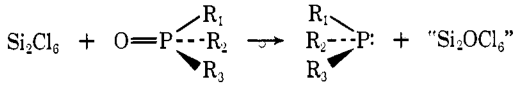
In the case of hexachlorodisilane, the silicon-containing product, "Si_2OCl_6," appears to be a mixture of silicon tetrachloride, hexachlorodisiloxane ($Cl_3SiOSiCl_3$), and higher molecular weight perchloropolysiloxanes.

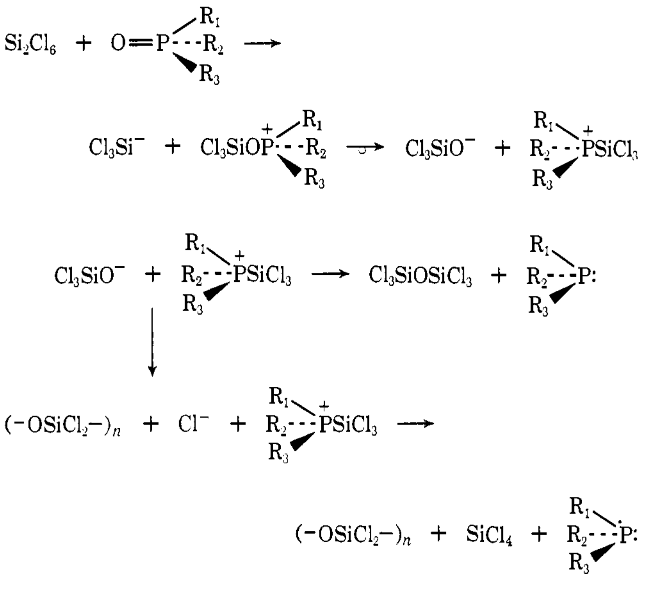


A typical procedure for such a reduction is the following. A solution of optically pure (+)-(*R*)-benzylmethylphenylphosphine oxide[3] (336 mg, 1.46 mmol), $[\alpha]_D$ +51.4° (methanol), in benzene (9 ml) was refluxed under N_2 with hexachlorodisilane (0.32 ml, *ca.* 1.9 mmol) for 15 min.[5] The reaction mixture was cooled to 0° and hydrolyzed by cautious addition of 30% aqueous sodium hydroxide (3 ml). Benzene (16 ml) was added and the organic layer was washed with water and dried (magnesium sulfate). Removal of solvent under reduced pressure gave the reduction product, benzylmethylphenylphosphine, as a clear, colorless oil, which could be isolated by rapid distillation (kugelrohr) at reduced pressure, bp 90–95° (0.01 mm). Reoxidation with excess hydrogen peroxide yielded (−)-(*S*)-benzylmethylphenylphosphine oxide, $[\alpha]_D$ −46.9° (methanol), optical purity 91%. Quaternization with excess *n*-propyl bromide in acetonitrile (*ca.* 60°, 10 hr) afforded (+)-(*S*)-benzylmethylphenyl-*n*-propylphosphonium bromide,[6] $[\alpha]_D$ +32.8° (methanol), optical purity 89%. The hydrogen peroxide oxidation and *n*-propylation of benzylmethylphenylphosphine proceed with retention of configuration at phosphorus.[7]

The ready availability of hexachlorodisilane, the simplicity and mildness of the reaction conditions (thus the reduction may be carried out in chloroform at room temperature), the high product yield (70–90%), and the high stereospecificity of the reduction (*ca.* 90%) make this a most convenient method for the preparation of optically active phosphines.

A tentative mechanism which we suggest to account for the observed stereochemistry and stoichiometry of the hexachlorodisilane reduction of optically active acyclic phosphine oxides is represented by Scheme I. The intervention of trichlorosilyl anion as a reaction intermediate has also been suggested in the base-catalyzed decomposition of hexachlorodisilane with tri-*n*-butylamine[8] and triphenylphosphine.[9]

Scheme I



Hexachlorodisilane was also found to reduce amine oxides and sulfoxides. Typically, the reduction of 4-methylpyridine N-oxide to 4-methylpyridine could be readily effected in 60–70% yield by simply stirring a mixture of the N-oxide and hexachlorodisilane (molar ratio 1:1) in chloroform at room temperature for 1 hr. Likewise, the smooth reduction of diphenyl sulfoxide by hexachlorodisilane in benzene at room temperature for 1 hr yielded diphenyl sulfide (91%). The work-up procedure for these reactions was essentially the same as that described above.

Finally, we have found that reduction of cyclic phosphine oxides as well as of optically active acyclic phosphine sulfides with hexachlorodisilane proceeds with *retention* of configuration.[10] These results, as well as the mechanistic relevance of perchloropolysilanes in reductions of phosphine oxides with trichlorosilane in the presence of strongly basic tertiary amines,[4] will be discussed in detail in forthcoming papers.

