was crystallized from chloroform–hexane, and recrystallized from methylene chloride–hexane: mp 139–142°; pmr CH_3O, s, τ 6.54; naphthyl, d, τ 1.74, $J_{\mathrm{PCCH}} = 14$ Hz, 1 H. An analytical sample was sublimed at 160° (0.5 mm).

Anal. Calcd for $C_{23}H_{19}PO_2$: C, 77.08; H, 5.34; P, 8.64; mol wt, 358.11226. Found: C, 76.72; H, 5.45; P, 8.53; M^+ *m/e* 358.11874.

p-Anisyl-*β*-**naphthylphenylphosphine oxide (9)**, prepared in like manner, was obtained as a glass. Purified by chromatography on Florisil (eluate, ethyl acetate) and subsequent distillation (kugelrohr, bp 260° (0.50 mm)), the material was homogeneous by tlc on silica gel, eluting with ethyl acetate, methanol, or benzene: pmr CH_3O, s, τ 6.17; naphthyl, d, τ 1.72, $J_{\mathrm{PCCH}} = 14$ Hz, 1 H; mol wt: calcd for $C_{23}H_{19}PO_2$, M^+ *m/e* 358.11226 (found 358.11026).

Ethylmethyl-*n*-propylphosphine oxide (4), prepared from ethylmethylphosphinyl chloride and *n*-propylmagnesium bromide, was obtained as a colorless oil. Purified by distillation (kugelrohr, bp 90° (0.1 mm)), the material was homogeneous by glpc and transparent in the uv (ϵ_{210} 13, methanol); pmr CH_3P, d, τ 8.57, $J_{\mathrm{PCH}} = 14$ Hz.

Anal. Calcd for $C_6H_{15}PO$: C, 53.72; H, 11.27; mol wt, 134.08605. Found: C, 53.88; H, 11.20; M^+ *m/e* 134.08591.

Determination of Optical Purity by Pmr. (+)-(*S*)-2-Phenyl-2-methoxyethyl-1-d_2 Bromide (11). (+)-(*S*)-O-Methylmandelic acid (31 g, 187 mmol), mp 66.5–68°, $[\alpha]^{22}\mathrm{D}$ +162° (*c* 1.49, water) (lit.[25] $[\alpha]^{23}\mathrm{D}$ +162°), was esterified with diazomethane to yield (quantitatively) methyl (*S*)-O-methylmandelate (33.8 g, 187 mmol). After distillation (bp 59° (0.1 mm)), the ester had $[\alpha]^{25}\mathrm{D}$ +138° (*c* 1.0, methanol). A solution of 18 g (100 mmol) of this material in ether (50 ml) was added dropwise to a suspension of lithium aluminum deuteride (4.2 g, 100 mmol) in ether (150 ml), at a rate sufficient to maintain a rapid reflux. When addition was complete (*ca.* 45 min) the mixture was heated at reflux for an additional 15 min, cooled, and treated with ethyl acetate (10 ml) to consume excess lithium aluminum deuteride. The resulting mixture was hydrolyzed with water (4.2 ml), 15% sodium hydroxide solution (4.2 ml), and water (12.6 ml). The ether layer was dried over magnesium sulfate and concentrated on the rotary evaporator. The residue was distilled to yield (+)-(*S*)-**2-phenyl-2-methoxyethanol-1-d_2** (14.1 g, 91.5 mmol): bp 75° (1.0 mm); $[\alpha]^{22.7}\mathrm{D}$ +133° (neat); pmr CH_3O, s, τ 6.77; $\mathrm{C_6H_5}CH$, s, τ 5.75; OH, s, τ 6.83; $\mathrm{C_6H_5}$, s, τ 2.79. Methanesulfonyl chloride (9.6 g, 84 mmol) was added to a stirred solution of the alcohol (6.5 g, 42 mmol) in pyridine (100 ml). After 90 min, the mixture, which contained solid pyridine hydrochloride, was poured into an ice–water mixture (700 ml), and a precipitate formed. Removed by filtration, washed with water, and distilled (kugelrohr, 120° (0.025 mm)) the resulting (+)-(*S*)-**2-phenyl-2-methoxyethyl-1-d_2 methanesulfonate** (6.4 g, 28 mmol) had mp 46–49°; $[\alpha]^{24}\mathrm{D}$ +91.3°; pmr $CH_3\mathrm{SO_2}$, s, τ 7.11; CH_3O, s, τ 6.78; $\mathrm{C_6H_5}CH$, s, τ 5.58; $\mathrm{C_6}H_5$, s, τ 2.78. A solution of the methanesulfonate (6.3 g, 27 mmol) in dimethyl sulfoxide (25 ml) was added to sodium bromide (8.2 g, 80 mmol) in dimethyl sulfoxide (100 ml) at 80°. After stirring for 12 hr, the mixture was cooled, poured over ice (500 g), and extracted with two 300-ml portions of ether. The ethereal solution was washed with two 300-ml portions of water, dried over magnesium sulfate, and concentrated on the rotary evaporator. The residue was purified by distillation, bp 74° (0.2 mm),[26] to yield **11** (4.25 g, 19.6 mmol): $[\alpha]^{24}\mathrm{D}$ +73°; $n^{22.5}\mathrm{D}$ 1.5399; pmr CH_3O, s, τ 6.79; $\mathrm{C_6H_5}CH$, s, τ 6.03; $\mathrm{C_6}H_5$, s, τ 2.80. The over-all yield from the starting acid was 42%.

o-Anisyl-*β*-**naphthylphenyl-((*S*)-2-phenyl-2-methoxyethyl-1-d_2)-phosphonium Bromide.** Reduction of (−)-(*S*)-**7** (294 mg, $[\alpha]^{27}{}_{400}$ −28.5° (*c* 1.016, methanol)) with hexachlorodisilane provided the phosphine **14** (244 mg, $[\alpha]^{27}{}_{400}$ −43.8° (*c* 2.387, benzene)).[14] A portion (95 mg, 0.26 mmol) of this material was combined with **11** (650 mg, 2.3 mmol) in benzene (4 ml) and heated at reflux for 12 hr. The phosphonium bromide which precipitated was washed several times with ether, dissolved in methylene chloride, filtered, precipitated with hexane, and dried (60°, 0.05 mm): pmr (benzonitrile, 100 MHz) $-\mathrm{C_6H_4}OCH_3$, s, τ 6.26, 1.71 H, and τ 6.34, 1.29 H.

---

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

(26) W. M. Lauer and M. A. Spielman [*J. Am. Chem. Soc.*, 55, 4923 (1933)] give bp 117–118° (15 mm) for the racemic unlabeled bromide.

The Use of Hexachlorodisilane as a Reducing Agent. Stereospecific Deoxygenation of Acyclic Phosphine Oxides[1]

Klaus Naumann, Gerald Zon, and Kurt Mislow

Contribution from the Department of Chemistry, Princeton University,
Princeton, New Jersey 08540. Received June 2, 1969

Abstract: Optically active acyclic phosphine oxides are reduced by hexachlorodisilane to phosphines with a high degree of stereospecificity and with inversion of configuration. Mechanisms for these deoxygenations are suggested which account for the observed stereochemistry. Factors are discussed which are responsible for the racemization of the produced phosphines under the conditions of the reduction. The ready availability of hexachlorodisilane, the simplicity and mildness of the reduction conditions, the high product yield, and the high stereospecificity of the reaction make this a most convenient method for the preparation of optically active phosphines from phosphine oxides. In an extension of this study, octachlorotrisilane was found to reduce acyclic phosphine oxides to phosphines with nearly complete inversion of configuration, and hexachlorodisilane was found to reduce amine oxides to amines and sulfoxides to sulfides. It is suggested that perchloropolysilanes may also be implicated in the reduction of optically active phosphine oxides with trichlorosilane in the presence of strongly basic tertiary amines.

Optically active phosphines constitute a class of compounds which has occupied a central position in the study of organophosphorus reaction mechanisms and stereochemistry.[2] Reported pathways leading to the synthesis of such compounds are cathodic reduc-

---

(1) This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-B. For a preliminary communication, see K. Naumann, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, 91, 2788 (1969).

(2) For comprehensive reviews giving citations to the original literature, see (a) L. Horner, *Pure Appl. Chem.*, 9, 225 (1964); (b) W. E. McEwen in "Topics in Phosphorus Chemistry," Vol. 2, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, New York, N. Y., 1965, Chapter 1; (c) M. 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.

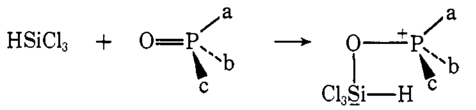
tion[3] or basic cleavage[4,5] of optically active phosphonium salts, reduction of optically active phosphine oxides with hydrides such as trichlorosilane,[6,7] and kinetic[5] or direct[8] resolution.

The ready availability of optically pure phosphine oxides of known absolute configuration by the recently developed Grignard synthesis[9] justified a search for a convenient, general method of reducing phosphine oxides to phosphines in high yield and with a high degree of stereospecificity: a combination of the two synthetic methods would provide a useful access route to phosphines of known absolute configuration and of high optical purity.

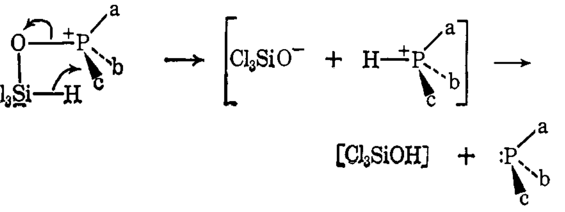
A necessary condition for such a reduction is that it proceeds under mild conditions, lest the produced phosphine racemize by thermally induced pyramidal inversion.[10] The use of trichlorosilane[6,11] meets this condition. The present work evolved as a consequence of preliminary studies, described in the following section, which were undertaken to examine the scope and mechanism of the trichlorosilane reduction.

Reduction of Phosphine Oxides with Trichlorosilane. Reduction of optically active phosphine oxides with trichlorosilane affords phosphines with net *retention* of configuration[6] and in high optical yield. However, Horner and Balzer observed[6] that in the presence of triethylamine, acyclic phosphine oxides afford phosphines with net *inversion* of configuration and in high optical yield, whereas in the presence of pyridine and N,N-diethylaniline the stereochemical course is *retention*.

To rationalize retention of configuration in the absence of base, Horner and Balzer suggested[6] complexation,[12] followed by intramolecular hydride transfer,[13] as shown in eq 1 and 2.

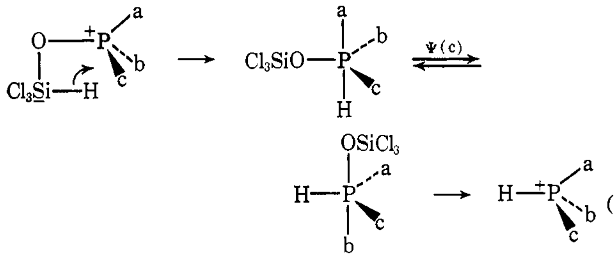


(1)



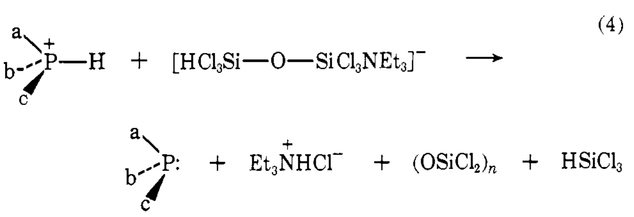
(2)

The proposed mechanism, in the absence of further data, appears to be a reasonable possibility, and it is only necessary to add that, if an intermediate is involved, and if hydride attack and trichlorosiloxy departure both follow the same stereochemical course, *i.e.*, equatorial or apical, pseudorotation[14] must intervene, as shown in eq 3 for the example of apical stereochemistry.



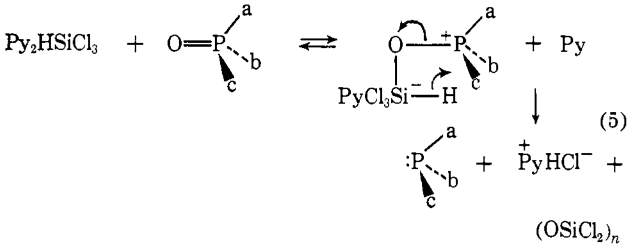
(3)

To rationalize inversion of configuration in the presence of triethylamine, Horner and Balzer[6] suggested complexation (eq 1), followed by *intermolecular* hydride transfer from a 1:1 triethylamine–trichlorosilane complex in an S_N2 reaction (apical–apical), as shown in eq 4.



(4)

The authors[6] suggested that the inefficacy of N,N-diethylaniline in reversing the stereochemical course from retention to inversion might be attributed to the possible absence of complexation with trichlorosilane. In the case of pyridine, which forms a 2:1 pyridine–trichlorosilane complex,[15] the authors[6] proposed the mechanism in eq 5.



