less soluble diastereomer of **1** having δ_P −84.24 ppm.

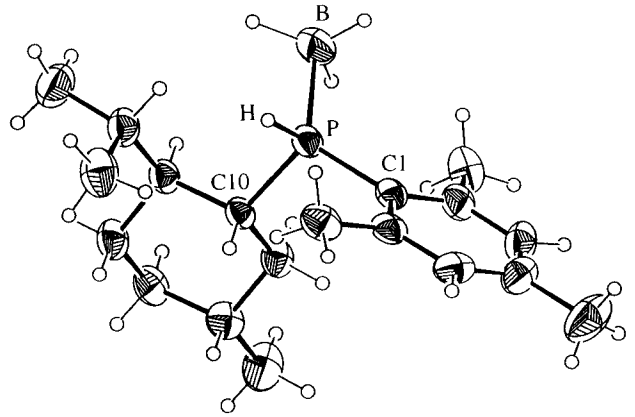
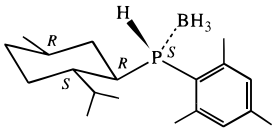
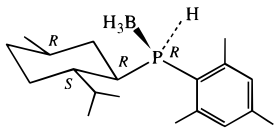


Figure 2. ORTEP view of (S_P)-**2** showing atom-labeling scheme of selected atoms. Thermal ellipsoids enclose 30% probability levels.



(S_P)-**2**



(R_P)-**2**

(c) Liberation of (R_P)-1 from (S_P)-2. In contrast to the prolonged heating required for the removal of the borane from tertiary phosphine−borane complexes,[12] the borane protecting group can be readily removed from (S_P)-**2**. Thus, treatment of (S_P)-**2** of 97% diastereomeric purity in benzene at room temperature with excess diethylamine quantitatively affords after 15 min (R_P)-**1** of identical diastereomeric purity to the starting material, as evidenced by $^{31}P\{^1H\}$ NMR spectroscopy. The deboranation of (S_P)-**2** is stereospecific and proceeds with retention of configuration at phosphorus. Under the conditions used, the liberated secondary phosphine showed no sign of epimerization at phosphorus after 1 week. Because of the ready isolation of (S_P)-**2** and its quantitative conversion into (R_P)-**1**, large quantities of the free secondary phosphine resolved at phosphorus are now available for subsequent syntheses, which are in progress.

(d) Crystal and Molecular Structure of (S_P)-2. The molecular structure of (S_P)-**2** is depicted in Figure 2. Crystal data for the compound are given in Table 1, and Table 2 contains the most important bond distances and angles for (S_P)-**2**. To our knowledge (S_P)-**2** is the first secondary phosphine−borane complex to be characterized by X-ray crystallography. The geometry around phosphorus is distorted from tetrahedral (Table 2). The P−H distance of 1.37(4) Å in (S_P)-**2** compares closely

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Table 1. Crystallographic Data for Compound (S_P)-**2**

formula	$C_{19}H_{34}B$
mol wt	304.268
crys syst	orthorhombic
space group	$P2_12_12_1$
a, Å	9.059(2)
b, Å	11.823(3)
c, Å	18.496(2)
V, Å^3	1980.9(6)
Z	4
cryst dimens, mm	0.06 × 0.26 × 0.27
d_{calcd}, g cm^{-3}	1.020
μ, cm^{-1}	11.4
X-ray radiation (graphite monochromator)	Cu Kα (λ = 1.5418 Å)
diffractometer	Rigaku AFC6R
T, °C	20(1)
2θ range, deg	4−120
no. of unique data	1708
no. of data used	1396
no. of variables	297
no. of restraints	97
R	0.045
R_w	0.048
GOF	3.11
F(000)	672

Table 2. Selected Bond Distances and Angles for (S_P)-**2**

P−H	1.37(4)	P−B	1.944(8)
P−C(1)	1.821(5)	P−C(10)	1.856(4)
H−P−B	104(2)	H−P−C(1)	106(2)
H−P−C(10)	99(2)	B−P−C(1)	122.5(3)
B−P−C(10)	115.9(3)	C(1)−P−C(10)	106.3(2)

with the corresponding distance in dimesitylphosphine[13] and in certain primary phosphine transition metal complexes.[14] The P−B bond distance of 1.94(3) Å is similar to the corresponding distance found in tertiary phosphine−borane complexes.[15]

Conclusion

The R_P diastereomer of (−)-menthylmesitylphosphine can be isolated with high configurational purity at phosphorus by fractional crystallization of the mixture epimeric at phosphorus from acetonitrile containing sodium acetylacetonate as proton scavenger or by displacement from the corresponding borane complex with diethylamine under mild conditions. The latter method is appropriate for the large-scale synthesis of the resolved secondary phosphine for subsequent syntheses.

