monomers about a 2_1 axis would result in intolerably close methyl group hydrogen atom contacts for the first and third molecules, the second and fourth and so on. Since there are no steric barriers to the formation of a second paired intermolecular hydrogen bond, the dimer configuration is strongly favored. Dimer formation should then be expected in other examples of highly hindered organophosphinic acids and organophosphoric acids. We are currently investigating the structures of several other organophosphorus compounds which are efficient extractants for heavy elements.

Supplementary Material Available: Listings of structure-factor amplitudes (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Work performed under the auspices of the U.S. Energy Research and Development Administration; (b) Hines Veterans Administration Hospital and Department of Biochemistry, Loyola University of Chicago; (c) Argonne National Laboratory.

(2) J. R. Ferraro, G. W. Mason, and D. F. Peppard, *J. Inorg. Nucl. Chem.*, **22**, 285 (1961).

(3) J. D. Dunitz and J. S. Rollett, *Acta Crystallogr.*, **9**, 327 (1956).

(4) (a) M. Calleri and J. C. Speakman, *Acta Crystallogr.*, **17**, 1097 (1964); (b) Mazhar-ul-Haque, C. N. Caughlan, and W. L. Moats, *J. Org. Chem.*, **35**, 1446 (1970); (c) F. P. Boer, *Acta Crystallogr., Sect. B*, **28**, 1201 (1972).

(5) (a) P. J. Wheatley, *J. Chem. Soc.*, 3722 (1962); (b) T.-T. Liang and K.-C. Chi, *Chem. Abstr.*, **63**, 12441*e* (1965); (c) F. Giordano and A. Ripamonti, *Acta Crystallogr.*, **22**, 678 (1967); (d) D. D. Swank and C. N. Caughlan, *Chem. Commun.*, 1051 (1968); (e) E. Alver and H. M. Kjoge, *Acta Chem. Scand.*, **23**, 1101 (1969); (f) D. Fenske, R. Mattes, J. Lons, and K. F. Tebbe, *Chem. Ber.*, **106**, 1139 (1973).

(6) H. Altenburg and D. Mosty, *Acta Crystallogr., Sect. B*, **27**, 1982 (1971).

(7) A. F. Berndt and R. Lamberg, *Acta Crystallogr., Sect. B*, **27**, 1092 (1971).

(8) Y. Okaya, *Acta Crystallogr.*, **20**, 712 (1966).

(9) J. Kraut, *Acta Crystallogr.*, **14**, 1146 (1961).

(10) D. F. Peppard, *Annu. Rev. Nucl. Sci.*, **21**, 365 (1971).

(11) E. K. Hulet and D. D. Bode, *MTP Int. Rev. Sci.*, **7**, 1 (1972).

(12) (a) G. W. Mason, A. F. Bollmeier, and D. F. Peppard, *J. Inorg. Nucl. Chem.*, **32**, 1011 (1970); (b) D. F. Peppard, G. W. Mason, A. F. Bollmeier, and S. Lewey, *ibid.*, **33**, 845 (1971).

(13) G. W. Mason and S. Lewey, *J. Inorg. Nucl. Chem.*, **36**, 911 (1974).

(14) An IBM 370/195 program written by H. A. Levy.

(15) (a) ORXFLS3 written by W. R. Busing and H. A. Levy; (b) FOURIER written by R. J. Dellaca and W. T. Robinson.

(16) ORFFE3 written by W. R. Busing and H. A. Levy.

(17) ORTEP written by C. Johnson.

(18) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, p 71.

(19) Reference 18, p 148.

(20) Reference 18, p 102.

(21) (a) C. H. Bushweller, J. A. Brunelle, W. G. Anderson, and H. S. Bilofsky, *Tetrahedron Lett.*, 3261 (1972); (b) J. B. Robert and J. D. Roberts, *J. Am. Chem. Soc.*, **94**, 4902 (1972); (c) C. H. Bushweller and J. A. Brunelle, *ibid.*, **95**, 5949 (1973); (d) C. H. Bushweller and J. A. Brunelle, *Tetrahedron Lett.*, 893 (1974); (e) C. H. Bushweller and M. Z. Lourandos, *Inorg. Chem.*, **13**, 2514 (1974).

(22) W. Hamilton and J. Ibers, "Hydrogen Bonding in Solids", W. A. Benjamin, New York, N.Y., 1968 pp 52–53.

(23) L. G. Vorontsova, *Z. Strukt. Khim.*, **7**, 240 (1966).

Nucleophilic Substitution at Phosphorus in Tertiary Phosphines. Evidence against Pseudorotation in a Potential Intermediate

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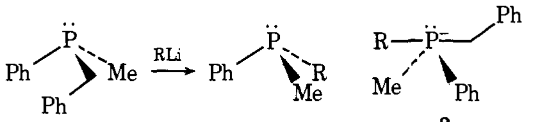
Abstract: The possibility of the formation of a hypervalent tetracoordinated phosphorus anion as an intermediate in nucleophilic substitution at phosphorus in tertiary phosphines was investigated. Treatment of (+)-$(S)_{\mathrm{P}}$-4-*tert*-butylphenylmethylphenylphosphine with *t*-BuLi resulted in displacement of phenyl and 4-*tert*-butylphenyl anions (in a ratio of 1.4:1, respectively) with complete inversion of configuration at phosphorus with both leaving groups. These data are used to show the absence of any pseudorotation in the potential intermediate (the hypervalent anion) and that the substitution may best be considered to be a classical SN2-type of process.