(5)

Our own interest in developing a useful synthesis of optically active phosphines of known absolute configuration prompted a further investigation of the factors which are responsible for the stereochemical outcome of

---

(3) L. Horner, H. Winkler, A. Rapp, A. Mentrup, H. Hoffmann, and P. Beck, *Tetrahedron Lett.*, 161 (1961), and subsequent papers.

(4) D. P. Young, W. E. McEwen, D. C. Valez, J. W. Johnson, and C. A. VanderWerf, *ibid.*, 359 (1964).

(5) G. Wittig, H. J. Cristau, and H. Braun, *Angew. Chem. Intern. Ed. Engl.*, 6, 700 (1967).

(6) L. Horner and W. D. Balzer, *Tetrahedron Lett.*, 1157 (1965).

(7) Reduction of optically active phosphine oxides with lithium aluminum hydride is accompanied by extensive racemization of the starting oxide, and the phosphines are obtained in a very low state of optical purity (P. D. Henson, K. Naumann, and K. Mislow, *J. Am. Chem. Soc.*, **91**, 5645 (1969)).

(8) T. H. Chan, *Chem. Commun.*, 895 (1968).

(9) O. Korpiun and K. Mislow, *J. Am. Chem. Soc.*, **89**, 4784 (1967); O. Korpiun, R. A. Lewis, J. Chickos, and K. Mislow, *ibid.*, **90**, 4842 (1968).

(10) Thus, methylphenyl-*n*-propylphosphine racemizes in decalin at 130° with a half-life of 301 min (L. Horner and H. Winkler, *Tetrahedron Lett.*, 461 (1964)).

(11) S. E. Cremer and R. J. Chorvat, *J. Org. Chem.*, **32**, 4066 (1967).

(12) Complexes between phosphine oxides and silicon tetrachloride have been reported (I. R. Beattie and M. Webster, *J. Chem. Soc.*, 3672 (1965); K. Issleib and H. Reinhold, *Z. Anorg. Allgem. Chem.*, **314**, 113 (1962)).

(13) A process which may be considered an intermolecular analog of this transfer reaction is the recently reported reduction of carbonium ions by organosilanes (F. A. Carey and H. S. Tremper, *J. Am. Chem. Soc.*, **90**, 2578 (1968)).

(14) For a recent discussion of pseudorotations in related systems, see F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

(15) H. J. Campbell-Ferguson and E. A. V. Ebsworth, *J. Chem. Soc.*, 705 (1967); U. Wannagat, K. Hensen, and P. Petesch, *Monatsh. Chem.*, **98**, 1407 (1967), and references cited therein.

the reductions with trichlorosilane.[16] A preliminary survey, using a variety of tertiary amines, immediately revealed that strong bases (pK_b < *ca.* 5) give phosphine with predominant inversion and weak bases (pK_b > *ca.* 7) give phosphine with predominant retention of configuration (Table I).[17] That complexation is irrelevant to the stereochemical outcome of the reduction is evidenced by the fact that both pyridine (a retention base) and trimethylamine (an inversion base) form complexes with trichlorosilane.[15] However, in contrast to the stability of the pyridine–trichlorosilane complex, which suffers no decomposition even at room temperature,[15] it has long been recognized that the trimethylamine–trichlorosilane adduct decomposes, even at temperatures well below 0°, into a mixture of chlorosilanes.[15,18] Our own investigations confirm the reactivity of such adducts. Thus, freshly prepared triethylamine–trichlorosilane "adduct" at room temperature showed the presence of triethylammonium salt by identity of the ir (4000–625-cm^{-1} region, Nujol mull) and pmr spectra with those of triethylammonium chloride. The seemingly total destruction of the trichlorosilane was indicated by the absence of the Si–H ir stretching frequency near 2250 cm^{-1}, by the absence of the Cl_3Si–H pmr signal near τ 3.9, and by the behavior of the sample on ethanolysis, which yielded no detectable quantities of triethoxysilane, a product which would have been expected[15] had the adduct suffered simple dissociation (eq 6).

$$\mathrm{HSiCl_3\cdot Et_3N \rightleftarrows HSiCl_3 + Et_3N \xrightarrow{EtOH} HSi(OEt)_3} \tag{6}$$

Table I. Reduction of Optically Active Benzylmethylphenylphosphine Oxide[a] with Trichlorosilane–Tertiary Amine Mixtures[b]

Amine	pK_b[c]	Stereochemistry of reduction	Product optical purity, %[d]
$CH(C_2H_4)_3N$[e]	3.05[f]	Inversion	78
$(C_6H_{11})_2NC_2H_5$	*Ca.* 3[g]	Inversion	86
$(C_2H_5)_3N$	3.26	Inversion	100
$(CH_3)_3N$	4.20	Inversion	81
$(CH_3)_2NCH_2C_6H_5$	5.07[h]	Inversion	94
$(C_2H_5)_2NC_6H_4CH_3$-*p*	6.91	Retention	79
$(C_2H_5)_2NC_6H_5$[i]	7.44	Retention	88
C_5H_5N[j]	8.81	Retention	50
$(CH_3)_2NC_6H_5$	8.84	Retention	58

[a] Optically pure, $[\alpha]_D$ +51.4° (methanol). [b] Five- to tenfold excess of trichlorosilane and tertiary amine (molar ratio = 1:1); benzene solvent; reflux 1–2 hr. [c] N. F. Hall and M. R. Sprinkle, *J. Am. Chem. Soc.*, **54**, 3469 (1932); values for pure water at 25°, except as noted. [d] Benzylmethylphenyl-*n*-propylphosphonium bromide; optical purity varied *ca.* ±10% depending on reaction conditions. [e] Quinuclidine. [f] C. A. Grob, A. Kaiser, and E. Renk, *Chem. Ind.* (London), 598 (1957). [g] Estimate based on value for diisopropylmethylamine, pK_b = 2.97 (solvent not reported); L. Spialter and J. A. Pappalardo, "The Acyclic Aliphatic Tertiary Amines," The Macmillan Co., New York, N. Y., 1965, p 161. [h] "International Critical Tables of Numerical Data, Physics, Chemistry, and Technology," Vol. 6, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p 292. [i] Data of Horner and Balzer; see ref 6. [j] Pyridine.

It thus appears, generally, that the stereochemistry of the reduction of optically active acyclic phosphine oxides with trichlorosilane in benzene[19] proceeds with retention of configuration, whether the reagent is uncomplexed (as in the absence of amine) or complexed (as in the presence of pyridine), but that the reduction may proceed with *inversion* of configuration when the reagent is no longer trichlorosilane itself, complexed or uncomplexed, but a product of base decomposition. This simple hypothesis, which is consistent with all of the reported data, is proposed as an alternative to the suggestions previously advanced[6] to account for the role of tertiary amines in the trichlorosilane reduction.

The following question remains: what are the products of trichlorosilane decomposition which give rise to phosphine with inverted configuration? An obvious possibility is the one indicated in eq 7.[20]

$$\begin{gathered}\mathrm{HSiCl_3 + Et_3N \rightleftarrows {}^{-}SiCl_3 + Et_3\overset{+}{N}H}\\ \mathrm{abcPO + Et_3\overset{+}{N}H \rightleftarrows abc\overset{+}{P}OH + Et_3N}\\ \mathrm{Cl_3Si^{-} + abc\overset{+}{P}OH \xrightarrow[\sigma]{} Cl_3Si\overset{+}{P}cba + {}^{-}OH}\\ \mathrm{HO^{-} + Cl_3Si\overset{+}{P}cba \longrightarrow [HOSiCl_3] + Pcba}\end{gathered} \tag{7}$$

The first step in this sequence, formation of trichlorosilyl anion from trichlorosilane and tertiary amine, has also recently been suggested by Benkeser and Smith,[21] who proposed that this anion is the reactive species in the dechlorination of polyhalo compounds. In the third step, a phosphorane is the likely intermediate. The silicon-containing final product of the reaction, trichlorosilanol, suffers further decomposition.[22] However, in view of the apparent complexity of the trichlorosilane–amine reaction,[19] other reasonable alternatives might be considered, and one of these was inspired by our observation that treatment of freshly prepared triethylamine–trichlorosilane "adduct" (a yellow, resinous material which in fact represents a mixture of reaction products; see above) with aqueous base causes evolution of hydrogen, suggesting[23a] the *possibility* of the presence of silicon–silicon bonds in one or more of

---

(16) In private correspondence, Professor Horner had kindly informed us that he had no plans to pursue the mechanistic aspects of this problem.

(17) This generalization obtains for tertiary amines only. Reductions of phosphine oxides with trichlorosilane in the presence of primary and secondary amines may take a different stereochemical course. Thus, for example, reduction of optically pure benzylmethylphenylphosphine oxide in the presence of piperidine (pK_b = 2.87 (Table I, footnote *c*)) affords 68% optically pure phosphine with net *retention* of configuration.

(18) A. B. Burg, *J. Am. Chem. Soc.*, 76, 2674 (1954).

(19) There is a marked solvent dependence on the course of the reaction. For example, reduction of optically active benzylmethylphenylphosphine oxide by trichlorosilane in the presence of N,N-diethyl-*p*-toluidine proceeds with retention of configuration (70–80% optical yield) in benzene and in di-*n*-butyl ether, but with inversion of configuration (60–70% optical yield) in acetonitrile. However, reduction in acetonitrile in the absence of amines or in the presence of amines weaker than N,N-diethyl-*p*-toluidine (such as N,N-diethylaniline) results in complete *racemization* under the same reaction conditions. This and related observations (Experimental Section) attest to the complexity of the reaction mechanism.

(20) From this point on, throughout the paper the letter sequences "abcPO" and "OPcba" symbolize enantiomeric phosphine oxides, and, similarly, "abcP" and "Pcba" symbolize enantiomeric phosphines.

(21) R. A. Benkeser and W. E. Smith, *J. Am. Chem. Soc.*, 90, 5307 (1968).

(22) H. J. Emeléus and A. J. E. Welch, *J. Chem. Soc.*, 1928 (1939); J. Goubeau and R. Warncke, *Z. Anorg. Allgem. Chem.*, **259**, 109 (1949).

(23) (a) G. Urry, *et al.*, *J. Inorg. Nucl. Chem.*, 26, 421, 427 (1964); (b) L. Troost and P. Hautefeuille, *Ann. Chim. Phys.*, 7, 452 (1871); G. Martin, *J. Chem. Soc.*, 105, 2836, 2860 (1914); G. Martin, *ibid.*, 107, 319 (1915); (c) G. Urry, *J. Inorg. Nucl. Chem.*, 26, 409 (1964).

Table II. Reductions of Optically Active Acyclic Phosphine Oxides, $(R)(CH_3)(C_6H_5)PO$, with Hexachlorodisilane

Phosphine oxide						Product phosphine or derivative				
Compd no.	R	Chirality[a]	$[\alpha]_D$,[b] deg	Optical purity, %[c]	Conditions[d]	No.[e]	Chirality	$[\alpha]_D$,[b] deg	Optical purity, %[c]	Yield, %[f]
1	$CH_2{=}CHCH_2$	*R*[g]	+21.0	100[g]	Benzene, reflux, 5 min	6	*R*[h]	−16.1	67[i]	73
2	*n*-C_3H_7	*R*	+16.0	80[j]	Benzene, 60°, 25 min	8	*R*[k]	−34.4	93[l,m]	82
3	$C_6H_5CH_2$	*R*	+51.4	100	Benzene, 70°, 10 min	7	*R*	+81[n]	95[l]	84
					Benzene, reflux, 30 min	3	*S*[a]	−46.9	91	
					Benzene, reflux, 30 min	8	*S*[k]	+32.8	90[l]	70
					Chloroform, 25°, 30 min	8	*S*[k]	+34.2	93[l]	59
4	*p*-$CH_3OC_6H_4$	*S*	−9.8	100[o]	Benzene, reflux, 30 min	4	*R*[a]	+9.2	94	62

[a] See ref 9. [b] Rotations refer to solvent methanol; *c* 1.0–3.0; 22–24°. The rotational prefixes used in the text refer to solvent methanol, except as noted. [c] Based on rotations reported in ref 9, except as noted. [d] Molar ratio $(R)(CH_3)(C_6H_5)PO{:}Si_2Cl_6$ = 1.0:1.1–1.5; $[(R)(CH_3)(C_6H_5)PO]$ = 0.15–0.20 *M*. [e] Numbers refer to formulas given in Chart I. [f] Yield of isolated final product based on starting phosphine oxide and assuming 100% conversion. [g] Reference 31. [h] Reference 2a. [i] Based on the value (24°) for the absolute rotation of **6** estimated by G. Zon, K. E. DeBruin, K. Naumann, and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7023 (1969). [j] Based on the value (20.0°) for the absolute rotation of **2** estimated by J. P. Casey, R. A. Lewis, and K. Mislow, *J. Am. Chem. Soc.*, **91**, 2789 (1969). [k] See ref 30. [l] Based on the value (36.8°) for the rotation of **8** reported in ref 3. [m] The higher optical purity of **8**, relative to **2**, appears to be due to optical fractionation of **8** during its isolation. [n] Rotation in toluene; $[\alpha]_D$ +45.8° (toluene) was the previously reported highest rotation; see ref 2a. [o] $[\alpha]_D$ −8° was the previously reported highest rotation; see ref 9.

the components of the "adduct," perhaps as part of a perchloropolysilane system formed by polymerization of dichlorosilylene[24] (eq 8).

$$Cl_3Si^- \longrightarrow [SiCl_2] + Cl^- \qquad (8)$$
$$n[SiCl_2] \longrightarrow (SiCl_2)_n$$

Perchloropolysilanes (Si_nCl_{2n+2}) are capable of functioning as reducing agents,[23b] and Urry,[23c] who observed that hexasilicon tetradecachloride (Si_6Cl_{14}) rapidly reduces metal halides, also recognized the possibility of using the same reagent "as a reducing agent for use in nonaqueous systems for reactions where hydride or metallic reducing agents are incompatible." This chain of reasoning led us to a test of perchloropolysilanes as possible stereospecific reducing agents of phosphine oxides. Surprisingly, considering the ready availability of the lower members of this series, hexachlorodisilane (Si_2Cl_6) and octachlorotrisilane (Si_3Cl_8), no work describing the deoxygenation of organic compounds with these reagents had, to the best of our knowledge, been heretofore reported. The present paper describes results of our studies in this area.