Experimental Section

All manipulations were performed under an argon atmosphere with use of the Schlenk technique. Diethyl ether, petroleum (bp 40−60 °C), *n*-hexane, benzene, and THF were freshly distilled from sodium benzophenone ketyl and stored under argon. Commercial acetonitrile was purified according to the reported four-step procedure.[10] Sodium acetylacetonate was prepared and isolated according to the procedure described in ref 16 and recrystallized from purified acetonitrile. Borane−dimethyl thioether was obtained from the Aldrich Chemical Co., Inc. NMR spectra were recorded on Varian XL 200E and VXR 300S spectrometers at the frequencies indicated and in the solvents specified with reference to Me_4Si (^{1}H), external 85% aqueous H_3PO_4 (^{31}P), and external BF_3·OEt_2 in $CDCl_3$ (^{11}B), with downfield shifts being positive. Optical rotations were measured with a Perkin-Elmer Model 241 polarimeter in a 1-dm cell at 20 °C. Mass spectra were recorded on a VG Micromass 7070F double-focusing mass spectrometer. Fast atom bombardment (FAB) mass spectra were recorded on a VG Analytical ZAB-2SEQ mass spectrometer (ionization: 30 keV Cs^+ ions) in a matrix of 3-nitrobenzyl alcohol. Elemental analyses were carried out by staff within the Research School of Chemistry.

[R_P-(1*R*,2*S*,5*R*)]/[S_P-(1*R*,2*S*,5*R*)]-Chloromenthylmesitylphosphine. A Grignard solution was prepared from (−)-menthyl chloride (54.32 g, 310.9 mmol) and magnesium turnings (8.72 g, 358.8 mmol) in THF (350 mL). This solution was added dropwise to a stirred solution of dichloromesitylphosphine (59.96 g, 271.2 mmol) in the same solvent (300 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and the solvent was removed in vacuo. The residue was extracted with petroleum ether (3 × 250 mL). The solvent was removed from the combined extracts to leave the crude product as a yellow oil consisting of a ca. 1:1 mixture of diastereomers epimeric at phosphorus. Yield: 85.75 g (98%). ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C, 80.98 MHz): δ 95.71 (s) and 102.59 (s) (diastereomers). The major impurity was unreacted dichloromesitylphosphine.

