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]

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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]

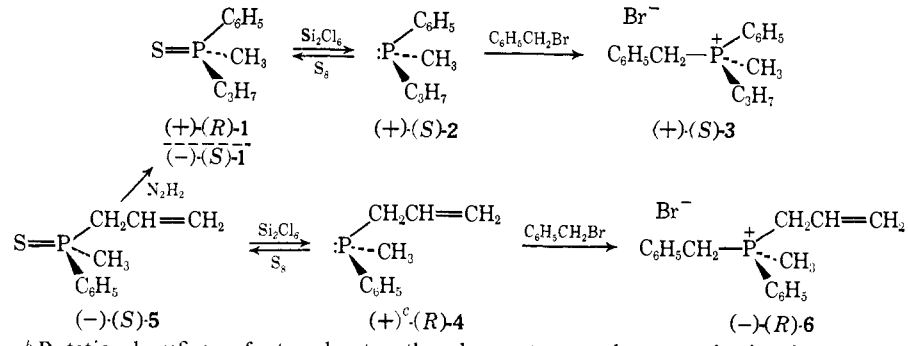
(9) Rotational prefixes and rotations used in the text refer to solvent methanol, unless specified otherwise.

(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).

Chart I[a,b]



[a] C_3H_7 = *n*-propyl. [b] Rotational prefixes refer to solvent methanol, except as noted. [c] Rotation in toluene.

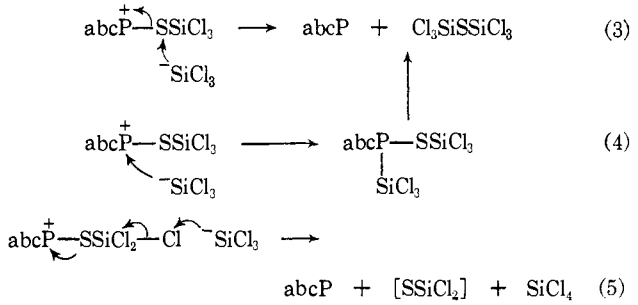
In the mechanism suggested[3] for the reduction of optically active acyclic phosphine oxides with Si_2Cl_6, inversion of configuration results from nucleophilic attack by trichlorosilyl anion on phosphorus in an intermediate trichlorosiloxyphosphonium ion, as shown in eq 1 (X = $OSiCl_3$, Y = $SiCl_3$).[14]

$$Y^- + abc\overset{+}{P}X \rightleftharpoons Y\overset{+}{P}cba + X^- \quad (1)$$

We assume that the first step in the reaction of phosphine sulfides with Si_2Cl_6, by analogy with the mechanism proposed[3] for the reaction of phosphine oxides, is nucleophilic attack of sulfur on silicon (eq 2). The next

$$abcPS + Si_2Cl_6 \longrightarrow abc\overset{+}{P}SSiCl_3 + {}^-SiCl_3 \quad (2)$$

step cannot be displacement on phosphorus with inversion, *i.e.*, eq 1 (X = $SSiCl_3$, Y = $SiCl_3$), but must involve either (a) attack of trichlorosilyl anion at sulfur (eq 3) or (b) attack at phosphorus, with retention (eq 4),[15,16] or (c) attack at chlorine (fragmentation, eq 5), in analogy to one of the possibilities discussed for the deoxygenation of quinuclidine N-oxide.[3] Variations on these mechanisms, involving various degrees of bond making

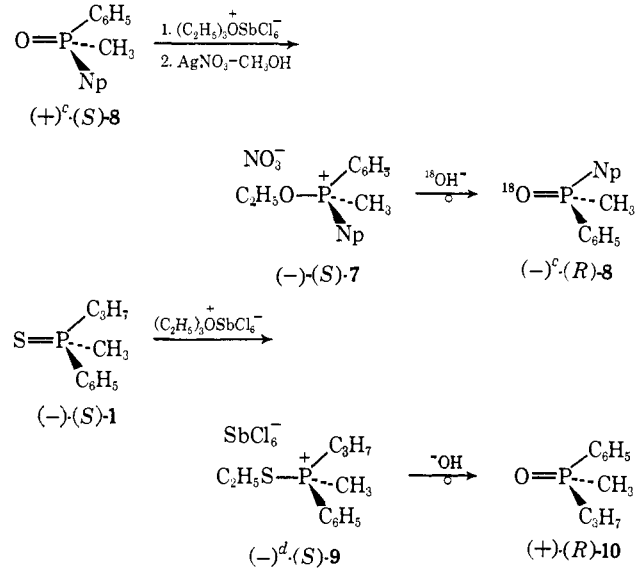


or breaking in the transition state, are easily envisaged.