Deoxygenation of Phosphine Oxides with Si_2Cl_6 and Si_3Cl_8. Stoichiometry and Products. Phosphines are prepared in generally high yields (70–90%) by reaction of the corresponding phosphine oxides with Si_2Cl_6 in refluxing benzene or in chloroform solution at room temperature (Experimental Section). The gross stoichiometry of the over-all reduction, represented by eq 9, requires an equimolar ratio of reagents.

$$R_3PO + Si_2Cl_6 \longrightarrow R_3P + \text{“}Si_2OCl_6\text{”} \qquad (9)$$

In an attempt to characterize the silicon-containing product, "Si_2OCl_6," benzylmethylphenylphosphine oxide was reduced with Si_2Cl_6 in benzene, in a molar ratio of 1:1. The yield of benzylmethylphenylphosphine was 88%. A glpc analysis revealed the presence of *ca.* 0.7 mol of silicon tetrachloride and *ca.* 0.3 mol of hexachlorodisiloxane ($Cl_3SiOSiCl_3$) per mole of phosphine. The material balance may consist of *ca.* 0.7 mol of perchloropolysiloxanes, $(OSiCl_2)_n$, which have been proposed as products in the trichlorosilane reduction of phosphine oxides.[6,25] A control experiment eliminated the possibility that silicon tetrachloride and perchloropolysiloxanes might have been formed as the products of a phosphine-catalyzed disproportionation of hexachlorodisiloxane (eq 10).[26]

$$Cl_3SiOSiCl_3 \longrightarrow SiCl_4 + [OSiCl_2] \qquad (10)$$

In reductions with Si_3Cl_8 under the same conditions, the gross stoichiometry, represented by eq 11, requires a 2:1 molar ratio of reagents (see Experimental Section).

$$2R_3PO + Si_3Cl_8 \longrightarrow 2R_3P + \text{“}Si_3O_2Cl_8\text{”} \qquad (11)$$

A glpc analysis of the products ("$Si_3O_2Cl_8$") revealed the presence of *ca.* 0.3 mol of silicon tetrachloride and *ca.* 0.1 mol of hexachlorodisiloxane per mole of phosphine. The material balance may consist of *ca.* 1.0 mol of perchloropolysiloxanes.

On the basis of the stoichiometries found for the two reductions, one may extrapolate to the generalization stated in eq 12, where *n* is the number of Si–Si bonds in the perchloropolysilane[28] ($n = 1,2, \cdots$).

$$nR_3PO + Cl(SiCl_2)_{n+1}Cl \longrightarrow nR_3P + Si_{n+1}O_nCl_{2n+4} \qquad (12)$$

Stereochemistry. Investigations carried out with a number of optically active acyclic phosphine oxides, which are listed in Table II, show that reduction with

---

(24) H. Gilman and G. D. Lichtenwalter, *J. Org. Chem.*, **24**, 1588 (1959); O. M. Nefedov and M. N. Manakov, *Angew. Chem. Intern. Ed. Engl.*, **5**, 1021 (1966); *cf.* also D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **49**, 1938 (1968).

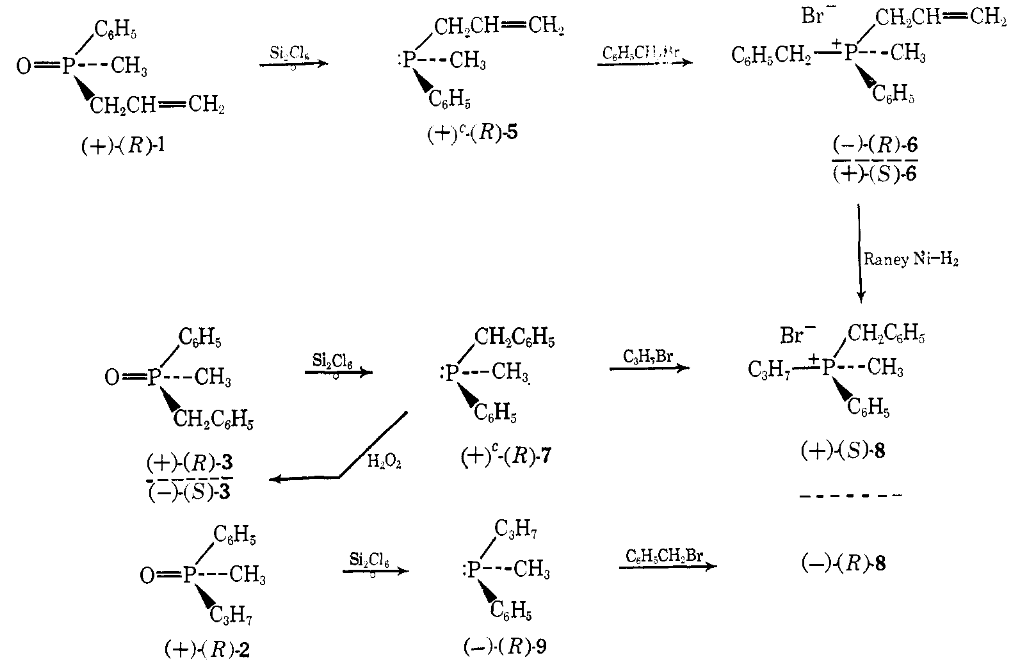
(25) H. Fritzsche, U. Hasserodt, and F. Korte, *Chem. Ber.*, **98**, 171 (1965).

(26) Hexachlorodisiloxane decomposes in the presence of tri-*n*-butylamine at *ca.* 135° to produce a mixture of starting material, silicon tetrachloride, and "higher boiling perchloropolysiloxanes."[27]

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

(28) Although the generalization stated in eq 12 refers specifically to linear perchloropolysilanes, it can easily be extended to the branched isomers of the same molecular formula, $Si_{n+1}Cl_{2n+4}$, or to the cyclic analogs, $Si_{n+1}Cl_{2n+2}$.

Chart I[a,b]



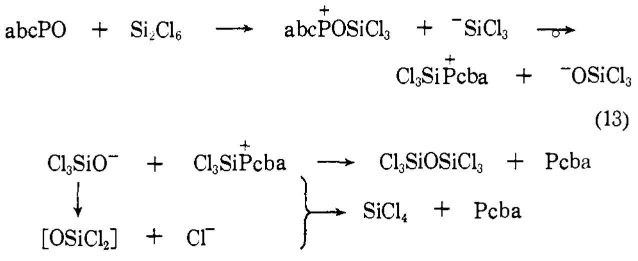
[a] C_3H_7 = *n*-propyl. [b] Hexachlorodisilane reductions are described in the text; for other reactions see ref 2. [c] Rotation in toluene.

Si_2Cl_6 in benzene or chloroform occurs with nearly complete inversion of configuration.[29] The stereochemical direction of the reductions was deduced from the configurational correlations summarized in Chart I. The absolute configurations of all of the compounds shown in Chart I have been previously established[2,9,30,31] and it follows that the reductions of **1**–**3** with Si_2Cl_6 proceed with inversion of configuration, granted that quaternization and hydrogen peroxide oxidation occur with retention of configuration.[2] In addition to the dialkylaryl- and diarylalkylphosphine oxides listed in Table II, Si_2Cl_6 was also found to reduce an optically active trialkylphosphine oxide with net inversion of configuration. Reduction of (−)-(*S*)-ethylmethyl-*n*-propylphosphine oxide,[32] $[\alpha]_{300}$ −1.9°, with Si_2Cl_6 gave ethylmethyl-*n*-propylphosphine which, upon reoxidation with hydrogen peroxide, yielded (87%) (+)-(*R*)-ethylmethyl-*n*-propylphosphine oxide, $[\alpha]_{300}$ +1.2°. Similarly, a triarylphosphine oxide, (−)-(*S*)-*o*-anisyl-β-naphthylphenylphosphine oxide (**10**),[32] $[\alpha]_{400}$ −28.5°, upon reduction with Si_2Cl_6 in refluxing benzene for 13 min, afforded (*S*)-*o*-anisyl-β-naphthylphenylphosphine (**11**), $[\alpha]_D$ −10.0° (benzene), in 98% yield. Upon reoxidation with hydrogen peroxide, this phosphine afforded (+)-(*R*)-**10** with $[\alpha]_{400}$ +9.0°, indicating extensive racemization of **11** under these particular reaction conditions (see below).

In an extension of these reductions to the next higher member of the homologous series of perchloropolysilanes, it was found that reduction of 81% optically pure (+)-**2** with Si_3Cl_8 in benzene gave, after quaternization with benzyl bromide, (−)-**8**, 81% optically pure, in 87% yield. The reduction therefore proceeded with inversion of configuration, by way of (−)-**9** (Chart I), and with complete stereospecificity.

It would thus appear that perchloropolysilanes in general reduce acyclic phosphine oxides with inversion of configuration and with high stereospecificity. In this connection, it is noteworthy that the pmr spectrum of the bismethylphenyl-*p*-anisylphosphine complex of nickel bromide exhibits resonance doubling of the *para* proton when the complex is prepared from racemic phosphine (due to the presence of *dl* and *meso* complexes), whereas only one signal is observed when the complex is prepared from phosphine obtained by Si_2Cl_6 reduction of the oxide (**4**).[33] This observation unequivocally demonstrates that the starting phosphine is optically pure, or nearly so, and thereby supports our contention that the Grignard synthesis of phosphine oxides[9] as well as the deoxygenation with Si_2Cl_6 proceed with nearly complete stereospecificity.

Mechanism. The observed stoichiometry and stereochemistry of Si_2Cl_6 reductions of acyclic phosphine oxides are satisfactorily accounted for by the scheme



$$\mathrm{abcPO} + \mathrm{Si_2Cl_6} \longrightarrow \mathrm{abc\overset{+}{P}OSiCl_3} + {}^{-}\mathrm{SiCl_3} \longrightarrow \mathrm{Cl_3Si\overset{+}{P}cba} + {}^{-}\mathrm{OSiCl_3} \tag{13}$$

$$\mathrm{Cl_3SiO^-} + \mathrm{Cl_3Si\overset{+}{P}cba} \longrightarrow \mathrm{Cl_3SiOSiCl_3} + \mathrm{Pcba}$$

$$\mathrm{Cl_3SiO^-} \longrightarrow [\mathrm{OSiCl_2}] + \mathrm{Cl^-};\quad [\mathrm{OSiCl_2}] + \mathrm{Cl^-} + \mathrm{Cl_3Si\overset{+}{P}cba} \longrightarrow \mathrm{SiCl_4} + \mathrm{Pcba}$$

shown in eq 13, which is akin to that in eq 7. The first step in both schemes involves nucleophilic attack by oxygen to give a phosphonium salt, $abcP^+OX$ (X = H or $SiCl_3$). This is followed by nucleophilic attack on phosphorus by trichlorosilyl anion, with concomitant inversion of configuration and formation of trichloro-

---

[29] By contrast, reduction of cyclic (phosphetane) oxides with Si_2Cl_6 results in retention of configuration, as discussed in an accompanying paper (K. E. DeBruin, G. Zon, K. Naumann, and K. Mislow, *J. Am. Chem. Soc.*, 91, 7027 (1969)).

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

[31] A. W. Herriott and K. Mislow, *ibid.*, 3013 (1968).

[32] R. A. Lewis and K. Mislow, *J. Am. Chem. Soc.*, 91, 7009 (1969).

[33] L. H. Pignolet and W. DeW. Horrocks, Jr., *ibid.*, **91**, 3976 (1969).

silylphosphonium and OX^- (hydroxide or trichlorosiloxy) ions. The intermediacy of a phosphorane is assumed. Finally, attack by OX^- on silicon in trichlorosilylphosphonium ion gives phosphine and $XOSiCl_3$ (trichlorosilanol or hexachlorodisiloxane).