We recently reported that nucleophilic displacement at phosphorus (SN$^{\mathrm{P}}$) by alkyllithium reagents on (+)-$(R)_{\mathrm{P}}$-benzylmethylphenylphosphine (**1**) occurs with complete inversion of configuration at phosphorus (eq 1).[1] A possible



(1)

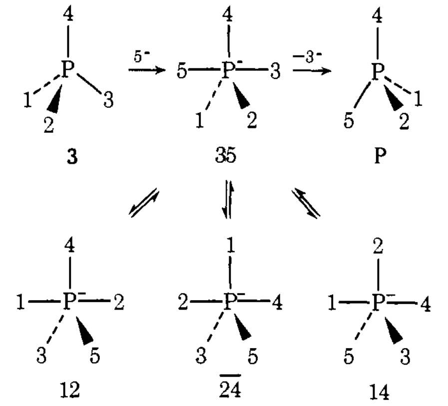
1

2

mechanism for this reaction would involve nucleophilic attack on the phosphine phosphorus atom, which could lead to a valence-expanded anionic intermediate (e.g., **2**).[2] This potential intermediate has one more electron than a phosphoranyl radical, some of which are known to be stereochemically nonrigid[3] due to pseudorotational processes (ψ).[4] As the analysis below will show, the stereochemical results of the SN$^{\mathrm{P}}$ reaction on **1**, with only one good leaving group, indicated, but did not prove, that **2** was stereochemically rigid. The use of a phosphine with poorer leaving groups than the benzyl anion might bestow a longer lifetime upon species analogous to **2**, potentially allowing ψ to become observable. It was thus of interest to investigate whether or not a stereochemical result other than complete inversion of configuration at phosphorus for an SN$^{\mathrm{P}}$ reaction was possible under more biased conditions than with substrate **1**. Before describing the specific substrate chosen, it is important to consider the potential pseudorotations in species analogous to **2**.

A hypervalent, tetracoordinated phosphorus anion (e.g., **2**) may be considered to be analogous to the neutral pentacoordinated phosphoranes, with the lone pair of electons (1p) replacing one of the ligands. Consequently, the analysis of pseudorotational interconversions of phosphoranes, as elegantly described in detail by Mislow,[4b,5] will be applied to the potential interconversions of the hypothetical tetracoordinated phosphorus anion intermediates. If one uses the descriptors 1, 2, 3, 4 to represent a substituted phosphine 123P4 (**3**) where 4 represents the 1p, and 3^- the *only leaving group*, and, further, 5^- represents the nucleophile of an alkyllithium, then Scheme I represents the types of transformations to be con-

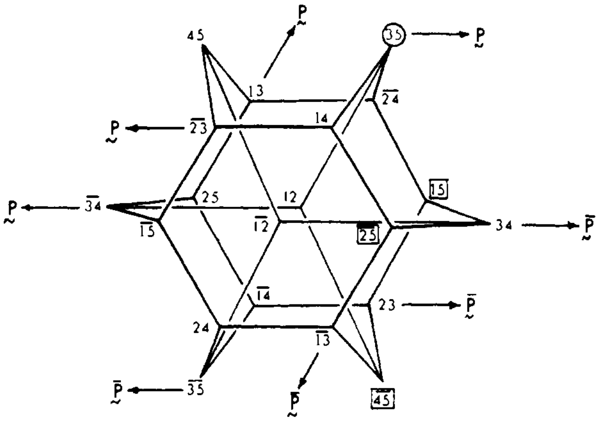
Scheme I. Generation of Hypothetical Tetracoordinate Phosphorus Anion Intermediates by Attack of Alkyl Anion (5^-) on Phosphine 3[a]



[a] See text for significance of numerical descriptors attached to phosphorus.

sidered in the following discussion. The chiral hypervalent anions may be described by the two apical descriptors, where the unbarred number represents a clockwise progression of the equatorial descriptors from lowest to highest, and the barred number, a counterclockwise progression.[4b] Scheme II uses a Desargues-Levi projection[4b] to illustrate the complete family of hypervalent anions which might be accessible with no restrictions to their interconversions via Berry pseudorotation. In addition, the entry points via apical attack of 5^- are shown either circled (attack backside of the leaving group 3) or boxed (attack other than backside of 3). Assuming apical leaving also,[6] the exit points must be from vertices with 3 as one of the double digit descriptors. The eight exit points are shown by arrows and give either **P** (inversion) or $\bar{\mathbf{P}}$ (retention). It is immediately obvious from Scheme II that if no restrictions are placed on (a) the direction of nucleophilic attack and (b) the various pseudorotamers accessible, a very complex situation might result.

Scheme II. Desargues–Levi Projection[a]



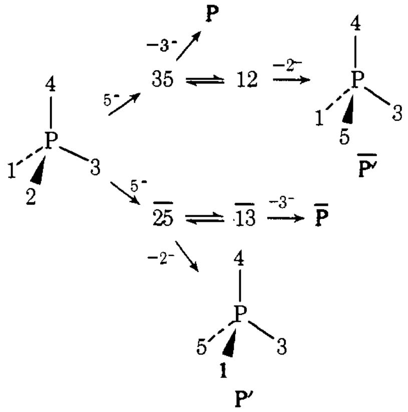
[a] Desargues–Levi projection illustrating the interconversions of hypothetical tetracoordinate phosphorus anion intermediates, some of which are shown in Scheme I. The vertices represent each isomer and also exit points to either **P** or $\bar{\mathbf{P}}$ via 3^- leaving apically. Entry points from 3 by apical attack of 5^- are shown by the double digit descriptor being either circled or boxed.

If one combines the various possibilities derived from (a) and (b) above, with the results from our previous work (eq 1),[1] then the following conclusions are possible: (case 1) if there are no restrictions either on the direction of nucleophilic attack, or on the accessible pseudorotamers, no ψ is possible;[7] (case 2) if there is no restriction on the direction of nucleophilic attack but if the 1p is *not* allowed to occupy an apical position[8] (4 cannot be one of the descriptors in Scheme II), no ψ is possible; (case 3) if only attack backside of the leaving group (3) is allowed, but there are no restrictions on the accessible pseudorotamers, no ψ is possible; (case 4) if only attack backside of the leaving group is possible and if the 1p is not allowed to occupy an apical position, then one ψ is possible, viz., $35 \rightleftharpoons 12$ (Scheme II).