According to the mechanisms in eq 3–5, the nucleophile, *i.e.*, trichlorosilyl anion, attacks sulfur, phosphorus, or chlorine in the mercaptophosphonium ion, with retention of configuration, in contrast to the oxygen analog, where attack takes place on the abc face of the phosphorus atom[15] with inversion of configuration. To test the generality of this difference in modes of nucleophilic displacement on abcP⁺OR and abcP⁺SR systems, the base-catalyzed hydrolysis of alkoxy- and alkylmercaptophosphonium salts was investigated.

Ethoxymethyl-β-naphthylphenylphosphonium nitrate (**7**), prepared by ethylation of (+)-(*S*)-methyl-β-naphthylphenylphosphine oxide[18] (**8**), $[\alpha]D$ +27° (chloroform),[19] gave (−)-**8**, $[\alpha]D$ −27° (chloroform), upon treatment with 0.5 *M* NaOH in 50% v/v H_2O–dioxane, containing 5.1 atom % ^{18}O/mole in the H_2O. The produced phosphine oxide contained 5.0 atom % ^{18}O/mole.[20] Similarly, alkaline hydrolysis of the ethylmercaptophosphonium salt, (−)-**9** (acetone), derived from 74% optically pure (−)-**1**, yielded (+)-**10**, which was 75% optically pure.[10] These results, summarized in Chart II, show that basic hydrolyses of acyclic mono-

Chart II[a,b]



[a] C_3H_7 = *n*-propyl; Np = β-naphthyl. [b] Rotational prefixes refer to solvent methanol, except as noted. [c] Rotation in chloroform. [d] Rotation in acetone.

alkoxy- and monoalkylmercaptophosphonium salts are highly stereospecific and proceed with complete inversion

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

(14) Throughout this paper, the letter sequences "abcP⁺X" and "XP⁺cba" symbolize enantiomeric phosphonium ions, and, similarly, "abcP" and "Pcba" symbolize enantiomeric phosphines. The intermediacy of phosphoranes is assumed.

(15) Apical attack at phosphorus with retention of configuration requires attack on one of three faces of the Sabc tetrahedron, *i.e.*, Sab, Sac, and Sbc. Attack on the fourth, or abc, face results in inversion. In addition, a pseudorotation is required in order to bring the departing group (Cl_3SiS^-) into an apical position; a close analogy is the mechanism of the trichlorosilane reduction of phosphine oxides.[3]

(16) The silicon-containing product from reaction according to eq 3 or 4 is hexachlorodisilthiane, $Cl_3SiSSiCl_3$. This compound has been previously described.[17]

(17) W. C. Schumb and W. J. Bernard, *J. Am. Chem. Soc.*, 77, 862 (1955); D. J. Panckhurst, C. J. Wilkins, and P. W. Craighead, *J. Chem. Soc.*, 3395 (1955); J. Goubeau and W. D. Hiersemann, *Z. Anorg. Allgem. Chem.*, 290, 292 (1957).

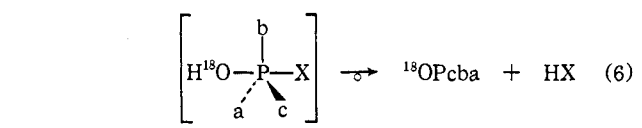
(18) O. Korpiun, R. A. Lewis, J. Chickos, and K. Mislow, *J. Am. Chem. Soc.*, 90, 4842 (1968).

(19) The previously reported[18] highest rotation of 8 is $[\alpha]D$ +25° (chloroform).

(20) These results parallel those observed for the base-catalyzed hydrolysis of optically active alkoxysulfonium salts (C. R. Johnson and D. McCants, Jr., *J. Am. Chem. Soc.*, 87, 5404 (1965)).