The first step of the sequence in eq 13, attack of the oxygen atom of abcPO on the silicon atom of Si_2Cl_6, is one of several modes of attack to which Si_2Cl_6 is vulnerable. Since in subsequent steps of the scheme shown in eq 13, trichlorosilyl, trichlorosiloxy, and chloride ions are postulated as reaction intermediates, these ions may themselves attack Si_2Cl_6 with expulsion of trichlorosilyl or chloride ions.

Even when "no-reactions" (such as the displacement of trichlorosilyl anion from Si_2Cl_6 by another trichlorosilyl anion) are omitted, it is immediately obvious that a great multiplicity of catenated species (some containing phosphorus and some not) may arise by nucleophilic displacements on silicon subsequent to the primary step; each new species is capable of giving rise to a new structural subset upon nucleophilic displacement at silicon, and each member of the subset in turn generates its own subset. To describe the dendritic growth of the reaction sequence would be futile,[34] and we shall restrict ourselves merely to two comments.

First, in view of the admitted complexity of the reaction,[34] eq 13, by application of the principle of parsimony, merely represents the simplest scheme consistent with stoichiometry and stereochemistry. With the exception of the trichlorosiloxyphosphonium ion, the individual intermediates here postulated all have precedent in the literature.[35] As a working model, the scheme in eq 13 accounts not only for stereochemistry but also for stoichiometry. In particular, the partitioning of the trichlorosiloxy ion among two reaction paths is reflected in the ratio of products in the reduction of **3** (see above). Evidently, 70% of the ion decomposes into chloride and perchloropolysiloxane; the chloride then reacts with trichlorosilylphosphonium ion to give silicon tetrachloride and phosphine. The other 30% reacts with trichlorosilylphosphonium ion to give hexachlorodisiloxane and phosphine.

Second, the formation of perchloropolysilanes from secondary reactions[34,37] in no way affects the stereochemical outcome of the reaction, since, as was shown above, Si_3Cl_8 and, by extrapolation, the higher perchloropolysilanes reduce phosphine oxides with the same stereochemistry as does Si_2Cl_6. Furthermore, it now becomes quite apparent that polysilanes may indeed function as active species in the reduction of phosphine oxides by trichlorosilane in benzene in the presence of strongly basic tertiary amines[6] (see above). In that reaction, perchloropolysilanes might be formed not only by polymerization of dichlorosilylene (eq 8), but also by a series of displacement reactions (eq 14 and its extensions) similar to those proposed[37] for the polymerization of Si_2Cl_6. Either reaction path would lead to formation of the requisite silicon–silicon bonds. It is noteworthy that hexamethyldisilane, $Si_2(CH_3)_6$, was found to be inert toward phosphine oxides even under vigorous reaction conditions (see Experimental Section). The difference in reactivity between Si_2Cl_6 and $Si_2(CH_3)_6$ parallels the observation that the stability of the silicon–silicon bond toward cleavage by ammonium chloride increases with increasing replacement of halogen by alkyl substituents.[38] That heterolysis of the silicon–silicon bond is more facile when X = Cl than when X = CH_3, whether the nucleophilic attack on Si_2X_6 occurs by phosphine oxide (eq 13) or by chloride ion, may be attributed to the stabilizing effect of electron-withdrawing substituents on silyl anions,[39] X_3Si^- being formed in both cases, in parallel with similar effect on carbanions.[40] For polysilanes of mixed composition,[41] intermediate behavior would be expected.

$$\begin{gathered}
HSiCl_3 + Et_3N \rightleftarrows {}^-SiCl_3 + Et_3\overset{+}{N}H \\
Cl_3Si^- + HSiCl_3 \longrightarrow Cl_3SiSiCl_2H + Cl^- \\
Cl_3SiSiCl_2H + Et_3N \rightleftarrows Cl_3SiSiCl_2^- + Et_3\overset{+}{N}H \qquad (14) \\
Cl_3SiSiCl_2^- + HSiCl_3 \longrightarrow Cl_3SiSiCl_2SiCl_2H + Cl^- \\
Cl_3SiSiCl_2^- + Cl_3SiSiCl_2H \longrightarrow Cl_3SiSiCl_2SiCl_3 + {}^-SiCl_2H
\end{gathered}$$

Factors Affecting the Optical Purity of the Products. Although the reduction itself is highly stereospecific, the starting phosphine oxide and the produced phosphine are both liable to racemization under the conditions of the reduction, mild though these be. For the compounds examined in the present work, the reductions, when carried out in refluxing benzene, are nearly complete in about 5 min, but if the contact time is extended beyond this period, the optical purity of the product decreases. For example, reduction of (+)-**2** with Si_2Cl_6 or Si_3Cl_8 in refluxing benzene yields (−)-**9** (isolated as the derivative (−)-**8**) in 80–90% yields and with an optical purity near 90%, *provided* the reaction mixture is quenched after 15 min or less; if the contact time is appreciably prolonged, the optical purity of **8** decreases markedly (see Experimental Section). Even more dramatically, when (+)-(*R*)-**10**, $[\alpha]_{400}$ +9.0°, prepared by hydrogen peroxide oxidation of (−)-(*S*)-**11**, $[\alpha]_D$ −10.0° (benzene), is reduced with Si_2Cl_6 in refluxing benzene for *1.5 min*, (+)-(*R*)-**11**, $[\alpha]_D$ +8.1° (benzene), is obtained. The over-all stereospecificity is attributable to the reduction step and is no less than 81%. By contrast, the optical yield of the product is reduced to only 31% when the contact time is increased to *13 min* (see above)!

---

[34] Among the possible uncharged catenated species which are formed in further reactions, there are the great variety of perchloropolysilanes, $Cl(SiCl_2)_nCl$, and perchloropolysiloxanes, $Cl[-(SiCl_2)_kO(SiCl_2)_lO(SiCl_2)_m-]Cl$. Among the possible phosphonium ions, one must consider the perchloropolysilylphosphonium ions, $Cl(SiCl_2)_nP^+cba$, and the perchloropolysiloxyphosphonium ions, $abcP^+O[-(SiCl_2)_kO(SiCl_2)_lO(SiCl_2)_m-]Cl$, and among the possible anions one must consider chloride, perchloropolysilyl, $[(SiCl_2)_nCl]^-$, and perchloropolysiloxy, $Cl[-(SiCl_2)_kO(SiCl_2)_lO(SiCl_2)_m-]O^-$. In addition, all the branched-chain isomers of the above must also be taken into account!

[35] Cooper and Gilbert[27] have reported that nucleophilic attack of tri-*n*-butylamine on Si_2Cl_6 and hexachlorodisiloxane displaces trichlorosilyl and trichlorosiloxy anions, respectively. A silylphosphonium salt has been described by Fritz,[36a] and Emeléus and Tufail[36b] suggested the intermediacy of a trichlorosilylphosphonium ion in the reaction of triphenylphosphine with Si_2Cl_6.

[36] (a) G. Fritz, *Fortschr. Chem. Forsch.*, **4**, 459 (1963); (b) H. J. Emeléus and M. Tufail, *J. Inorg. Nucl. Chem.*, **29**, 2081 (1967).

[37] Higher polysilanes may be formed in subsequent displacement reactions on silicon. The over-all stoichiometry of the polymerization has been formulated[27,36b] as $nSi_2Cl_6 = nSiCl_4 + (SiCl_2)_n$, with initiation by catalytic amounts of amine or phosphine. See, also, U. Wannagat, K. Hensen, and F. Vielberg, *Monatsh. Chem.*, **99**, 431 (1968).

[38] C. J. Wilkins, *J. Chem. Soc.*, 3409 (1953).

[39] For a comprehensive review of organosilylmetallic compounds see D. Wittenberg and H. Gilman, *Quart. Rev.* (London), **13**, 116 (1959).

[40] D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, Chapter 1.

[41] M. Kumada and K. Tamao in "Advances in Organometallic Chemistry," Vol. 6, F. G. A. Stone and R. West, Ed., Academic Press, New York, N. Y., 1968, p 19 ff.

$$\begin{tikzcd}[column sep=small]
\text{abcP} + \text{XY} \arrow[r, phantom, "\rightleftharpoons"] & \text{abc}\overset{+}{\text{P}}\text{X} + \text{Y}^- \arrow[r, phantom, "\overset{\circ}{\underset{\circ}{\rightleftharpoons}}"] \arrow[d, shift right, "\circ"'] & \text{Y}\overset{+}{\text{P}}\text{cba} + \bar{\text{X}} \arrow[r, phantom, "\rightleftharpoons"] \arrow[d, shift left, "\circ"] & \text{XY} + \text{Pcba} \\
\text{Pcba} + \text{XY} \arrow[r, phantom, "\rightleftharpoons"] & \text{X}\overset{+}{\text{P}}\text{cba} + \text{Y}^- \arrow[r, phantom, "\overset{\circ}{\underset{\circ}{\rightleftharpoons}}"] \arrow[u, shift right, "\circ\,\text{X}^-"'] & \text{abc}\overset{+}{\text{P}}\text{Y} + \text{X}^- \arrow[r, phantom, "\rightleftharpoons"] \arrow[u, shift left, "\text{Y}^-\,\circ"] & \text{XY} + \text{abcP}
\end{tikzcd} \tag{15}$$

$$\begin{aligned}
\text{abc}\overset{+}{\text{P}}\text{X} + \text{Pcba} &\rightleftharpoons \text{abcP} + \text{X}\overset{+}{\text{P}}\text{cba} \\
\text{abc}\overset{+}{\text{P}}\text{Y} + \text{Pcba} &\rightleftharpoons \text{abcP} + \text{Y}\overset{+}{\text{P}}\text{cba}
\end{aligned} \tag{16}$$

$$\begin{tikzcd}[column sep=small]
\text{abcPO} + \text{XY} \arrow[r, phantom, "\rightleftharpoons"] & \text{abc}\overset{+}{\text{P}}\text{OX} + \text{Y}^- \arrow[r, phantom, "\overset{\circ}{\underset{\circ}{\rightleftharpoons}}"] \arrow[d, shift right, "\circ"'] & \text{Y}\overset{+}{\text{P}}\text{cba} + \text{O}\bar{\text{X}} \arrow[d, shift left, "\circ"] \\
\text{OPcba} + \text{XY} \arrow[r, phantom, "\rightleftharpoons"] & \text{XO}\overset{+}{\text{P}}\text{cba} + \text{Y}^- \arrow[r, phantom, "\overset{\circ}{\underset{\circ}{\rightleftharpoons}}"] \arrow[u, shift right, "\circ\,\text{OX}^-"'] & \text{abc}\overset{+}{\text{P}}\text{Y} + \text{OX}^- \arrow[u, shift left, "\text{Y}^-\,\circ"]
\end{tikzcd} \tag{17}$$

The racemization of **9** and other phosphines is *chemically* induced, since the conditions are too mild for significant thermal racemization.[10] Although the complexity of the reaction (see above) does not permit a definition of all possible pathways, the transformations shown in eq 15 and 16 adequately account for the results ($X = SiCl_3$, $Y = Cl$), as well as for the racemization of phosphine oxides (eq 17), which is discussed below. In all of these formulations, and those discussed below, the intermediacy of pentacovalent phosphorus compounds is assumed, and indeed such phosphoranes may function importantly in the racemization process which may to a significant extent be the result of pseudorotation.

All but one of the intermediates in eq 15–17 are present in the reaction mixture, according to the mechanism shown in eq 13, and the remaining one, $abcP^+Cl$, is readily generated by nucleophilic attack of chloride ion on phosphorus (with inversion at phosphorus) (eq 15 and 17) or of phosphorus on chlorine (with retention at phosphorus) (eq 15). The racemization of **9** by catalytic quantities of iodine (Experimental Section) provides additional evidence for the mechanisms in eq 15 and 16, with $X = Y = I$. In addition, as stated above, phosphoranes intervene. There is some precedent for transition states (or intermediates) similar to those here postulated in the racemization of phosphine oxides,[42a] as well as of phosphines.[42b,c] Support for the role of silicon tetrachloride in the racemization was obtained in a control experiment: 56% optically pure (−)-**9** was completely racemized after having been in contact with silicon tetrachloride (molar ratio 1:1) in benzene for *ca.* 30 min at 60°.[43]

In contrast to its behavior toward silicon tetrachloride, **9** showed no significant loss of optical activity when placed in contact with Si_2Cl_6 (molar ratio 1:1) in benzene for 60 min at 82°. Although mechanisms for racemization are available in principle, according to the scheme in eq 15 and 16 (with $X = Y = SiCl_3$, or $X = Si_2Cl_5$ and $Y = Cl$), the rates appear to be relatively slow in the case of Si_2Cl_6.