Thus, our previous work[1] had eliminated any ψ if cases 1–3 applied, but left one ψ possible with case 4. This ψ would be invisible since only 35 could lead to product. It is important to note that the previous work did not eliminate the possibility that only one tetrahedral face was being attacked, since only the benzyl group was observed to be displaced from **1**. We had noted previously that phenyl anion displacement from a dialkylphenylphosphine did not occur.[9] We felt that in order to have the potential to observe this remaining possible ψ, a chiral phosphine with two similar leaving groups, e.g., 2^- and 3^- in **3** would have to be studied.

Scheme III illustrates what might be expected under the conditions of case 4 if ψ were to occur in the hypervalent anions prior to expulsion of the leaving groups. Here, there is a single ψ that does not place the 1p apically, but that allows access to either enantiomeric precursor of either $\mathrm{S_N^P}$ product, depending on which face is attacked. Thus, examination of the enantiomeric purity of the two products **P** and **P′** should give definitive information concerning the only remaining possibility for ψ in the hypothetical tetracoordinated phosphorus anion intermediates. A chiral phosphine bearing two similar leaving groups was synthesized and subjected to $\mathrm{S_N^P}$ conditions.

Scheme III. Potential Stereochemical Results of $\mathrm{S_N^P}$ via Hypervalent Anions on a Chiral Phosphine 3 Which has Two Leaving Groups, 2^- and 3^-, under Case 4 (see text) Restrictions[a]



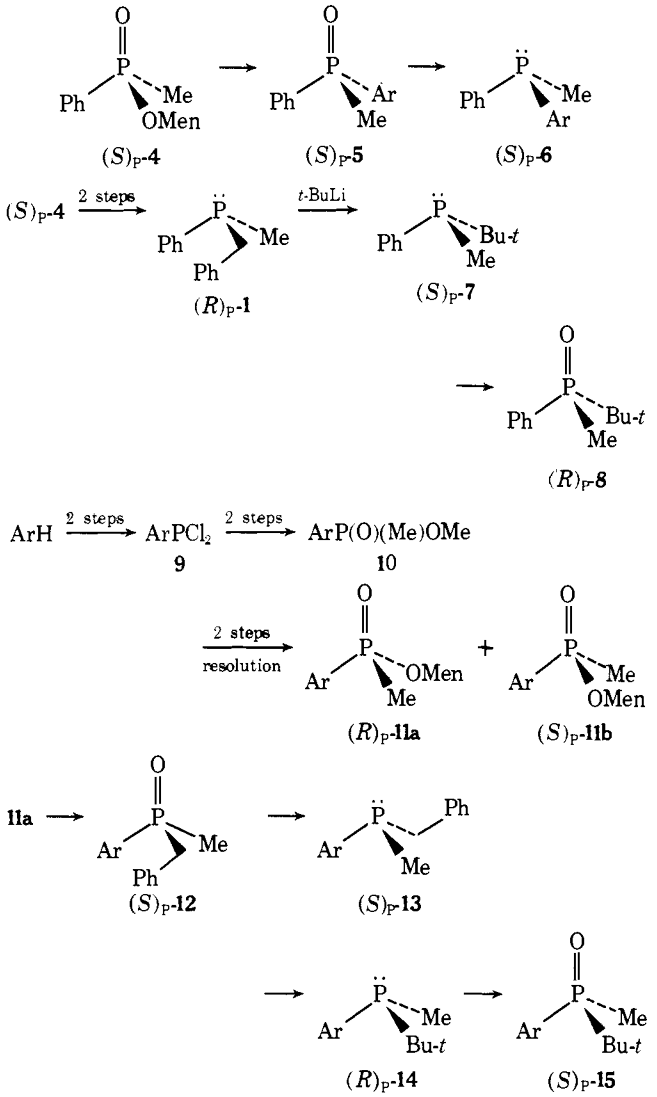
[a] See Scheme I for further details concerning descriptors.

Results and Discussion

The substrate chosen to investigate the above described problem, (+)-(S)$_\mathrm{P}$-(4-*tert*-butylphenyl)methylphenylphosphine (**6**), was obtained from the known[10] (S)$_\mathrm{P}$-menthyl methylphenylphosphinate (**4**), by methods similar to those described earlier[1,10] (Scheme IV). It was felt that substrate **6** had the following attractive features: (a) the phenyl and 4-*tert*-butylphenyl groups are of comparable leaving ability; (b) there are essentially two identical tetrahedral faces to be attacked by the nucleophile; (c) the leaving group abilities of the aryl groups are considerably poorer than that of benzyl, potentially allowing a longer lifetime for hypervalent anions to equilibrate (e.g., $35 \rightleftharpoons 12$ Scheme III).