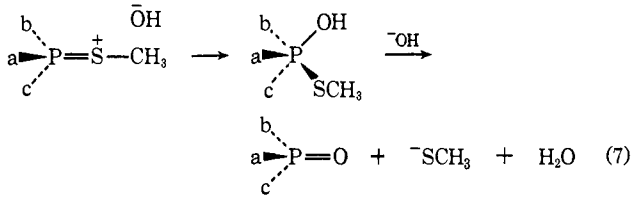
of configuration. This result is in harmony with the extensively investigated base-catalyzed hydrolyses of acyclic alkylarylphosphonium salts to phosphine oxides (eq 1, X = alkyl or aryl, Y = OH), which also proceed with inversion of configuration.[21]

A mechanism for the base-catalyzed hydrolysis of **7** which is consistent with the observed complete inversion of configuration and incorporation of ^{18}O tracer, and which is similar to those previously proposed for related displacements,[21] is shown in eq 6 (X = OC_2H_5).



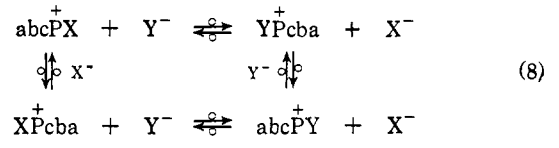
$$H^{18}O^- + abcP^+X \rightleftharpoons \left[H^{18}O-\overset{b}{\underset{a\ \ c}{P}}-X\right] \rightarrow {}^{18}OPcba + HX \quad (6)$$

The same mechanism also accommodates the observation that alkaline hydrolysis of **9** (X = SC_2H_5) gives ethylmercaptan and **10** with essentially complete inversion. This conclusion differs from the one previously advanced by Horner, who interpreted[13] the low[22] stereospecificity for conversion of (+)-**1** to (−)-**10**, by successive treatment of **1** with methyl iodide and alkali, as indicating attack of hydroxide on phosphorus from both the back side (inversion, eq 6, X = SCH_3) and from the front side (retention, eq 7). The discrepancy



$$\begin{matrix} b & \bar{O}H \\ a & P^+=S-CH_3 \\ c & \end{matrix} \longrightarrow \begin{matrix} b & OH \\ a & P \\ c & SCH_3 \end{matrix} \xrightarrow{{}^-OH} \begin{matrix} b & \\ a & P=O \\ c & \end{matrix} + {}^-SCH_3 + H_2O \quad (7)$$

may perhaps be explained by partial racemization of methylmercaptomethylphenylpropylphosphonium iodide *before* the hydrolysis step, which itself proceeds with complete or nearly complete inversion. Such a racemization could involve the conversions shown in eq 8 (X = SCH_3, Y = I); in addition, pentacoordinate intermediates (phosphoranes) may intervene to cause racemization by pseudorotation. A similar scheme has been discussed in the preceding paper.[3]

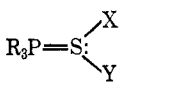


$$\begin{array}{ccccc} abcP^+X & + & Y^- & \rightleftharpoons & YP^+cba + X^- \\ \updownarrow\ X^- & & & & Y^-\ \updownarrow \\ XP^+cba & + & Y^- & \rightleftharpoons & abcP^+Y + X^- \end{array} \quad (8)$$

The base-catalyzed hydrolysis experiments described above clearly indicate that the Si_2Cl_6 desulfurization with retention of configuration is an "anomalous" process. Although, on the basis of our data, it is not possible to distinguish between the suggested alternatives described in eq 3–5, some discussion of an interpretive character is offered below.

In principle, fragmentation (eq 5) could be distinguished from displacement (eq 3 and 4) by an analysis of the silicon-containing products; however, such an analysis is complicated by the fact that both hexachlorodisilthiane and $(SSiCl_2)_n$ are capable of thermal decomposition into silicon sulfide, SiS_2, and silicon tetrachloride.[24] In addition, there exists the possibility that such decompositions may be catalyzed by the phosphine reduction product, in a manner similar to that reported for the amine-catalyzed decomposition of hexachlorodisiloxane ($Cl_3SiOSiCl_3$).[25] The fact that chemical racemization of the produced phosphine does not occur, under the reduction conditions employed, coupled with the demonstration[3] that silicon tetrachloride racemizes optically active phosphines under conditions which are milder than those used for the desulfurizations, suggests that the concentration of silicon tetrachloride is not appreciable. Therefore it appears that eq 5 does not represent an important reaction pathway.