Silicon tetrachloride also racemizes phosphine oxides, although not as readily as phosphines.[45] Thus, when optically pure **3** was heated with silicon tetrachloride (molar ratio 1:1) in benzene at 82° for 120 min, the recovered **3** (after work-up with base) was 16% optically pure. The mechanism for racemization can easily be evolved by analogy with previously reported mechanisms,[42] and as shown in eq 17 and 18, where $X = SiCl_3$ and $Y = Cl$.

$$\text{abc}\overset{+}{\text{P}}\text{OX} + \text{OPcba} \rightleftharpoons \text{abcPO} + \text{XO}\overset{+}{\text{P}}\text{cba} \tag{18}$$

Another pathway, which may be viewed as a variant of eq 17, is shown in eq 19; intermediates involving the $[POP]^+$ system have been invoked before.[46]

$$\begin{aligned}
&\text{abc}\overset{+}{\text{P}}\text{Y} + \text{abcPO} \overset{\circ}{\underset{\circ}{\rightleftharpoons}} \\
&\qquad \text{abc}\overset{+}{\text{P}}\text{O}\overset{+}{\text{P}}\text{cba} + \text{Y}^- \overset{\circ}{\underset{\circ}{\rightleftharpoons}} \text{OPcba} + \text{Y}\overset{+}{\text{P}}\text{cba}
\end{aligned} \tag{19}$$

These racemization processes are markedly accelerated in the polar solvent acetonitrile. Thus, optically pure **3** was completely racemized after having been in contact with silicon tetrachloride (molar ratio 1:1) in acetonitrile at room temperature for 20 min. Similarly, reduction of optically pure **3** with Si_2Cl_6 in acetonitrile at reflux temperature for 10 min afforded racemic **7** (36% yield, isolated as derivative **8**) and recovered (24%) **3** which was 8% optically pure; evidently both **3** and **7** are racemized by Si_2Cl_6 and silicon tetrachloride according to schemes in eq 15–19, with $X = SiCl_3$ or Si_2Cl_5 and $Y = Cl$ or $SiCl_3$. The increased rates of racemization are consistent with the scheme advanced in eq 15–19, in which ionization and heterolysis play important roles, but the intervention of new reaction paths cannot be excluded in light of the admitted complexity of the reaction.[19,34]

The generality of the scheme outlined in eq 17 is further illustrated by our observation that **3** is readily racemized by acetyl chloride ($X = Ac$, $Y = Cl$) or phosphorus trichloride ($X = PCl_2$, $Y = Cl$) in acetonitrile at room temperature; earlier observations[42a] are similarly accommodated.

Deoxygenation of Amine Oxides and Sulfoxides with Si_2Cl_6. In connection with the preceding work, we

---

[42] (a) D. B. Denney, A. K. Tsolis, and K. Mislow, *J. Am. Chem. Soc.*, 86, 4486 (1964); L. Horner and H. Winkler, *Tetrahedron Lett.*, 3271 (1964); (b) L. Horner and H. Winkler, *ibid.*, 455 (1964); D. B. Denney and N. E. Gershman, *ibid.*, 3899 (1965); (c) T. J. Katz, C. R. Nicholson, and C. A. Reilly, *J. Am. Chem. Soc.*, **88**, 3832 (1966).

[43] Racemization schemes may also be formulated involving $(R_3P)_2$-$SiCl_4$ complexes[12,44] by a suitable modification of eq 15 and 16.

[44] G. A. Ozin, *Chem. Commun.*, 104 (1969).

[45] Small quantities of racemic phosphine oxide are generally recovered from Si_2Cl_6 reductions. By the same token if the crude isolated phosphine is oxidized prior to purification by distillation or chromatography, the optical purity of the resulting phosphine oxide is generally a few per cent below that of the oxide obtained by oxidation of the purified phosphine or of the phosphonium salt obtained upon quaternization of the crude isolated phosphine.

[46] J. Michalski and M. Mikolajczyk, *Chem. Commun.*, 35 (1965); *Tetrahedron Lett.*, 1779 (1965).

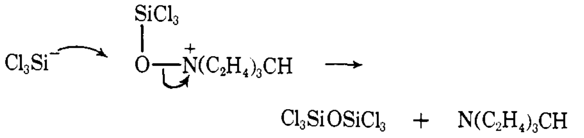
Table III. Reductions of Amine Oxides and Sulfoxides with Hexachlorodisilane[a]

Compound	Conditions	Product(s) or derivative	Yield, %[b]
$4\text{-}CH_3C_5H_4NO$[c]	Benzene, reflux, 11 hr	$4\text{-}CH_3C_5H_4N$	74
	Chloroform, 25°, 1.0 hr	$4\text{-}CH_3C_5H_4N$	60[d]
$CH(C_2H_4)_3NO$[e]	Chloroform, 25°, 1.5 hr	$CH(C_2H_4)_3N \cdot HOC_6H_2(NO_2)_3$[f]	55
$(C_6H_5)_2SO$	Benzene, 25°, 1.0 hr	$(C_6H_5)_2S$	91
$(C_6F_5)_2SO$[g]	Benzene, reflux, 22 hr[h]	$(C_6F_5)_2S$	73
$CH_3S(O)Ar$[i]	Benzene, 25°, 1.0 hr	CH_3SAr[i] + $ClCH_2SAr$[i] (1.7:1.0)[j]	83[k]
	Benzene, 25°, 1.0 hr	CH_3SAr[i] + $ClCH_2SAr$[i] (0.4:1.0)[j]	100[k]
	Chloroform, 25°, 1.0 hr	CH_3SAr[i] + $ClCH_2SAr$[i] (3.6:1.0)[j]	86[k]

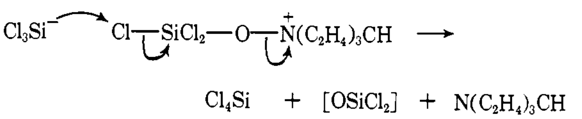
[a] Molar ratio of amine oxide or sulfoxide, Si_2Cl_6 = 1:1, except as noted. [b] Yield of isolated final product based on starting amine oxide or sulfoxide, except as noted, and assuming 100% conversion. [c] 4-Methylpyridine N-oxide. [d] Determined by quantitative glpc analysis. [e] Quinuclidine N-oxide. [f] Quinuclidine picrate. [g] We thank Mr. J. D. Gust for this preparation and reduction (see Experimental Section). [h] Molar ratio $(C_6F_5)_2SO:Si_2Cl_6$ = 1:2. [i] Ar = *p*-tolyl. [j] Molar ratio of methyl *p*-tolyl sulfide to chloromethyl *p*-tolyl sulfide as determined by pmr analysis. [k] Yield of total product, taking account of the product distribution as specified.

briefly explored the potential of Si_2Cl_6 as a deoxygenating agent for oxides of nitrogen and sulfur.[47]

Amine Oxides. Amine oxides are readily reduced with Si_2Cl_6 to the corresponding amines under mild conditions and in moderate yields (Table III).[48] The facile reduction of quinuclidine N-oxide with Si_2Cl_6 is of significant mechanistic interest, since the bicyclic structure necessarily precludes any inversion mechanism by backside attack on nitrogen. If, following the scheme in eq 13, the first step is formation of trichlorosilyl- and trichlorosiloxyquinuclidinium ions, the subsequent step must be nucleophilic attack of trichlorosilyl anion either on oxygen (displacement, eq 20), or on chlorine (fragmentation, eq 21). Since the silicon-containing products in eq 21 are capable of arising from hexachlorodisiloxane, which is produced according to the scheme in eq 20, and since the disproportionation reaction in eq 10 *may* be reversible, it would be difficult to distinguish between these two mechanistic pathways. The important point is that, given the appropriate structural constraints, Si_2Cl_6 is capable of deoxygenating oxides with *retention* of configuration. The implications for phosphine oxides are discussed in an accompanying paper.[29]

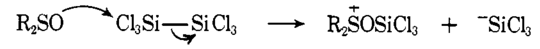


$$\mathrm{Cl_3Si^-}\quad \mathrm{O(SiCl_3)\text{—}\overset{+}{N}(C_2H_4)_3CH} \longrightarrow \mathrm{Cl_3SiOSiCl_3 + N(C_2H_4)_3CH} \quad (20)$$



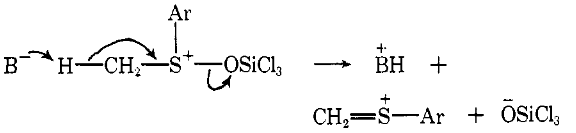
$$\mathrm{Cl_3Si^-}\quad \mathrm{Cl\text{—}SiCl_2\text{—}O\text{—}\overset{+}{N}(C_2H_4)_3CH} \longrightarrow \mathrm{Cl_4Si + [OSiCl_2] + N(C_2H_4)_3CH} \quad (21)$$

Sulfoxides. As with amine oxides, reduction of sulfoxides by Si_2Cl_6 was found to proceed smoothly under mild conditions, and in moderate yields (Table III). This method therefore compares favorably with those employing other reducing agents,[49] including lithium aluminum hydride.[50] With strongly electron-withdrawing substituents, somewhat more vigorous conditions are required, as exemplified for the reduction of bispentafluorophenyl sulfoxide. These observations are consistent with mechanisms for deoxygenation which parallel those suggested for the deoxygenation of phosphine oxides (eq 13) and quinuclidine oxide (eq 20 and 21): the initial step, formation of trichlorosilyl and trichlorosiloxysulfonium ions (eq 22), is followed by nucleophilic attack of trichlorosilyl anion on sulfur (displacement), on oxygen (displacement), or on chlorine (fragmentation). Since stereochemical studies are precluded, and for other reasons discussed in the preceding section, we are unable to distinguish between these three alternatives.

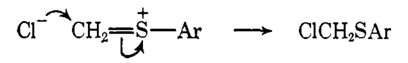


$$\mathrm{R_2SO}\quad \mathrm{Cl_3Si\text{—}SiCl_3} \longrightarrow \mathrm{R_2\overset{+}{S}OSiCl_3 + {}^-SiCl_3} \quad (22)$$

A fourth mode of attack on the initially formed trichlorosiloxysulfonium ion is possible for sulfoxides containing α-hydrogens, such as methyl *p*-tolyl sulfoxide: deprotonation and fragmentation to an ylide[51] (eq 23). Any anion (B) could serve as the initiating base, and chloride ion, which is present in the reaction mixture as previously described, might attack the ylide to form the observed Pummerer product,[51] chloromethyl *p*-tolyl sulfide (eq 24). As always in this highly complex reaction system, numerous alternative pathways remain. Thus, silicon tetrachloride, which is everpresent (see, for example, eq 10), might react with the sulfoxide to form trichlorosiloxysulfonium and chloride ions; fragmentation (eq 23) and recombination (eq 24) would account for the Pummerer product.[52,53] No evidence could be



$$\mathrm{B^-}\quad \mathrm{H\text{—}CH_2\text{—}\overset{+}{S}(Ar)\text{—}OSiCl_3} \longrightarrow \mathrm{B\overset{+}{H} + CH_2{=}\overset{+}{S}\text{—}Ar + \bar{O}SiCl_3} \quad (23)$$



$$\mathrm{Cl^-}\quad \mathrm{CH_2{=}\overset{+}{S}\text{—}Ar} \longrightarrow \mathrm{ClCH_2SAr} \quad (24)$$

---

(47) In preliminary studies with other systems, it was found that reduction of *trans*-stilbene oxide with Si_2Cl_6 in methylene chloride at room temperature leads to a mixture of products (whose identity is yet to be established), that reduction of benzophenone with Si_2Cl_6 in refluxing benzene affords a mixture of products, including trace amounts of tetraphenylethylene, and that nitrobenzene is not reduced by Si_2Cl_6 or by trichlorosilane in refluxing benzene.

(48) For a review which discusses other reduction methods for amine oxides, see E. Ochiai, "Aromatic Amine Oxides," Elsevier Publishing Corp., Amsterdam, 1967, p 184 ff.

(49) (a) M. Bögemann, *et al.*, in Houben-Weyl's "Methoden der organishen Chemie," Vol. 9, Georg Thieme Verlag, Stuttgart, 1955, p 218, and references cited therein; J. P. A. Castrillon and H. H. Szmant, *J. Org. Chem.*, **30**, 1338 (1965); (b) T. H. Chan, A. Melnyk, and D. N. Harpp, *Tetrahedron Lett.*, 201 (1969).

(50) E. N. Karaulova and G. D. Gal'pern, *Zh. Obshch. Khim.*, **29**, 3033 (1959).

(51) S. Oae and M. Kise, *Tetrahedron Lett.*, 2261 (1968); C. R. Johnson and W. G. Phillips, *J. Am. Chem. Soc.*, **91**, 682 (1969), and references cited therein.

(52) M. F. Lappert and J. K. Smith [*J. Chem. Soc.*, 3224 (1961)] have reported that the reaction of dimethyl sulfoxide with silicon tetrachloride gives chloromethyl methyl sulfide.