Authentic samples of the oxides of the anticipated $\mathrm{S_N^P}$ products derived from **6** and *t*-BuLi were prepared as outlined in Scheme IV. Phosphine (S)$_\mathrm{P}$-**7**, obtained essentially optically pure from (R)$_\mathrm{P}$-**1**,[1,10] gave the optically pure phosphine oxide (R)$_\mathrm{P}$-**8**.[11] The absolute configurations at phosphorus in **14** and **15** were established from the configuration of the chiral pre-

Scheme IV. Synthetic Routes to Phosphines **6**, **7**, and **14** and Their Corresponding Oxides (Ar = 4-*t*-Bu C_6H_4)



cursor, (*R*)$_P$-**11a.** The absolute configurations at phosphorus in **11a** and **11b** were readily assigned by comparison of their ^1H NMR spectra with those of (*S*)$_P$-**4** and its (*R*)$_P$ isomer, whose absolute configurations had been firmly established.[10a,12] Particularly useful in this regard was a doublet at δ 0.35, present in the (*S*)$_P$ isomers but not in the (*R*)$_P$ isomers of **4** and **11**. This doublet was due to one of the diastereotopic methyl groups of the isopropyl moiety on the menthyl group.[10a,12] Optical purity in **11** was determined readily by integration of the P-CH_3 doublets, which differed in chemical shift by ca. 3 Hz in **11a** and **11b**. The stereochemistry of the conversions **11a** → (*S*)$_P$-**12** and (*S*)$_P$-**12** → (*S*)$_P$-**13** is well established,[10] and that of (*S*)$_P$-**13** → (*R*)$_P$-**14** is established by analogy with the conversion (*R*)$_P$-**1** → (*S*)$_P$-**7**, studied previously.[1]

Treatment of (*S*)$_P$-**6** ($[\alpha]_D^{25}$ +4.2°) in hexane-TMEDA with *t*-BuLi (fivefold excess) in pentane at room temperature for 10 min, followed by an aqueous ammonium chloride quench, gave **7** (13%) and **14** (19%).[13] The reaction mixture was treated immediately with excess H_2O_2 to give the three oxides in essentially the same yields as obtained from the phosphines. The phosphine oxides **8** and **15** were then separated by thermal gradient sublimation and gave the rotations shown in Table I, along with rotations for the optically pure material. Comparison of the signs of the rotations of the isolated oxides with those of the authentic materials establishes the chiralities of **8** and **15** as (*R*)$_P$ and (*S*)$_P$, respectively. In addition, the percent ee (enantiomeric excess) in the isolated (*R*)$_P$-**8** and (*S*)$_P$-**15** are calculated to be 74 and 76%, respectively (identical within experimental error). Although it was not possible to establish the optical purity of (*S*)$_P$-**4** independently, it should be noted that the sample used had $[\alpha]_D$ +4.2° which is 75% of the maximum observed ($[\alpha]_D$ +5.6°) in this work. Since the products of SN^P had % ee $\simeq$ 75% and since no optical resolution is possible in the SN^P process, the implication is that the sample with $[\alpha]_D$ +5.6° is optically pure, and that the sample used in the SN^P experiments had % ee = 75%. These data correspond to displacement of both leaving groups with complete inversion of configuration at phosphorus.

Table I. Optical Rotations of Phosphine (*S*)$_P$-**6** and the Oxides of the Phosphines Obtained by SN^P on (*S*)$_P$-**6**[a]

	(*S*)$_P$-**6**	(*R*)$_P$-**8**	(*S*)$_P$-**15**
Authentic (optically pure)	+5.6°[b]	+21.7°	−42.3°[d]
SN^P on (*S*)$_P$-**6**	+4.2°[c]	+16.1°	−32.1°

[a] $[\alpha]_D^{25}$(*c* 1-4, C_6H_6). [b] See text for discussion of optical purity. [c] Rotation of phosphine used for the SN^P reaction. [d] Calculated, see experimental section.

It thus appears that SN^P occurs via a process which *does not allow even one pseudorotation* (which would interconvert isomers of very similar potential energy) as outlined in Scheme III. If **35** or **25** are in fact intermediates, they must reside in potential wells with barriers to ejection of the leaving groups lower than the barrier to pseudorotation. Thus for all intents and purposes nucleophilic substitution at phosphorus in tertiary phosphines is a classical SN2 process with no formation of an intermediate.[14]

Experimental Section

Melting points and boiling points are uncorrected. Proton magnetic spectra were obtained on Perkin-Elmer R-12, Varian A-60, or Varian HA-100 instruments. Mass spectra were determined on a CEC-21-100 high resolution instrument or a DuPont 21-491 instrument. A Perkin-Elmer 141 polarimeter was used to obtain optical rotations. Gas chromatographic analyses were performed on a Varian-Aerograph Model 2700 instrument (thermal conductivity detector) using 5% SE 30 on Gas Chrom Q packed in stainless steel columns (6 ft by 0.188 in.). Peak area measurements were obtained with the aid of a Vidar 6300 digital integrator. Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz. *All phosphine manipulations were carried out in nitrogen atmospheres.*

(−)-(*S*)$_P$-(4-*tert*-Butylphenyl)methylphenylphosphine Oxide (3). Optically pure (*S*)$_P$-menthyl methylphenylphosphinate[10a] (4.0 g, 13.6 mmol) in dry (molecular sieves 4A) benzene (100 ml) was added to a 1.0 M ethereal solution of 4-*tert*-butylphenylmagnesium bromide (95 ml, 95 mmol). The ether was then distilled until the head temperature reached 71° and the resulting mixture was boiled under reflux for 17 h. The cooled mixture was quenched with saturated ammonium chloride (100 ml), the layers were separated, and the aqueous layer was extracted with chloroform (4 × 100 ml). The combined organic extracts were dried ($MgSO_4$), concentrated on a rotary evaporator, followed by heating up to 160° at 10 μ. The residue was crystallized and recrystallized from cyclohexane, followed by sublimation (110°, 10 μ) to give **5** as white buttons (1.4 g, 38%), mp 126–127°, $[\alpha]_D^{25}$ −17.4° (*c* 2.98, C_6H_6). The ^1H NMR spectrum gave absorptions at δ_{CDCl_3} (Me_4Si) 8.0–7.3 (m, 9-H), 2.0 (d, J = 12.6 Hz, 3-H), and 1.31 (s, 9-H). The mass spectrum exhibited a molecular ion at *m/e* 272.