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(4) Hydrides have been employed in the stereospecific reduction of phosphine oxides to phosphines, a particularly valuable reagent being trichlorosilane, whose utilization for this purpose was pioneered by L. Horner and W. D. Balzer, *Tetrahedron Lett.*, 1157 (1965).

(5) Reduction is generally complete in 15 min or less. An increase in contact time causes chemical racemization of the produced phosphines.

(6) A. F. Peerdeman, J. P. C. Holst, L. Horner, and H. Winkler, *Tetrahedron Lett.*, 811 (1965).

(7) L. Horner, *Pure Appl. Chem.*, **9**, 225 (1964).

(8) G. D. Cooper and A. R. Gilbert, *J. Amer. Chem. Soc.*, **82**, 5042 (1960).

(9) H. J. Emeléus and M. Tufail, *J. Inorg. Nucl. Chem.*, **29**, 2081 (1967).

(10) To our knowledge, the reduction of optically active phosphine sulfides to optically active phosphines by hexachlorodisilane represents the first reported stereospecific reduction of such compounds.

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A General Method for Determining the Optical Purity of Phosphines[1]

Sir:

Contemporary techniques for obtaining optically active phosphines and their derivatives[2] are not complemented by any single widely applicable method for the determination of optical purities in this class of compounds. Enantiomeric ratios, and consequently optical purities, may be reliably estimated by nmr analysis of the diastereomers which are obtained when enantiomers are suitably derivatized with optically active reagents.[3] We wish to communicate at this time our experience with one such reagent, 2-phenyl-2-methoxyethyl bromide (**1**), which possesses all of the requisite attributes: it is easily obtained in optically pure form, it reacts quantitatively with phosphines (**2**) to give 2-phenyl-2-methoxyethylphosphonium bro-

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(1) This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-B.

(2) For a recent review, see N. J. Gallagher and I. D. Jenkins in "Topics in Stereochemistry," Vol. 3, N. L. Allinger and E. L. Eliel, Ed., John Wiley & Sons, Inc., New York, N. Y., 1968, Chapter 1.

(3) M. Raban and K. Mislow in "Topics in Stereochemistry," Vol. 2, N. L. Allinger and E. L. Eliel, Ed., John Wiley & Sons, Inc., New York, N. Y., 1967, Chapter 4.

Table I. Chemical Shift Nonequivalence of Diastereotopic Protons in Some 2-Phenyl-2-methoxyethylphosphonium Bromides (**3**)

Starting phosphine (2)				Δν, Hz, at 60 MHz		
R_1	R_2	R_3	Solvent	OCH_3[a]	PCH_3[b]	Anisyl OCH_3
Methyl	Cyclohexyl	Benzyl[c]	D_2O	2.7	0.5	
Methyl	Phenyl	*n*-Propyl[d]	D_2O	4.2	9.2	
Methyl	Phenyl	*p*-Anisyl	D_2O	0.9	*e*	*e*
Methyl	Phenyl	*o*-Anisyl	D_2O	2.2	5.8	3.3
Methyl	Phenyl	*o*-Anisyl	$(CD_3)_2CO$	6.0	3.0	2.3
Phenyl	β-Naphthyl	*o*-Anisyl	$CDCl_3$	1.5		1.9
Phenyl	β-Naphthyl	*o*-Anisyl	C_6H_5CN	*e*		4.2

[a] Refers to the methoxyl group derived from **1**. [b] J_{PCH} = 13.5–14.5 Hz. [c] At 60 MHz, the benzyl methylene protons in both diastereomers appear as broadened A_2 (rather than AB) spin systems, split by phosphorus. Δν for the two diastereomers is 2.5 Hz; J_{PCH} is 15 Hz for each. [d] Using **4**, Δν for OCH_3 and PCH_3 protons is 5.1 and 7.4 Hz, respectively. Δν for the diastereotopic methine protons is 9 Hz; J_{PCCH} is 7.5 Hz for each. [e] Only a broad signal was observed at 60 MHz.

mides (**3**), and, by virtue of the chemical shift nonequivalence observed for the diastereotopic protons in the product mixture, it provides a convenient means for estimating the optical purity of aliphatic, aromatic, and mixed tertiary phosphines.[4]

$$\underset{\mathbf{1}}{C_6H_5CH(OCH_3)CH_2Br} + \underset{\mathbf{2}}{PR_1R_2R_3} \longrightarrow \underset{\mathbf{3}}{C_6H_5CH(OCH_3)CH_2P^+R_1R_2R_3Br^-}$$

Reduction of optically pure methyl (*S*)-O-methylmandelate[5] with lithium aluminum hydride gives 2-phenyl-2-methoxyethanol (bp 75° (1 mm)); mesylation under standard conditions, followed by treatment of the mesylate with sodium bromide in DMSO at 80° (12 hr), affords **1**, bp 59° (0.5 mm), $n^{22.5}$D 1.5419, [α] D +73° (methanol), in 40–80% over-all yield from O-methylmandelic acid. Where signals from the methylene protons in **3** interfere with the pmr analysis, the reagent of choice is 2-phenyl-2-methoxyethyl-1-d_2 bromide (**4**), $n^{22.5}$D 1.5399, [α]D +73° (methanol), prepared as above by reduction with lithium aluminum deuteride.