(53) It is unlikely that reaction between methyl *p*-tolyl sulfide and Si_2Cl_6 gives rise to the α-chlorinated product, and a control experiment confirmed that this is not the case.

obtained for the formation of mercaptals in the reduction of methyl *p*-tolyl sulfoxide with Si_2Cl_6 under the conditions listed in Table III.[54] Finally, in connection with the work described in this section, we note that the deoxygenation of sulfoxides by intramolecular rearrangement of trimethylsilyl groups has been described.[55]

Experimental Section[56]

Reaction of Triethylamine and Trichlorosilane. Triethylamine was refluxed (2 days) over barium oxide, distilled under nitrogen, and was stored over potassium hydroxide pellets. Trichlorosilane was treated with quinoline to remove hydrogen chloride and was isolated by fractional distillation under nitrogen. Traces of ethanol and water were removed from chloroform solvent by passage through a column of aluminum oxide (Woelm, Basic, Activity Grade 1) and benzene was dried *in vacuo* over a sodium mirror. All reactions were carried out in a standard vacuum system, which contained a detachable reaction vessel equipped with a magnetic stirring bar and nmr sample tubes such that portions of a reaction solution could be removed *in vacuo*. Samples for ir analyses were prepared in a plastic dry bag under nitrogen atmosphere and as mulls using excess Nujol to prevent hydrolysis.

A solution of triethylamine (6.1 g, 0.060 mol) in chloroform (20 ml) was treated with trichlorosilane (3.6 g, *ca.* 0.027 mol) at 0° for 15 min. The pmr spectrum of this homogeneous light green solution was essentially identical with that of an authentic chloroform solution of triethylamine and triethylammonium chloride (mole ratio = 1:1). Addition of ethanol (4.22 g, 0.092 mol) to the reaction solution at room temperature caused rapid precipitation of a white crystalline material which was separated by filtration, washed with ether, and identified as triethylammonium chloride (7.7 g, 0.056 mol) by comparison of its melting point and ir spectrum with an authentic sample. The filtrate was concentrated by removal of solvent at reduced pressure and yielded 2.82 g of a viscous pale green residue. The pmr spectrum (chloroform–benzene solvent) of this material consisted solely of two complex multiplets at τ *ca.* 5.9–6.5 ($SiOCH_2CH_3$) and τ *ca.* 8.4–9.1 ($SiOCH_2CH_3$). The absence of an absorption at τ *ca.* 5.8 indicated the absence of detectable amounts of triethoxysilane. The ir spectrum (neat) of the residue displayed very strong absorptions at *ca.* 1100 cm^{-1} (Si–O) but did not show any strong absorption at *ca.* 2200 cm^{-1} ($(EtO)_3Si–H$ stretch), a finding which confirmed the absence of triethoxysilane.

The reaction of triethylamine and trichlorosilane at room temperature (mole ratio *ca.* 1:1) in benzene caused rapid precipitation of a light yellow material. All volatile materials were removed at room temperature, leaving a yellow mass whose pmr spectrum was similar to that described above and whose ir spectrum (4000–625 cm^{-1}, Nujol mull) was identical with that of triethylammonium chloride. Treatment of this yellow resinous material (0.524 g) with 25% aqueous potassium hydroxide caused vigorous evolution of hydrogen (*ca.* 2.7 mmol).

Optically Active Phosphine Oxides. Alkylmethylphenylphosphine oxides **1–3** and *p*-anisylmethylphenylphosphine oxide (**4**) were prepared from menthyl (*S*)-methylphenylphosphinate using the appropriate Grignard reagent, as previously described.[9] The preparations of optically active ethylmethyl-*n*-propylphosphine oxide and *o*-anisyl-β-naphthylphenylphosphine oxide (**10**) are reported elsewhere.[32]

Reduction of Benzylmethylphenylphosphine Oxide (3) with Trichlorosilane–Amine Mixtures. To ensure optimum chemical and optical yields of the product, the reductions were carried out with rigorous exclusion of oxygen,[57] *i.e.*, under a high-purity nitrogen or argon atmosphere, and with dried solvents and reagents from which oxygen had been carefully removed. A five- to tenfold excess of trichlorosilane–amine mixture (molar ratio *ca.* 1:1) was used and reaction mixtures were refluxed for 1–2 hr.

A. **Benzene Solvent.** The following procedure is typical of the general method used for the reduction of **3** with trichlorosilane–amine mixtures. A benzene solution (4 ml) of optically pure (+)-(*R*)-**3** (200 mg, 0.87 mmol), $[\alpha]_D$ +51.4°, was refluxed with trichlorosilane (0.45 ml, *ca.* 4.5 mmol) and N,N-diethyl-*p*-toluidine (0.76 ml, 4.3 mmol) for 1.5 hr. The homogeneous reaction mixture was cooled to 0°, diluted with benzene (15 ml), and hydrolyzed by cautious addition of 30% aqueous sodium hydroxide (3 ml). The organic layer was washed with water and dried (magnesium sulfate). An aliquot (15 ml) of this benzene solution was concentrated by removal of solvent under reduced pressure. N,N-Diethyl-*p*-toluidine was removed from the oily residue by rapid distillation (kugelrohr) at reduced pressure, bp *ca.* 50° (0.02 mm), to afford the crude reduction product, benzylmethylphenylphosphine, **7**: pmr PCH_3, d, τ 8.77, J_{PCH} = 4.0 Hz; $PCH_2C_6H_5$, m, τ 6.98; aromatic, m, τ *ca.* 2.3–3.0. Quaternization of **7** was carried out with a tenfold excess of *n*-propyl bromide in acetonitrile (1 ml) (*ca.* 60°, 6 hr). To avoid optical fractionation, ether was used to precipitate and wash the product, (−)-(*R*)-benzylmethylphenyl-*n*-propylphosphonium bromide, **8** (170 mg, 74%); mp 190–195°, $[\alpha]_D$ −28.9°, optical purity 79%; pmr PCH_3, d, τ 7.49, J_{PCH} = 14 Hz; $PCH_2C_6H_5$, d (apparent A_2 spin system), τ 5.27, J_{PCH} = 16 Hz.

Reductions of (+)-(*R*)-**3** with trichlorosilane in the presence of dicyclohexylethylamine and N,N-dimethylaniline occurred under homogeneous reaction conditions whereas use of quinuclidine, trimethylamine, triethylamine, benzyldimethylamine, and pyridine led to heterogeneous reaction mixtures throughout the reduction.

B. **Acetonitrile Solvent.** Reductions in refluxing acetonitrile were carried out in the same manner as described above for benzene, with the exception that benzene was added to the reaction mixture after alkaline hydrolysis. Whereas reduction of (+)-(*R*)-**3** with trichlorosilane in the presence of either N,N-diethyl-*p*-toluidine (homogeneous conditions) or triethylamine (heterogeneous conditions) afforded (+)-(*S*)-**8** with predominant (60 and 90%, respectively) inversion of configuration, the use of trichlorosilane itself led to isolation of racemic **8** in 48% yield. Reaction of (+)-(*R*)-**3** (230 mg, 1.0 mmol) without the usual excess of trichlorosilane (0.1 ml, *ca.* 1.0 mmol) led to rapid evolution of hydrogen (0.33 mmol) at low temperatures (*ca.* 0°) and, after subsequent refluxing, did not afford any detectable amounts of **8**. Recovered **3** was racemic. In the presence of pyridine (heterogeneous conditions) or N,N-diethylaniline (homogeneous conditions), no gas evolution was observed and racemic **8** was obtained (*ca.* 80%).

C. **Di-*n*-butyl Ether Solvent.** Optically pure (+)-(*R*)-**3** was added to a heterogeneous mixture of N,N-diethyl-*p*-toluidine and trichlorosilane in di-*n*-butyl ether and the mixture was heated at 70° for 2 hr. Alkaline hydrolysis and work-up were carried out as described above for the reduction in benzene, and afforded (40%) (−)-(*S*)-**8**, $[\alpha]_D$ −20.9°, optical purity 57% (retention).

Stoichiometry for Reduction of Benzylmethylphenylphosphine Oxide (3) with Si_2Cl_6. A solution of racemic **3** (460 mg, 2.0 mmol) in benzene (10 ml) was refluxed under nitrogen with Si_2Cl_6 (0.34 ml, *ca.* 2.0 mmol) for 30 min. The reaction mixture was cooled to 0° and toluene (0.210 ml, 2.0 mmol) was added as an internal standard for quantitative glpc analysis, using a 6-ft 10% silicone rubber SE-30 on 60–80 mesh Chromosorb W column at 70°, helium flow rate 55 cc/min. The molar ratios of $SiCl_4$/toluene and $Cl_3SiOSiCl_3$/toluene were obtained by multiplying the experimentally determined peak area ratios by 0.64, a factor which was used to correct for differences in thermal conductivities. Results indicated that *ca.* 1.4 mmol of $SiCl_4$ and *ca.* 0.6 mmol of $Cl_3SiOSiCl_3$ were present in the product mixture. Identification of the products was based on comparison of their glpc retention time (relative to air) with those for authentic $SiCl_4$ and $Cl_3SiOSiCl_3$, 0.87 and 7.56 min,

---

[54] Chan, Melnyk, and Harpp[49b] have reported that reduction of various sulfoxides having α-hydrogens with trichlorosilane produces mixtures of sulfides and mercaptals.

[55] A. G. Brook and D. G. Anderson, *Can. J. Chem.*, 46, 2115 (1968).

[56] Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Pmr spectra were recorded on a Varian A-60A spectrometer and refer to *ca.* 10% solution in deuteriochloroform, with tetramethylsilane as internal standard. All rotations refer to solvent methanol and to *c* 1–3 g/100 ml, except as noted. Optical rotations at the D line were measured on a Schmidt and Haensch visual polarimeter, and at other wavelengths on a Cary 60 spectropolarimeter. Mass spectra were obtained with an AEI MS-9 high-resolution mass spectrometer. We thank the National Science Foundation for providing the funds for the purchase of the mass spectrometer under Grant No. GP-5200.

[57] That the presence of oxygen during reductions of optically active phosphine oxides causes a significant decrease in the optical purity both of the reduction product and of the recovered starting material was apparent from the following experiment. Reduction of (+)-(*R*)-**3** with trichlorosilane in the presence of triethylamine (molar ratio 1.0:1.3:1.3) in refluxing benzene (for 30 min) under an atmosphere of dry air afforded, after quaternization with *n*-propyl bromide, 36% optically pure (+)-(*R*)-**8** in 16% yield, and recovered (+)-(*R*)-**3**, 12% optically pure, in 55% yield. Repetition of this experiment using Si_2Cl_6 yielded 57% optically pure (+)-(*R*)-**8** in 35% yield, and recovered (−)-(*S*)-**3**, 3% optically pure, in 23% yield.

respectively. The yield of benzylmethylphenylphosphine (**9**) was 88%.

As a control experiment, a solution of benzylmethylphenylphosphine (176 mg, 0.82 mmol), $Cl_3SiOSiCl_3$ (0.15 ml), and toluene (131 mg, 1.43 mmol) in benzene (7 ml) was refluxed for 30 min. Glpc analysis, as described above, indicated that the relative ratio $Cl_3SiOSiCl_3$/toluene (0.86 ± 0.03) was not significantly different from this same ratio (0.88 ± 0.03) measured before heating and that no $SiCl_4$ was present. Hence $Cl_3SiOSiCl_3$ is not decomposed by phosphine under these reaction conditions.

Stoichiometry of Reduction of Triphenylphosphine Oxide with Si_3Cl_8. A solution of triphenylphosphine oxide (1.315 g, 4.73 mmol) in benzene (10 ml) was refluxed under nitrogen with Si_3Cl_8 (1.58 mmol) for 1 hr. An aliquot (*ca.* 5 ml) was removed and was hydrolyzed by addition to 20% aqueous sodium hydroxide (5 ml). The benzene layer was separated, dried (magnesium sulfate), and concentrated by removal of solvent under reduced pressure to yield 0.5 g of a white crystalline residue, mp 80–130°. Glpc analysis of this material, on a 2-ft 10% silicone rubber SE-30 on 60–80 mesh Chromosorb W column at 245°, helium flow rate 160 cc/min, indicated a ratio of peak areas of triphenylphosphine to triphenylphosphine oxide of 2.18; after multiplication by a factor (0.71) to correct for thermal conductivity differences, a molar ratio of triphenylphosphine to triphenylphosphine oxide of 1.54 was obtained. The quantity x of triphenylphosphine reduction product was $x = (1.54)(4.73)/2.54 = 2.87$ mmol. The remaining reduction mixture was refluxed for a total of 20 hr and was analyzed in the same manner as described above. Results for this determination showed that 2 mol of phosphine oxide was reduced per mole of Si_3Cl_8.