Anal. Calcd for $C_{17}H_{21}OP$: C, 74.97; H, 7.77. Found: C, 74.94; H, 7.93.

(+)-(*S*)$_P$-(4-*tert*-Butylphenyl)methylphenylphosphine (6). A solution of the above oxide **5** (1.3 g, 4.8 mmol) and hexachlorodisilane (1.9 g, 7.0 mmol) in degassed benzene was immersed in an oil bath at 100° for 7 min, cooled in an ice bath, and quenched with 20% aqueous sodium hydroxide (25 ml). The layers were separated, and the benzene solution was diluted to 50 ml and washed with degassed water (2 × 50 ml) and brine (10 ml). The dried ($MgSO_4$) solution was concentrated and the residue was distilled (short path) to give **6** as a colorless oil (0.60 g, 49%); bp 120° (20 μ); $[\alpha]_D^{25}$ +5.6° (*c* 2.29, C_6H_6); MS, *m/e* 256 (M^+). The ^1H NMR spectrum exhibited absorptions at δ_{CDCl_3} (Me_4Si) 7.35 (m, 9-H), 1.59 (d, *J* = 3.5 Hz, 3-H), and 1.28 (s, 9-H).

Anal. Calcd for $C_{17}H_{21}P$: C, 79.66; H, 8.26. Found: C, 79.87; H, 8.41.

A similar run on a larger scale gave an 83% yield of **6**, but of lower optical purity: $[\alpha]_D^{25}$ +3.9° (*c* 2.37, C_6H_6).

(−)-(*S*)$_P$-*tert*-Butylmethylphenylphosphine (7). Optically pure (+)-(*R*)$_P$-benzylmethylphenylphosphine (1.0 g, 3.7 mmol) in hexane (60 ml) and TMEDA (1 ml) was treated at room temperature with a 1.2 M pentane solution of *t*-BuLi (9.3 ml, 11.7 mmol) for 0.25 h. Degassed, saturated ammonium chloride (50 ml) was added, the layers were separated, and the organic layer was dried ($MgSO_4$) and concentrated. The residue was distilled under vacuum to give **7** as a colorless liquid (0.30 g, 45%), bp 55° (10 μ), $[\alpha]_D^{25}$ −43.1° (*c* 4.56, C_6H_6), lit.[11] $[\alpha]_D$ +29.5° (C_6H_6, estimated 62% ee for (*R*)$_P$-**7**).

(+)-(*R*)$_P$-*tert*-Butylmethylphenylphosphine Oxide (8). The above phosphine **7** (200 mg, 1.22 mmol) in benzene (2 ml) was stirred with 30% hydrogen peroxide (1 ml) for 10 min. The layers were separated, the aqueous layer was extracted with benzene (2 × 3 ml), and the combined organic extracts were dried ($MgSO_4$) and concentrated. The residue was purified by thermal gradient sublimation (50°, 10 μ) to give the phosphine as a very hydroscopic white solid (100 mg, 42%), mp 98–99°, $[\alpha]_D^{25}$ +21.5° (*c* 2.22, MeOH), +21.7° (*c* 1.83, C_6H_6), lit.[2] $[\alpha]_D$ +14.9° (MeOH, estimated 71% ee).

4-*tert*-Butylphenyldichlorophosphine (9). Bis(diethylamino)chlorophosphine[15] (125 g, 0.59 mol) in dry ether (300 ml) was added with vigorous stirring to a 0.9 M ethereal solution of 4-*tert*-butylphenylmagnesium bromide (800 ml, 0.72 mol) at −78°. The resulting mixture was warmed to room temperature, filtered, and concentrated, and the residue was distilled to give the crude 4-*tert*-butylphenylbis(diethylamino)phosphine as a colorless oil (100 g, 55%), bp 145–150° (5 μ). The ^1H NMR spectrum exhibited absorptions at δ_{CDCl_3} (Me_4Si) 7.4 (narrow m, 2-H), 3.4–2.8 (pair overlapping q, *J* = 7 Hz, centered at δ 3.23 and 3.07, 4-H), 1.35 (s, 9-H), and 1.16 (t, *J* = 7 Hz, 6-H); the presence of an impurity, however, was indicated by an absorption at δ 1.40 (ca. 10% of the *t*-Bu peak of the bis(diethylamino)phosphine).

A solution of the above crude aminophosphine (100 g, 0.32 mol) in dry ether (100 ml) was added with vigorous stirring to dry hydrochloric acid (47.8 g, 1.3 mol) in dry ether (300 ml) at −78°. The mixture was warmed to room temperature and stirred overnight. The resulting mixture was filtered, concentrated, and distilled to give **9** as a colorless oil (70 g, 90%), bp 93–95° (100 μ). The molecular ion mass cluster gave a typical dichloro pattern, with a molecular ion at *m/e* 234 (^{35}Cl). The ^1H NMR spectrum exhibited absorptions at δ_{CDCl_3} (Me_4Si) 7.9–7.4 (m, 4-H) and 1.32 (s, 9-H).

Anal. Calcd for $C_{10}H_{13}Cl_2P$: C, 51.09; H, 5.57. Found: C, 51.34; H, 5.82.

Methyl 4-*tert*-Butylphenylmethylphosphinate (10). A solution of methanol (20.4 g, 0.64 mol) in pentane (70 ml) was added dropwise to a vigorously stirred solution of the above chloride **9** (68.2 g, 0.29 mol) in dry pentane (300 ml) and pyridine (51 g, 0.64 mol) at 0°. The mixture was stirred for 0.5 h after warming to room temperature, then filtered, and concentrated to give the crude dimethyl 4-*tert*-butylphenylphosphonite (66 g, 100%). The ^1H NMR spectrum of the crude material gave absorptions at δ_{CDCl_3} (Me_4Si) 7.5 (m, 4-H), 3.55 (d, *J* = 10.3 Hz, 6-H), and 1.32 (s, 9-H).