When various representative racemic phosphines (**2**) were heated under reflux for 7 hr with a twofold excess of **1** in oxygen-free dry benzene, **3** precipitated from solution. After addition of hexane (to complete precipitation), the mixture of diastereomers was isolated and dried, and the pmr spectrum was recorded. The chemical shift differences of diastereotopic protons are listed in Table I. There is a pronounced doubling of resonance signals and an appreciable solvent effect. Given that the reaction is essentially quantitative,[6] that quaternization proceeds stereospecifically with retention of configuration at phosphorus,[7] that thermal racemization of **2** is minimized by the mildness of the reaction conditions,[8] and that no racemization at the asymmetric carbon center can take place, the method thus lends itself ideally to the stated purpose.

To test the accuracy of the method, methylphenylpropylphosphine (**5**), [α]D −8.6° (toluene), obtained by hexachlorodisilane reduction[9] of methylphenylpropylphosphine oxide (**6**), [α]D +10.5° (methanol), was quaternized with **4**. From the relative intensities of the diastereotopic OCH_3 and PCH_3 pmr signals in the phosphonium salt (Table I), an optical purity of 44% was calculated[3] for the precursor **5**. A portion of the same sample of **5** was oxidized with hydrogen peroxide to the phosphine oxide, **7**, [α]D −8.8° (methanol),[10] and another portion quaternized with benzyl bromide to the P-benzylphosphonium salt, **8**, [α]D −16.0° (methanol). It follows that the absolute rotations of **5**, **7**, and **8** are 19.5, 20.0, and 36.4°, respectively, in good accord with the highest rotations reported[7,11] for these compounds, 18.4, 19.6, and 36.8°, respectively.

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(4) Where applicable, doubling of nmr signals of tetrahedral bis(phosphine)nickel(II) bromide complexes in chloroform (W. D. Horrocks, Jr., private communication) or of phosphine oxides in chiral solvents (W. H. Pirkle, private communication) may also be employed.

(5) J. Jacobus, M. Raban, and K. Mislow, *J. Org. Chem.*, 33, 1142 (1968).

(6) As judged by the ratio of intensities of the signals due to the diastereotopic protons, which is unity within the precision of the measurements. When racemic **2** and *racemic* **1** are allowed to react, however, this ratio deviates from unity by as much as 10%, reflecting[6] the difference in the rate constants of formation of the diastereomeric phosphonium salts.

(7) L. Horner, *Pure Appl. Chem.*, **9**, 225 (1964).

(8) For example, methylphenylpropylphosphine (**5**) racemizes in decalin at 130° with a half-life of 301 min (L. Horner and H. Winkler, *Tetrahedron Lett.*, 461 (1964)).

(9) K. Naumann, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 2788 (1969).

(10) From a comparison of the specific rotations of **6** and **7**, it follows that the hexachlorodisilane reduction[9] proceeded with only 84% net inversion. As detailed in a forthcoming paper, the incomplete stereospecificity can be attributed to chemical racemization of produced **5** under the conditions of the reduction.

(11) D. B. Denney and J. W. Hanifin, Jr., *Tetrahedron Lett.*, 2177 (1963).

(12) (a) Public Health Service Postdoctoral Fellow, 1968–1969; (b) Public Health Service Predoctoral Fellow, 1968–1969.

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Conformational Analysis of the 2,5-Di-*t*-butylcyclohexanol System. Evaluation of the Steric Effect of the *t*-Butyl Group in Cyclohexane Chair and Twist-Boat Conformations[1]

Sir:

Conformational analysis of the cyclohexane ring system has demonstrated that the chair form is appreciably more stable than the boat or twist-boat form. Allinger and Freiberg[2] have measured the enthalpy and entropy difference between *trans*- and *cis*-1,3-di-*t*-butylcyclohexane to be 5.9 ± 0.6 kcal/mol and +4.9

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(1) Research supported by the Alred P. Sloan Foundation.

(2) N. L. Allinger and L. A. Freiberg, *J. Amer. Chem. Soc.*, **82**, 2393 (1960).