Reduction of Optically Active Phosphine Oxides with Si_2Cl_6. All operations were carried out with complete exclusion of oxygen as described above, since the produced phosphines rapidly scavenge even trace amounts of oxygen and are thus reoxidized to phosphine oxides. Commercially available Si_2Cl_6 (Alfa Inorganics) left no higher boiling residue on distillation, bp 75° (70 mm). *Since there is some danger of detonation on distillation, undistilled Si_2Cl_6 should be used;* in our experience, there is no effect on the stereospecificity of the reduction. Hexachlorodisilane reacts with moisture in air and should be handled accordingly. The concentration of phosphine oxide was generally *ca.* 0.15–0.20 *M* and an excess of Si_2Cl_6 (*ca.* 1.3 equiv) was used since it was found that use of less than *ca.* 1 equiv of Si_2Cl_6 led to products of lower optical purity. Prolonged reaction times were avoided in order to prevent racemization of the product and *reaction times of 5 min or less in refluxing benzene are recommended.* Alkaline hydrolysis of the reduction mixture was used to terminate the reaction. Some typical reductions in benzene are described below. The only significant change in procedure for reductions in chloroform is use of lower reaction temperatures (see Table II).

Benzylmethylphenylphosphine Oxide (3). A solution of optically pure (+)-(*R*)-**3** (210 mg, 0.91 mmol), $[\alpha]_D$ +51.4°, in benzene (5 ml) was refluxed with Si_2Cl_6 (0.21 ml, *ca.* 1.2 mmol) for 10 min. The yellow reaction mixture was cooled to 0° and was hydrolyzed by cautious addition of 30% aqueous sodium hydroxide (3 ml). Benzene (10 ml) was added, and the organic layer was washed twice with 2-ml portions of water and dried (magnesium sulfate). Removal of solvent under reduced pressure from an aliquot of this benzene solution gave the crude reduction product, benzylmethylphenylphosphine, **7**, as a clear, colorless oil which was isolated in 84% yield by rapid distillation (kugelrohr) at reduced pressure, bp 90–95° (0.01 mm), $[\alpha]_D$ +81° (toluene). Quaternization of **7** with excess *n*-propyl bromide was carried out as described above and afforded (+)-(*S*)-**8** (70%), mp 195–196°, $[\alpha]_D$ +35.1°, optical purity 95%.

***o*-Anisyl-β-naphthylphenylphosphine Oxide (10).** A solution of (−)-(*S*)-*o*-anisyl-β-naphthylphenylphosphine oxide[32] (**10**) (294 mg, 0.86 mmol), $[\alpha]_{400}$ −28.5°, in benzene (5 ml) was refluxed with Si_2Cl_6 (0.20 ml, *ca.* 1.2 mmol) for 13 min. After alkaline hydrolysis and work-up as described above for reduction of **3**, the residual viscous material was rapidly chromatographed on silica gel, using ethyl acetate as eluent, to afford *o*-anisyl-β-naphthylphenylphosphine (**11**) (244 mg, 98%) as a colorless viscous oil, $[\alpha]_D$ −10.0°, $[\alpha]_{400}$ −43.8° (benzene). Reoxidation of **11** was effected by treatment with a tenfold excess of aqueous hydrogen peroxide at room temperature for 30 min with benzene as solvent. The aqueous layer was separated and extracted with chloroform and the combined organic layers were dried (magnesium sulfate). Removal of solvent under reduced pressure yielded (+)-**10**, $[\alpha]_{400}$ +9.0°. Reduction of this material with Si_2Cl_6, following the procedure described above *except* that the reaction mixture was refluxed for only 1.5 min, yielded (+)-**11**, $[\alpha]_D$ +8.1°, $[\alpha]_{400}$ +35.5° (benzene), in 70% yield.

Ethylmethyl-*n*-propylphosphine Oxide. A solution of (−)-(*S*)-ethylmethyl-*n*-propylphosphine oxide[32] (160 mg, 1.2 mmol), $[\alpha]_{300}$ −1.9°, in benzene (5 ml) was refluxed with Si_2Cl_6 (0.23 ml, *ca.* 1.4 mmol) for 30 min. The reaction mixture was cooled to 0°, hydrolyzed by addition of 30% aqueous sodium hydroxide (1.5 ml), and washed twice with 1-ml portions of water to remove any unreacted starting phosphine oxide. Reoxidation of the benzene solution of ethylmethyl-*n*-propylphosphine with aqueous hydrogen peroxide followed by work-up as described above for **11** gave ethylmethyl-*n*-propylphosphine oxide as a partially crystalline oil, which was isolated as a hygroscopic solid (139 mg, 87%) by rapid distillation (kugelrohr) at reduced pressure, bp *ca.* 75° (0.01 mm), $[\alpha]_{300}$ +1.2°.

Reduction of Benzylmethylphenylphosphine Oxide (3) with Si_2Cl_6 in Acetonitrile. A solution of optically pure (+)-(*R*)-**3** (90 mg, 0.39 mmol), $[\alpha]_D$ +78° (acetonitrile), in acetonitrile (3 ml) was refluxed with Si_2Cl_6 (0.085 ml, *ca.* 0.5 mmol) for 10 min. Benzene (5 ml) was added to the heterogeneous reaction mixture and work-up was followed by quaternization of **7** with *n*-propyl bromide (as described above) to yield (45 mg, 36%) racemic **8**. The filtrate obtained from isolation of **8** was concentrated by removal of solvent under reduced pressure. Sublimation (120°, 0.01 mm) of the residue afforded (+)-(*R*)-**3** (21 mg, 24%), $[\alpha]_D$ +6.6° (acetonitrile), optical purity 8%.

Reduction of Methylphenyl-*n*-propylphosphine Oxide (2) with Si_3Cl_8. Commercially available Si_3Cl_8 (Alfa Inorganics) was used without further purification and the usual precautions against the presence of oxygen were followed (see above). A solution of 80% optically pure (+)-(*R*)-**2** (251 mg, 1.41 mmol), $[\alpha]_D$ +16.0°, in benzene (9 ml) was refluxed with Si_3Cl_8 (0.24 ml, *ca.* 1.0 mmol) for 5 min. Alkaline hydrolysis and work-up of the reaction mixture, as described above for reduction of **3** with Si_2Cl_6, afforded a benzene solution which was concentrated by removal of solvent under reduced pressure. The crude product, methylphenyl-*n*-propylphosphine, **9**, was treated with a tenfold excess of benzyl bromide (*ca.* 50°, 2 hr). Isolation of the quaternization product, as described above, yielded (−)-(*R*)-benzylmethylphenyl-*n*-propylphosphonium bromide (**8**) in 87% yield, mp 192–196°, $[\alpha]_D$ −29.7°, optical purity 81%.

Attempted Reduction of Phosphine Oxides with Hexamethyldisilane. A solution of triphenylphosphine oxide (840 mg, 3.0 mmol) in benzene (3 ml) was refluxed for 48 hr with hexamethyldisilane, which was prepared according to the method of Wilson and Smith[58] and identified by pmr and mass spectral analyses. Glpc analysis was carried out directly on the reaction mixture, using a 2-ft 10% silicone rubber SE-30 on 60–80 mesh Chromosorb W column at 240°, helium flow rate 150 cc/min, and indicated that no detectable amount of triphenylphosphine was present. Repetition of this procedure using tri-*n*-butylphosphine oxide (42-hr reflux) gave similar results upon glpc analysis (column temperature, 190°).

Effect of Contact Time on Optical Purity in Reductions of Methylphenyl-*n*-propylphosphine Oxide (2) with Si_2Cl_6 and Si_3Cl_8. A solution of 80% optically pure (+)-(*R*)-**2** (190 mg, 1.04 mmol), $[\alpha]_D$ +16.0°, in benzene (6.3 ml) was refluxed (82°) with Si_2Cl_6 (1.04 mmol). Aliquots (0.65 ml) were removed at various time intervals and were quenched by addition to 30% aqueous sodium hydroxide (1 ml). Work-up and quaternization of the reduction product, methylphenyl-*n*-propylphosphine, **9**, with excess benzyl bromide were carried out as described above and afforded, in 80–90% yields, (−)-(*R*)-benzylmethylphenyl-*n*-propylphosphonium bromide (**8**). After 25, 35, and 45 min, the optical purity of **8** was 56, 23, and 1%.

The same procedure was used to study the reduction of 80% optically pure (+)-(*R*)-**2** (240 mg, 1.32 mmol) with Si_3Cl_8 (0.66 mmol) in benzene (8 ml) at 70°. After 6, 15, 30, 45, and 60 min, the optical purity of **8** was 81, 76, 64, 49, and 5%.

Racemization of Methylphenyl-*n*-propylphosphine (9) with Iodine. A solution of 56% optically pure (−)-(*R*)-methylphenyl-*n*-propylphosphine (33 mg, 0.2 mmol) in benzene–acetonitrile (3 ml, 2:1) was heated with iodine (7 mg, *ca.* 0.03 mmol) at *ca.* 50° for 1.5 hr. The reaction mixture was treated with a fivefold excess of benzyl bromide and was heated at *ca.* 50° for 2 hr to afford racemic **8** (41 mg, 60%).

Racemization of Methylphenyl-*n*-propylphosphine (9) with Silicon Tetrachloride. A solution of 56% optically pure (−)-(*R*)-methyl-

---

(58) G. R. Wilson and A. G. Smith, *J. Org. Chem.*, 26, 557 (1961).

phenyl-*n*-propylphosphine (50 mg, *ca.* 0.3 mmol) in benzene (3 ml) was heated with silicon tetrachloride (68 mg, *ca.* 0.4 mmol) at 60° in a temperature-controlled polarimeter cell and the loss of optical activity was continuously monitored at 400 mμ. Racemization was complete after *ca.* 23 min. The solution was cooled to 0° and was hydrolyzed with 30% aqueous sodium hydroxide (1 ml). Work-up and quaternization with benzyl bromide, as described above for **9**, afforded (77%) racemic **8**.

Attempted Racemization of Methylphenyl-*n*-propylphosphine (9) with Si_2Cl_6. A solution of 78 ± 3% optically pure (−)-(*R*)-methylphenyl-*n*-propylphosphine (*ca.* 0.25 mmol) was refluxed (82°) with Si_2Cl_6 (67 mg, *ca.* 0.25 mmol) in benzene (2.5 ml) for 1 hr. Alkaline hydrolysis and work-up of the reaction mixture, followed by quaternization of **9** as described above, afforded (96%) (−)-(*R*)-**8**, $[\alpha]_D$ −28°, optical purity 74%.

Racemization of Benzylmethylphenylphosphine Oxide (3) with Silicon Tetrachloride. A. Benzene Solvent. A solution of optically pure (+)-(*R*)-benzylmethylphenylphosphine oxide (40 mg, *ca.* 0.17 mmol), $[\alpha]_D$ +51.4°, in benzene (3 ml) was refluxed with silicon tetrachloride (0.23 ml, *ca.* 2.0 mmol) for 2 hr. The reaction mixture was hydrolyzed with 30% aqueous sodium hydroxide (1 ml), the aqueous layer was extracted with chloroform, and the combined extracts were dried (magnesium sulfate). Removal of solvent under reduced pressure gave crude **3**, which was purified by sublimation (see above) to yield (+)-(*R*)-**3**, $[\alpha]_D$ +8.4°, optical purity 16%.

B. Acetonitrile Solvent. A solution of optically pure (+)-(*R*)-**3** (230 mg, 1.0 mmol) in acetonitrile (3 ml) was treated with silicon tetrachloride (0.12 ml, *ca.* 1.0 mmol) at 25° for 20 min. The reaction mixture was hydrolyzed and was worked up as described above to afford racemic **3** in essentially quantitative yield.

Racemization of Benzylmethylphenylphosphine Oxide. A. With Acetyl Chloride. A solution of optically pure (+)-(*R*)-benzylmethylphenylphosphine oxide (80 mg, 0.35 mmol), $[\alpha]_D$ +51.4°, in acetonitrile (1 ml) was treated with acetyl chloride (14 mg, *ca.* 0.18 mmol) at room temperature and the loss of optical activity was monitored at 589 mμ. Racemization was complete after *ca.* 150 min.

B. With Phosphorus Trichloride. A solution of (+)-(*R*)-benzylmethylphenylphosphine oxide (58 mg, 0.25 mmol) in acetonitrile (2 ml) was treated with phosphorus trichloride (196 mg, *ca.* 1.4 mmol) at room temperature and the loss of optical activity was monitored at 589 mμ. Racemization was complete after *ca.* 4 min.