The crude phosphonite (66 g, 0.29 mmol) was added portionwise to methyl iodide (2 g, 0.014 mol) while maintaining the temperature between 105 and 115° using both the exothermicity of the reaction and a heat gun. Additional portions of methyl iodide (ca. 1 g) were added occasionally. The dark residue was distilled to give the phosphinate **10** as a colorless oil (49.6 g, 73%), bp 135–138° (0.5 mm), which solidified on standing, mp 99–104° (103–105° after thermal gradient sublimation), MS, *m/e* 226 (M^+). The ^1H NMR spectrum showed absorptions at δ_{CDCl_3} (Me_4Si) 8.7 (m, 4-H), 3.13 (d, *J* = 11 Hz, 3-H), 1.67 (d, *J* = 14.5 Hz, 3-H), and 1.36 (s, 9-H).

Anal. Calcd for $C_{12}H_{19}O_2P$: C, 63.70; H, 8.46. Found: C, 63.70; H, 8.57.

(−)-(*R*)$_P$-Menthyl 4-*tert*-Butylphenylmethylphosphinate (11a). The above phosphinate **10** (47.7 g, 0.211 mol) in carbon tetrachloride (200 ml) was treated portionwise with phosphorus pentachloride (47.9 g, 0.23 mol) at 60°. The mixture was stirred at 60° for 2 h, filtered, concentrated, and distilled to give the crude 4-*tert*-butylphenylmethylphosphinyl chloride (41 g, 84%), bp 127–129° (40 μ), which solidified to a hygroscopic solid, mp 60–65°. The ^1H NMR spectrum of the crude material was consistent with the chloride: δ_{CDCl_3} (Me_4Si) 7.75 (m, 4-H), 2.21 (d, *J* = 14.5 Hz, 3-H), and 1.35 (s, 9-H).

The above crude phosphinyl chloride (23 g, 0.10 mol) in dry ether (100 ml) was added in one portion to a solution of *l*-menthol (15.8 g, 0.10 mol) in ether (50 ml) and pyridine (8.0 g, 0.10 mol) at 15°. The mixture was allowed to stand overnight, then extracted with water (3 × 100 ml) and brine (100 ml) and dried ($MgSO_4$). Concentration of the resulting solution gave the diastereomeric mixture of menthyl phosphinates as a very viscous oil (33 g, 92%). The ^1H NMR spectrum in the aliphatic region was indicative of the diastereomeric mixture: δ_{CDCl_3} (Me_4Si) 1.69 (d, *J* = 14.5 Hz), 1.64 (d, *J* = 14.5 Hz), 1.33 (s), 0.90 (complex m) and 0.30 (d, *J* = 6.5 Hz). Since all attempts to crystallize this material failed, it was chromatographed on silica gel (1.4 kg) using pentane–ether (3:1, v/v) as eluent, and 1-l. fractions were monitored for weight of residue and optical rotation. Although early fractions gave $[\alpha]_D^{25}$ −4.4° (*c* 3.2, C_6H_6), further fractions were combined with these to give a very viscous oil, which was distilled (Kugelrohr, 135° (20 μ)) to give the menthyl phosphinate **11a** as a clear, very viscous oil (4.0 g, 11% based on starting chloride), which solidified on standing for 2 weeks: mp 61–63°; $[\alpha]_D^{25}$ −7.3° (*c* 2.58, C_6H_6); MS, *m/e* 350 (M^+). The ^1H NMR spectrum showed absorptions at δ_{CDCl_3} (Me_4Si) 7.6 (m, 4-H), 4.3 (m, 1-H), 1.64 (d, *J* = 14.5 Hz, 3-H), 1.33 (s, 9-H), three overlapping doublets at 0.96 (*J* = 7.0 Hz, 3-H), 0.89 (*J* = 7.0 Hz, 3-H), and 0.79 (*J* = 5.0 Hz). The above sharp absorptions at δ 1.7–0.8 were superimposed upon a diffuse multiplet due to the substituted cyclohexyl ring and the isopropyl methine protons (9-H). The percent ee [(*R*)$_P$–(*S*)$_P$] was estimated to be >92 by NMR (comparison of the doublets at δ 1.69 and 1.64) and ca. 94 by assuming that $[\alpha]_D^{25}$ −4.4° (vide supra) was of optically pure material.

Anal. Calcd for $C_{21}H_{35}O_2P$: C, 71.97; H, 10.07. Found: C, 71.68; H, 10.26.

Further elution led ultimately to the collection of tail fractions which were distilled (Kugelrohr, 135° (20 μ)) to give a viscous oil (3.0 g, 8%) which solidified on standing: mp 66–69°; $[\alpha]_D^{25}$ −83.0° (*c* 5.26, C_6H_6); MS, *m/e* 350 (M^+). The ^1H NMR spectrum exhibited absorptions at δ_{CDCl_3} (Me_4Si) 7.6 (m, 4-H), 4.0 (m, 1-H), 1.69 (d, *J* = 14.5 Hz, ca. 2.7-H, vide infra), 1.64 (d, *J* = 14.5 Hz, ca. 0.3-H, vide infra), 1.33 (s, 9-H), 0.92 (d, *J* = 5.0 Hz, 3-H), 0.83 (d, *J* = 7.0 Hz, 3-H), and 0.30 (d, *J* = 7.0 Hz, 3-H). The above sharp absorptions at δ 1.7–0.8 were superimposed upon a diffuse multiplet due to the substituted cyclohexyl ring and isopropyl methine protons. The percent ee [(*S*)$_P$–(*R*)$_P$] was estimated to be 84 (by comparison of the doublets at δ 1.69 and 1.64), which leads to a calculated $[\alpha]_D$ −90° for the (*S*)$_P$-menthyl phosphinate **11b.**