[R_P-(1*R*,2*S*,5*R*)]/[S_P-(1*R*,2*S*,5*R*)]-Menthylmesitylphosphine ((R_P/S_P)-1). A solution of (R_P/S_P)-chloro(menthyl)mesitylphosphine (86.75 g, 267.1 mmol) in diethyl ether (300 mL) was added dropwise with stirring to a suspension of LAH (13.56 g, 357.3 mmol) in the same solvent (375 mL) at 0 °C. The reaction mixture was stirred at room temperature for 3 h. Water (14 mL), aqueous sodium hydroxide (14 mL, 15% w/v), and water (41.5 mL) were then added dropwise to the vigorously stirred reaction mixture cooled in ice. After 1 h, the mixture was filtered and the solid was washed with diethyl ether. The combined extracts were dried over $MgSO_4$. Filtration, followed by removal of the solvent in vacuo, gave 69.50 g of the crude product. Seven consecutive recrystallizations of this material from highly purified acetonitrile over the temperature range +80 to −28 °C afforded the pure product as colorless needles: yield 36.81 g (48%), mp 79−88 °C. Anal. Calcd for $C_{19}H_{31}P$: C, 78.6; H, 10.8. Found: C, 78.6; H, 11.1. ^{31}P{^{1}H} NMR (CD_3CN, 20 °C, 80.98 MHz): δ −63.47 (s, S_P diastereomer, 43%), −85.15, (s, R_P diastereomer, 57%). MS (70 eV): 290.1 amu [M$^{\bullet+}$]. Six consecutive recrystallizations of the (R_P/S_P)-**1** mixture from highly purified acetonitrile (50 mL of solvent per gram of compound) containing Na[acac] (0.04% w/v) from 60 to 35 °C yielded the major R_P diastereomer of 94% diastereomeric purity: yield 0.18 g (0.5%), mp 84−88 °C. [α]$_D$ −186 (*c* 0.273, CH_3CN containing 0.04% Na[acac]). ^{1}H NMR (CD_3CN containing 0.04% Na[acac], 23 °C, 299.95 MHz): δ 0.714 (d, $^3J_{HH}$ = 6.60 Hz, 3 H, CH*Me*), 0.84 (d, $^3J_{HH}$ = 6.00 Hz, 3 H, CH*Me*$_2$), 0.95 (d, $^3J_{HH}$ = 6.90 Hz, 3 H, CH*Me*$_2$), 0.70−1.36 (m, 6 H, unresolved, menthyl-*H*), 1.62−1.76 (m, 2 H, unresolved, menthyl-*H*), 1.96−2.08 (m, 1 H, C*H*Me$_2$), 2.13−2.23 (m, 1 H, PCH), 2.23 (s, 3 H, *p*-CH_3), 2.47 (s, 6 H, *o*-CH_3), 4.37 (d of d, $^1J_{HP}$ = 215.36 Hz, $^3J_{HH}$ = 5.85 Hz, 1 H, PH), 6.90−6.93 (m, 2 H, *m*-CH). (Detailed analyses of the regions of the ^{1}H NMR spectrum corresponding to most menthyl-*H* protons gave inconsistent assignments in this and subsequent compounds.) ^{31}P{^{1}H} NMR (C_6D_6, 20 °C, 80.98 MHz): δ −84.24. IR (KBr): ν_{PH} 2318 cm^{-1}. MS *m*/*z* 290 ([M]$^{\bullet+}$). Spectroscopic details for the minor S_P diastereomer (not isolated) are the following: ^{1}H NMR (CD_3CN containing 0.04% Na[acac], 23 °C, 299.95 MHz): δ 0.708 (d, $^3J_{HH}$ = 6.60 Hz, 3 H, CH*Me*), 0.77 (d, $^3J_{HH}$ = 6.90 Hz, 3 H, CH*Me*$_2$), 0.94 (d, $^3J_{HH}$ = 6.90 Hz, 3 H, CH*Me*$_2$), 0.68−1.35 (m, 5 H, unresolved, menthyl-*H*), 1.48−1.58 (m, 1 H, unresolved, menthyl-*H*), 1.63−1.73 (m, 2 H, unresolved, menthyl-*H*), 1.75−1.89 (m, 1 H, PCH), 2.22 (s, 3 H, *p*-CH_3), 2.37 (s, 6 H, *o*-CH_3), 2.38−2.48 (m, 1 H, C*H*Me$_2$), 3.90 (d of d, $^1J_{HP}$ = 216.56 Hz, $^3J_{HH}$ = 9.45 Hz, 1 H, PH), 6.86−6.90 (m, 2 H, *m*-CH). ^{31}P{^{1}H} NMR (C_6D_6, 20 °C, 80.98 MHz): δ −62.62; IR (KBr): ν_{PH} 2338 cm^{-1}.

[S_P-(1*R*,2*S*,5*R*)]-(−)-Menthylmesitylphosphine−Borane ((S_P)-2). Borane−dimethyl thioether (1.60 mL, 10 M in Me_2S, 16.0 mmol) was added over 10 min to a solution of (R_P/S_P)-**1** (4.76 g, 16.4 mmol, S_P:R_P = 54:46) in benzene (100 mL) with stirring. After 18 h, the solvent was removed in vacuo, and the residue was treated with *n*-hexane (50