Deoxygenation of Amine Oxides with Si_2Cl_6. 4-Methylpyridine N-Oxide. A solution of 4-methylpyridine N-oxide (210 mg, 1.93 mmol) in chloroform (5 ml) was stirred with Si_2Cl_6 (0.33 ml, *ca.* 1.93 mmol) at room temperature for 1 hr, following the initially exothermic reaction which occurred on mixing. The reaction mixture was cooled to 0° and was hydrolyzed with 20% aqueous sodium hydroxide (3 ml). The aqueous layer was extracted four times with 5-ml portions of chloroform and the combined extracts were dried (magnesium sulfate). Removal of solvent under reduced pressure gave the crude reduction product, 4-methylpyridine, as a light brown oil, which was identified by comparison of its ir and pmr spectra with those of authentic material and by conversion to 4-methylpyridine picrate, mp 166–168° (ethanol) (lit.[59] mp 166–167°). Quantitative glpc analysis using naphthalene as an internal standard on a 6-ft 10% silicone rubber SE-30 on 60–80 mesh Chromosorb W column at 125°, helium flow rate 160 cc/min, indicated that the yield of 4-methylpyridine was 60%. Similar results were obtained upon deoxygenation in benzene (Table III). The same procedure was used for reduction of 4-methylpyridine N-oxide in benzene; however more vigorous reaction conditions were necessary (see Table III).

Quinuclidine N-Oxide. A solution of quinuclidine (105 mg, 0.94 mmol), mp 150–157° (lit.[60] mp 158°), in methanol (5 ml) was oxidized with hydrogen peroxide following the oxidation procedure described by Cope and Ciganek.[61] A negative phenolphthalein spot test[61] for quinuclidine was obtained after reaction for 48 hr at room temperature. Decomposition of excess hydrogen peroxide was effected by *cautious* addition of a small amount of 5% platinum-on-carbon powder. Removal of solvent under reduced pressure afforded a colorless, viscous oil which solidified after dehydration (*ca.* 50°, 0.01 mm) to yield (114 mg, 95%) hygroscopic white crystals,[62] mp *ca.* 110° dec, M^+, *m/e* 127. The ir spectrum (Nujol mull) of this material confirmed the absence of quinuclidine and featured a strong band at 940 cm^{-1} (N–O stretch[63]). The pmr spectrum was also consistent with the assigned quinuclidine N-oxide structure and showed only aliphatic absorptions: ON(CH_2CH$_2$)$_3$CH, m, τ 6.60, and ON(CH$_2$$CH_2$)$_3$*CH*, m, τ 7.95, with each absorption occurring at *ca.* 0.5 ppm lower field than the corresponding absorptions in quinuclidine.

A solution of quinuclidine N-oxide (31 mg, 0.25 mmol) in chloroform (5 ml) was stirred with Si_2Cl_6 (0.042 ml, *ca.* 0.25 mmol) at room temperature for 1.5 hr. The reaction mixture was hydrolyzed and worked up as described above for 4-methylpyridine N-oxide. Removal of solvent under reduced pressure at room temperature afforded the crude reduction product, as a partially crystalline oil. The ir and pmr spectra of this residue indicated the presence of quinuclidine, in addition to some contaminants. A solution of the crude residue in ethanol (3 ml) was added to a hot solution of picric acid (90 mg, 0.4 mmol) and the mixture was slowly cooled to room temperature. The yellow crystalline product was recrystallized from ethanol to yield 46 mg (55%) of long yellow needles, mp 283–284°, whose ir spectrum (Nujol mull) was identical with that of an authentic sample of quinuclidine picrate, mp 283–285° (lit.[60] mp 275–276°).

Deoxygenation of Sulfoxides with Si_2Cl_6. Diphenyl Sulfoxide. A solution of diphenyl sulfoxide (142 mg, 0.7 mmol) in benzene (5 ml) was stirred with Si_2Cl_6 (0.12 ml, *ca.* 0.7 mmol) at room temperature for 1 hr. Hydrolysis and work-up were carried out as described above for 4-methylpyridine N-oxide, with substitution of water for 20% aqueous sodium hydroxide, to afford a pale green oil. Rapid distillation (kugelrohr) at reduced pressure, bp *ca.* 100° (0.1 mm), yielded diphenyl sulfide (119 mg, 91%), identified by comparison of its ir, pmr, and mass spectrum with those of an authentic sample.

Bispentafluorophenyl Sulfoxide. A solution of thionyl chloride (5.66 g, 0.048 mol) in ether (5 ml) was added dropwise to pentafluorophenylmagnesium bromide (0.096 mol) in ether (100 ml) at 0° under nitrogen. Ether (20 ml) was added and the mixture was hydrolyzed by addition of saturated aqueous ammonium chloride. The ether layer was separated, washed with water, treated with activated charcoal, and dried (magnesium sulfate). Sublimation (90°, 0.05 mm) of the residue obtained after removal of solvent under reduced pressure afforded a white crystalline material which was chromatographed on silica gel, eluting with hexane and then with chloroform. The product from the chloroform eluate was recrystallized from hexane to yield (12.65 g, 70%) bispentafluorophenyl sulfoxide, mp 76.5–77.5°. Attempts to prepare the sulfoxide by oxidation of the sulfide were uniformly unsuccessful in the face of the extraordinary chemical inertness of the sulfide.

Anal. Calcd for $C_{12}F_{10}SO$: C, 37.71; F, 45.71; S, 8.35. Found: C, 37.80; F, 50.01; S, 8.66.

A solution of bispentafluorophenyl sulfoxide (300 mg, 0.79 mmol) in benzene (10 ml) was refluxed with Si_2Cl_6 (0.25 ml, *ca.* 1.5 mmol) for 22 hr. Alkaline hydrolysis (10% aqueous potassium hydroxide) followed by work-up as described for diphenyl sulfoxide afforded an oil which was chromatographed on silica gel, using hexane as the eluent. The eluate was recrystallized from methanol–water (9:1) to yield white plates (210 mg, 73%), mp 85–86°, which were identified as bispentafluorophenyl sulfide by comparison of melting point and ir spectrum with the corresponding properties of authentic material, prepared by the method of Cohen, *et al.*[64]

Methyl *p*-Tolyl Sulfoxide. Reduction of a solution of methyl *p*-tolyl sulfoxide (155 mg, 1.0 mmol) with Si_2Cl_6 (0.17 ml, *ca.* 1.0 mmol) in benzene (5 ml) at room temperature for 1 hr was carried out in the same manner as described above for diphenyl sulfoxide. Glpc analysis of the crude reduction product on a 6-ft 10% silicone rubber SE-30 on 60–80 mesh Chromosorb W column at 170°, helium flow rate 160 cc/min, indicated the presence of methyl *p*-tolyl sulfide, plus a major quantity of a second component. A portion of the latter was collected from the glpc column and identified as chloromethyl *p*-tolyl sulfide by comparison of its ir and pmr

---

[59] G. R. Clemo and W. M. Gourlay, *J. Chem. Soc.*, 478 (1938).

[60] J. Meisenheimer, *Ann.*, **420**, 190 (1920).

[61] A. C. Cope and E. Ciganek, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 612.

[62] Elemental analysis of this material was consistent with a hydrated form of quinuclidine N-oxide. However, attempts to prepare a completely anhydrous sample of this material were frustrated by its decomposition at reduced pressures and temperatures above *ca.* 70°.

[63] The general region of N–O ir stretching frequencies in aliphatic *t*-amine N-oxides is *ca.* 950–970 cm^{-1} (see ref 48).

[64] S. C. Cohen, M. L. N. Reddy, and A. G. Massey, *J. Organometal. Chem.*, **11**, 563 (1968).

spectra with those from an authentic sample prepared by the method of Bordwell and Pitt.[65] The molar ratio of methyl *p*-tolyl sulfide to chloromethyl *p*-tolyl sulfide was *ca.* 0.4:1.0 as determined by integration of pmr intensities. The recovery of reduction products (161 mg) was essentially quantitative. The results of a duplicate reduction in benzene (note the change in ratio) and of another run in chloroform are listed in Table III.

---

[65] F. G. Bordwell and B. M. Pitt, *J. Am. Chem. Soc.*, 77, 572 (1955).

The Stereospecific Desulfurization of Acyclic Phosphine Sulfides with Hexachlorodisilane and the Alkaline Hydrolysis of Monoalkoxy- and Monoalkylmercaptophosphonium Salts. Stereochemistry and Mechanism[1]

Gerald Zon, Kenneth E. DeBruin,[2] Klaus Naumann, and Kurt Mislow

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. *Received June 2, 1969*

Abstract: The first stereospecific desulfurization of a phosphine sulfide is reported: optically active acyclic phosphine sulfides are reduced to phosphines by hexachlorodisilane in high optical yields and with *retention* of configuration. This result is in contrast to the reduction of optically active acyclic phosphine oxides which, as shown previously, undergo reduction by the same reagent with *inversion* of configuration. In a parallel study, it was found that *both* ethoxymethyl-β-naphthylphenylphosphonium *and* ethylmercaptomethylphenylpropylphosphonium salts undergo basic hydrolysis with complete *inversion* of configuration at phosphorus, to give the corresponding phosphine oxides. Mechanisms for these reactions are suggested which account for the observed stereochemistry.

In the preceding paper,[3] it was shown that optically active acyclic phosphine oxides are deoxygenated by hexachlorodisilane (Si_2Cl_6) to phosphines with high stereospecificity and with inversion of configuration. As an extension of this study, we investigated the possibility of achieving the stereospecific desulfurization of phosphine sulfides to phosphines by Si_2Cl_6. Additional impetus for such an investigation arose from the fact that no information concerning the stereochemistry of desulfurization of optically active phosphine sulfides appears to have been reported, even though methods[4] for such conversions are available; stereochemical studies of optically active phosphine sulfides have been limited either to their syntheses,[5–7] or to their conversion to the corresponding optically active phosphine oxides.[6]

Optically active methylphenylpropylphosphine sulfide, (+)-(*R*)-**1**,[8,9] was prepared[6] from (+)-(*S*)-methylphenylpropylphosphine (**2**). Based on the rotation of the product of quaternization of **2** with benzyl bromide, (+)-(*S*)-**3**, the phosphine was 58% optically pure. Assuming complete retention of asymmetry, our sample of (+)-(*R*)-**1** was therefore 58% optically pure. Reduction of this sample with Si_2Cl_6 in refluxing benzene afforded (+)-(*S*)-**2**, which upon quaternization with benzyl bromide yielded 63% optically pure (+)-(*S*)-**3**.[10] Both steps, sulfurization *and* desulfurization, therefore proceeded with complete or nearly complete retention of configuration at phosphorus (Chart I).

Similarly (see Chart I), (*R*)-allylmethylphenylphosphine (**4**), prepared by Si_2Cl_6 reduction of the oxide,[3] was converted to the sulfide, (−)-(*S*)-**5**, by treatment with elemental sulfur.[11] The optical purity of **5** was 74%, as judged by the optical purity of (−)-(*S*)-**1** obtained upon diimide reduction[11,12] of **5**. Reduction of this sample of **5** gave **4**, which upon sulfurization gave 70% optically pure **5**, and upon quaternization with benzyl bromide gave the P-benzylphosphonium salt, (−)-(*R*)-**6**. Again, both sulfurization and desulfurization were thus shown to proceed with complete or nearly complete retention of configuration at phosphorus. From the rotation of the product of quaternization, $[\alpha]_D$ −17.0°, the absolute rotation of **6** is calculated to be $[\alpha]_D$ 24°; this is significantly higher than the highest previously reported[13] rotation, 15.7°.

---

[1] This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-B. A portion of this work was reported in a preliminary communication: K. Naumann, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, **91**, 2788 (1969).

[2] U. S. Public Health Service Postdoctoral Fellow, 1967–1969, supported by the National Cancer Institute.

[3] K. Naumann, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7012 (1969).

[4] F. Hein, K. Issleib, and H. Rabold, *Z. Anorg. Allgem. Chem.*, 287, 208 (1956); L. Horner, H. Hoffmann, and P. Beck, *Ber.*, **91**, 1583 (1958); **92**, 2088 (1959); L. Maier, *Helv. Chim. Acta*, **47**, 2137 (1964); K. D. Berlin, T. H. Austin, M. Peterson, and M. Nagabhusanam in "Topics in Phosphorus Chemistry," Vol. 1, M. Grayson and E. J. Griffith, Ed., Interscience Publishers, New York, N. Y., 1964, Chapter 2, p 49.

[5] W. C. Davies and F. G. Mann, *J. Chem. Soc.*, 276 (1944).

[6] L. Horner and H. Winkler, *Tetrahedron Lett.*, 175 (1964).

[7] D. P. Young, W. E. McEwen, D. C. Velez, J. W. Johnson, and C. A. VanderWerf, *ibid.*, 359 (1964).

[8] Absolute configurations are based on the work of A. F. Peerdeman, J. P. C. Holst, L. Horner, and H. Winkler, *Tetrahedron Lett.*, 811 (1965), and the correlations described in ref 6. The sulfurization step is believed to occur with retention of configuration.[6,7]

[9] Rotational prefixes and rotations used in the text refer to solvent methanol, unless specified otherwise.

[10] Since the error limits for the optical purity of **3** are *ca.* ±3%, the values for the two comparable optical purities are not considered to differ significantly.

[11] We thank Dr. Arthur W. Herriott and Mr. W. B. Farnham for this preparation.

[12] For the analogous diimide reduction of an optically active allyl sulfoxide, see P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *J. Am. Chem. Soc.*, **90**, 4869 (1968).