(−)-(*S*)$_P$-Benzyl(4-*tert*-butylphenyl)methylphosphine Oxide (12). The above (*R*)$_P$-menthyl phosphinate (**11a**) (3.9 g, 10.8 mmol) in dry benzene (70 ml) was added to a 1.1 M ether solution of benzylmagnesium chloride (150 ml, 165 mmol), and the ether was distilled until the head temperature reached 71°. The resulting mixture was refluxed overnight, and the cooled mixture quenched with saturated ammonium chloride (70 ml). The layers were separated, the aqueous layer was extracted with chloroform (4 × 50 ml), and the combined extracts were dried ($MgSO_4$) and concentrated. The residue was pumped on at 100° (10 μ) and then crystallized and recrystallized from cyclohexane to give the phosphine oxide **12** (1.5 g, 49%) as a white solid: mp 158–161°; $[\alpha]_D^{25}$ −37.3° (*c* 2.52, C_6H_6); MS, *m/e* 286 (M^+). The ^1H NMR spectrum exhibited absorptions at δ_{CDCl_3} (Me_4Si) 7.4 (m, 9-H), 3.28 (d, *J* = 15 Hz, 2-H), 1.63 (d, *J* = 12.5 Hz, 3-H), and 1.33 (s, 9-H).

Anal. Calcd for $C_{18}H_{23}OP$: C, 75.50; H, 8.10. Found: C, 75.41; H, 7.96.

(−)-(*S*)$_P$-*tert*-Butyl(4-*tert*-butylphenyl)methylphosphine Oxide (15). A benzene solution (30 ml) of phosphine oxide **12** (1.40 g, 4.90 mmol) was treated at room temperature with hexachlorodisilane (2.2 g, 8.2 mmol), and the resulting mixture was immersed in an oil bath at 90° for 8 min, then cooled in an ice bath. The reaction mixture was treated with 20% sodium hydroxide (30 ml), the layers were separated, and the aqueous layer was extracted with benzene (2 × 30 ml). The combined organic extracts were washed with degassed water, dried ($MgSO_4$), and concentrated. The residue was distilled (Kugelrohr, 120° (5 μ)) to give (S)$_P$-benzyl(4-*tert*-butylphenyl)methylphosphine (**13**) (0.80 g, 60%), $[\alpha]_D^{25}$ −69.7° (c 3.10, C_6H_6), MS, *m/e* 270 (M^+). The ^1H NMR spectrum featured absorptions at δ_{CDCl_3} (Me_4Si) 7.2 (m, 9-H), 3.00 (m, 2-H), 1.30 (s, 9-H), and 1.25 (d, J = 3.5 Hz, 3-H). This phosphine showed a great tendency to air oxidize and was not characterized by elementary analysis.

The phosphine (**13**) (515 mg, 1.91 mmol) in ether (20 ml) and TMEDA (2.4 g, 21 mmol) was treated with 1.6 M *tert*-butyllithium in pentane (10 ml, 16 mmol) at 25° for 1 h. The reaction mixture was quenched with saturated ammonium chloride (10 ml), and the layers were separated. The organic layer was dried ($MgSO_4$), concentrated, and distilled (Kugelrohr, 100° (10 μ)) to give (R)$_P$-*tert*-butyl(4-*tert*-butylphenyl)methylphosphine (**14**) as a colorless liquid (131 mg, 29%), $[\alpha]_D^{25}$ +30.6° (c 3.76, C_6H_6). Exact mass calcd for $C_{15}H_{15}P$, 236.1694; found, 236.1690. The ^1H NMR spectrum exhibited absorptions at δ_{CDCl_3} (Me_4Si) 7.4 (m, 4-H), 1.32 (s) and ca. 1.31 (d, $J \simeq 3.5$ Hz) (1.32 + 1.31 absorptions: 12-H), and 0.97 (d, J = 12.0 Hz, 9-H). A small amount of phosphine oxide impurity (ca. 5%) was evident from a doublet at δ 1.72 (vide infra). This phosphine showed a great tendency to oxidize and was not characterized by elemental analysis.

The above phosphine (**14**) (100 mg, 0.42 mmol) was dissolved in benzene (2 ml) and stirred for several minutes with 30% hydrogen peroxide (1 ml). The layers were separated, the aqueous layer was extracted with benzene (2 × 2 ml), and the combined organic extracts were washed with brine (1 ml), dried ($MgSO_4$), and concentrated. The residue was purified by thermal gradient sublimation to give the phosphine oxide (**15**) as a white crystalline solid (91 mg, 86%): mp 168–173°; $[\alpha]_D^{25}$ −38.0° (c 2.80, C_6H_6); MS, *m/e* 252 (M^+). The ^1H NMR spectrum exhibited absorptions at δ_{CDCl_3} (Me_4Si) 7.6 (m, 4-H), 1.72 (d, J = 12 Hz, 3-H), 1.33 (s, 9-H), and 1.15 (d, J = 15 Hz, 9-H). To determine the enantiomeric purity, an ^1H NMR spectrum was run on the sample in (+)-(S)-2,2,2-trifluorophenylethanol[16] and perdeuteriobenzene (1:1, v/v) which resolved the diastereotopic phosphorus methyl protons; δ (Me_4Si) 1.20 (d, J = 12 Hz, major) and 1.13 (d, J = 12 Hz?, one absorption superimposed on C-Bu-t absorption, minor), along with absorptions at δ 1.33 (s) and 0.79 (d, J = 15 Hz) due to the *tert*-butyl groups. Integration of multiple scans gave the % ee = 90. This leads to a calculated $[\alpha]_D$ −42.3°.