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mL). The mixture was heated briefly to 60 °C and filtered. Slow cooling of the filtrate to −74 °C afforded colorless crystals that were filtered off, washed with *n*-hexane, and dried in vacuo. The product was dissolved in *n*-hexane (40 mL) at 65 °C, and the solution was filtered and cooled to 4 °C. A crystalline fraction (2.77 g) having (R_P)-**2**/(S_P)-**2** = 7:93 separated. A second crystalline fraction (0.91 g) of similar diastereomeric purity was obtained by allowing the filtrate to stand for 1 d and then concentrating it to ca. 50% and cooling it to 4 °C. The combined crystalline fractions were dissolved at 40 °C in *n*-hexane (93 mL), and the solution was cooled over 5 h to −74 °C. The recrystallized material was collected, washed with *n*-hexane, and dried in vacuo: yield 3.30 g (66.2%) (97% diastereomeric purity), mp 110 °C (epimerization), $[\alpha]_D^{20}$ −84.5 (*c* 0.883, CH_2Cl_2). Anal. Calcd for $C_{19}H_{34}BP$: C, 75.0; H, 11.3; P, 10.2. Found: C, 74.8; H, 11.6; P, 10.2. ^{1}H NMR (C_6D_6, 23 °C, 299.94 MHz): δ 0.65 (d, ^3J(HH) = 6.9 Hz, 3 H, CH*Me*$_2$), 0.68 (d, ^3J(HH) = 6.3 Hz, 3 H, CH*Me*), 0.94 (d, ^3J(HH) = 6.9 Hz, 3 H, C*H*Me$_2$), 0.63−1.00 (m, 3 H, unresolved, menthyl-*H*), 1.25−2.32 (br m, 3 H, BH_3), 1.40−1.66 (m, 4 H, unresolved, menthyl-*H*), 1.90−2.10 (m, 1 H, unresolved, menthyl-*H*), 1.98 (s, 3 H *p*-Me), 2.19 (sept of d, $^3J(HH_{Me})$ = 6.8 Hz, $^3J(HH_{ring})$ = 2.4 Hz, 1 H, C*H*Me$_2$), 2.45 (s, 6 H, *o*-Me), 5.83 (d of d of quart., ^1J(HP) = 369.2 Hz, $^3J(HH_{borane})$ = 6.8 Hz, $^3J(HH_{ring})$ = 3.7 Hz, 1 H, PH), 6.62 (d, ^4J(HP) = 2.4 Hz, 2 H, *m*-CH). ^{1}H{^{11}B} NMR (C_6D_6, 25 °C, 299.94 MHz): δ 1.76 (additional d of d, ^2J(HP) = 13.4 Hz, ^3J(HH) = 6.8 Hz, 3 H, BH_3). ^{31}P{^{1}H} NMR (C_6D_6, 25 °C, 121.42 MHz): δ −20.15 (br). ^{11}B{^{1}H} NMR (C_6D_6, 25 °C, 96.23 MHz): δ −38.86 (br). FAB-MS: *m*/*e* 290 amu ($[M-BH_3]^{\bullet+}$).

Recovery of (R_P)-1 from (S_P)-2. (S_P)-**2** of 97% diastereomeric purity was dissolved in benzene-d_6 (0.5 mL) and a 10-fold excess of diethylamine was added at room temperature. After 15 min, the quantitative liberation of (R_P)-**1** of 97% diastereomeric purity was indicated by ^{11}B{^{1}H} and ^{31}P{^{1}H} NMR spectroscopy.

Melting and Sublimation of (S_P)-2. A small sample of (S_P)-**2** of 97% purity was heated to 130 °C and maintained at this temperature for 5 min. The ^{31}P{^{1}H} NMR spectrum of the melt in C_6D_6 after this period indicated 12.5% epimerization at phosphorus. Sublimation of (S_P)-**2** of similar purity at 100 °C (0.5 mmHg) proceeded without epimerization at phosphorus, according to the ^{31}P{^{1}H} NMR spectrum of the sublimate in C_6D_6.

Crystal Structure Analysis. Crystal data for (S_P)-**2** are given in Table 1. Intensity data were collected using $\omega-2\theta$ scans of width $(1.31 + 0.3 \tan\theta)°$ in ω and a scan speed of 16° min^{-1}. The intensities of three representative reflections were measured after every 150 reflections and showed a 3% decrease in intensity; a decay correction was applied. Data were also corrected for absorption (transmission range: 0.749−0.919). The structure was solved by direct methods[17] and difference Fourier techniques. Anisotropic displacement factors were used for all non-hydrogen atoms. Hydrogen atom parameters were refined, but those within the hydrocarbon groups required restraints on bond lengths and angles. The absolute configurations were assigned by means of refinement of a Flack enantiomorph−polarity parameter[18] (final value $x = -0.02(5)$) and concurs with the known chirality of (1*R*,2*S*,5*R*)-(−)-menthol. Refinement continued until all shift/error ratios were <0.05. Least-squares refinement was performed using full-matrix methods. The maximum and minimum peaks in the final difference Fourier map corresponded to +0.31(4) and −0.13(4) e Å^{-3}. Data reduction and refinement computations were performed with Xtal3.2;[19] atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from ref 20. Selected interatomic distances and angles are given in Table 2.

Supporting Information Available: For (S_P)-**2**, text detailing the X-ray analysis, figures showing the structures, and tables of bond distances and angles, thermal parameters for non-hydrogen atoms, calculated hydrogen atom parameters, least-squares planes, and selected torsion angles (16 pages). Ordering information is given on any current masthead page.

IC951494H

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