Anal. Calcd for $C_{15}H_{25}OP$: C, 71.40; H, 9.99. Found: C, 71.11; H, 9.61.

The Reaction of *tert*-Butyllithium with (+)-(S)$_P$-(4-*tert*-Butylphenyl)methylphenylphosphine (6). A 1.22 M pentane solution of *tert*-butyllithium (20 ml, 24 mmol) wa added at room temperature to a solution of the phosphine (1.06 g, 4.13 mmol) in dry hexane (75 ml) and TMEDA (2.8 g, 24 mmol) and the reaction mixture was stirred at room temperature for 0.5 h. A saturated solution of ammonium chloride (100 ml) was added, the layers were separated, and the organic layer was dried ($MgSO_4$). Analysis by GLC revealed only three peaks corresponding in retention times to PhP(Me)Bu-t, 4-t-BuC_6H_4P(Me)Bu-t, and 4-t-BuC_6H_4P(Me)Ph in mole ratios of 13:19:68 (corrected for thermal response factors). Dichloromethane (25 ml) and 30% hydrogen peroxide (10 ml) were added and the resulting mixture was stirred at room temperature for 1 h. Analysis by GLC indicated that the phosphines had reacted completely and three new peaks were present corresponding in retention times to PhP(O)(Me)Bu-t, 4-t-BuC_6H_4P(O)(Me)Bu-t, and 4-t-BuC_6H_4P(O)(Me)Ph in mole ratios of 11:17:72. The two layers were separated, and the organic layer was dried ($MgSO_4$) and concentrated to give a viscous residue (1.01 g), which solidified on standing. This was separated into its components using a number of thermal gradient sublimations coupled with GLC monitoring of the various zones obtained. Care was taken to isolate as much as possible the entire amount of each component, since some optical fractionation did occur in the various zones of the sublimate. The rotations of the product phosphine oxides thus obtained were: PhP(O)(Me)Bu-t, $[\alpha]_D^{25}$ +16.1° (c 1.63, C_6H_6); 4-t-BuC_6H_6P(O)(Me)Bu-t, $[\alpha]_D^{25}$ −32.1° (c 3.14, C_6H_6). These rotations correspond to % ee's: PhP(O)(Me)Bu-t, 74; 4-t-BuC_6H_4P(O)(Me)Bu-t, 76.

A similar, duplicate run gave essentially the same results.

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References and Notes

(1) E. P. Kyba, *J. Am. Chem. Soc.*, **97**, 2554 (1975).

(2) The existence of such a species as an intermediate has been proposed; G. Wittig and A. Maercker, *J. Organomet. Chem.*, **8**, 191 (1967).

(3) For recent studies in this area: (a) D. Griller and K. H. Ingold, *J. Am. Chem. Soc.*, **97**, 1813 (1975), and references contained therein; (b) I. H. Elson, M. J. Parrott, and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 586 (1975); (c) H.-W. Tan and W. G. Bentrude, *J. Am. Chem. Soc.*, **96**, 5950 (1974).

(4) (a) F. H. Westheimer, *Acc. Chem. Res.*, 1, 70 (1968), and references contained therein; (b) K. Mislow, *ibid.*, **3**, 321 (1970), and references contained therein; (c) I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Ramirez, *Ibid.*, **4**, 288 (1971), and references contained therein; (d) E. L. Muetterties and R. A. Schunn, *Q. Rev., Chem. Soc.*, **20**, 235 (1966); (e) J. I. Musher in "Conformational Analysis, Scope and Present Limitations", G. Chiurdoglu, Ed., Academic Press, New York, N.Y., 1971, pp 177–189.

(5) I wish to thank the referee for pertinent comments concerning the use of graph theory to analyze this potentially very complicated situation.

(6) A set of arguments similar to those which assume apical attack and exit may also be developed for equatorial attack and exit and lead to the same conclusions.

(7) For example, if in Scheme II, 15 were produced, one ψ would produce 23 whch would give **P** (retention). Even if 23 were, for some reason, not a reasonable exit point further ψ could lead to either 35 or $\overline{35}$ and thus to at least partially racemic product. Since only complete inversion of configuration was observed, case 1 must not allow any ψ, and only attack backside of 3 leads to product. Similar arguments also apply to the conclusions reached in cases 2 and 3.

(8) A lone pair of electrons can be considered as a group having the least possible electronegativity; therefore, its apicophilicity[4a] should be extremely low, making pseudorotamers with 4 as one of the double digit descriptors in Scheme II inaccessible.

(9) E. P. Kyba and C. W. Hudson, *Tetrahedron Lett.*, 1869 (1975).

(10) (a) O. Korpiun, R. A. Lewis, J. Chickos, and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4842 (1968); (b) K. Naumann, B. Zon, and K. Mislow, *ibid.*, **91**, 7012 (1969).

(11) R. A. Lewis, K. Naumann, K. E. DeBruin, and K. Mislow, *J. Chem. Soc. D*, 1010 (1969).

(12) R. A. Lewis, O. Korpiun, and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4847 (1968).

(13) The yield of recovered **4** was 68%. This phosphine was clearly less prone to S_N^P than Ph_2PMe, as established in competition experiments where **4** gave only 25% S_N^P compared to Ph_2PMe[9] which gave 43% S_N^P.

(14) A similar conclusion was reached for nucleophilic substitution in isoelectronic, though rather dissimilarly substituted, "pentacoordinate" sulfur compounds; R. Tang and K. Mislow, *J. Am. Chem. Soc.*, **91**, 5644 (1969).

(15) P. G. Chantrell, C. A. Pearce, C. R. Toyer, and R. Twaits, *J. Appl. Chem.*, 563 (1964).

(16) W. H. Pirkle, S. D. Beare, and R. L. Muntz, *J. Am. Chem. Soc.*, **91**, 4574 (1969).