Displacement on phosphorus with retention of configuration (eq 4) is unlikely if the results of the basic hydrolysis of **9** are to be taken as a guide to the stereochemistry of nucleophilic displacements at phosphorus in mercaptophosphonium salts. Therefore, attack of trichlorosilyl anion on the sulfur atom of trichlorosilylmercaptophosphonium ion (eq 3) remains as the most likely mechanistic alternative. That attack at sulfur competes successfully with attack on phosphorus may be the result of stabilization in intermediates or transi-



11a, X = Y = $SiCl_3$
b, X = OH; Y = C_2H_5

tion states such as **11a**, due to (3p → d)π bonding: not only is such multiple bonding ruled out for the oxygen analog, but any conceivable intermediate with tricoordinate oxygen would be destabilized by charge separation. However, while these considerations account for the difference in the stereochemistry of reductions of acyclic phosphine oxides and sulfides with Si_2Cl_6, they fail to account for the difference in stereochemistry between Si_2Cl_6 reduction of phosphine sulfides and basic hydrolysis of mercaptophosphonium salts. Evidently, in contrast to **11a**, stabilization of intermediates or transition states such as **11b** does not play an important role, but the reasons for this distinction are not yet understood.[26]

Displacements at phosphorus and sulfur described in this work do not appear to parallel similar displacements at silicon.[28] Both R_3SiSCH_3 and $R_3SiSSiR_3$ suffer nucleophilic displacement at silicon with inversion, whereas displacement at silicon in the oxygen analogs

(21) For an excellent review, see 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.

(22) Based on the estimated[23] values for the absolute rotations of **2** (19.5° (toluene)) and **10** (20.0°), the data of Horner and Winkler[6] indicate that the conversion of 94% optically pure (+)-**2** to (+)-**1** by sulfurization (retention), followed by successive treatment of (+)-**1** with methyl iodide and hydroxide, yielded (−)-**10** of 32% optical purity.

(23) J. P. Casey, R. A. Lewis, and K. Mislow, *J. Am. Chem. Soc.*, **91**, 2789 (1969).

(24) Panckhurst, *et al.*,[17] have reported that hexachlorodisilthiane suffers essentially complete decomposition into silicon sulfide and silicon tetrachloride within 3 hr at *ca.* 180° (neat), whereas thermal decomposition of $(SSiCl_2)_n$ occurs at *ca.* 220° (neat) according to the equation $2(SSiCl_2)_n \rightarrow n SiS_2 + n SiCl_4$.

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

(26) Taking hydroxide and trichlorosilyl ions as hard and soft bases,[27] respectively, and the P^+ terminal as a hard acid[27] compared to the oxygen or sulfur atom attached thereunto, the Si_2Cl_6 reduction of acyclic phosphine oxides with inversion now becomes the apparent anomaly.

(27) R. G. Pearson and J. Songstad, *J. Am. Chem. Soc.*, 89, 1827 (1967), and references cited therein.

(28) L. H. Sommer and W. D. Korte, *ibid.*, 89, 5802 (1967); L. H. Sommer and J. McLick, *ibid.*, 89, 5806 (1967).

occurs with retention *or* inversion, depending on the nature of the nucleophile.[29]

Experimental Section[30]

Reduction of Optically Active Phosphine Sulfides with Si_2Cl_6. The general procedure used for desulfurization of optically active phosphine sulfides with Si_2Cl_6 was similar to that previously described[3] for the reduction of optically active acyclic phosphine oxides with this same reagent. To obtain moderate yields (*ca.* 60–70%) of the desulfurization product when using benzene as solvent, the heterogeneous reaction mixtures were refluxed for 6 hr, with rigorous exclusion of oxygen.[3]

Methylphenylpropylphosphine Sulfide (1). A solution of 62% optically pure[23] (−)-(*S*)-methylphenylpropylphosphine oxide[18] (**10**) (337 mg, 1.85 mmol), $[\alpha]D$ −12.3°, in benzene (10 ml) was refluxed with Si_2Cl_6 (0.63 ml, *ca.* 3.7 mmol) for 15 min. The 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). An aliquot (3 ml) of this benzene solution was concentrated by removal of solvent under reduced pressure and quaternization of the crude reduction product, methylphenylpropylphosphine (**2**), was carried out with a tenfold excess of benzyl bromide (*ca.* 60°, 3 hr). To avoid optical fractionation, ether was used to precipitate and wash the product, benzylmethylphenylpropylphosphonium bromide, **3** (88.5 mg, 95%), mp 182–194°, $[\alpha]D$ +21.5°, optical purity[23] 58%. Assuming complete retention[13] of configuration and asymmetry in the quaternization step, the produced phosphine, **2**, was 58% optically pure. The remaining benzene solution of **2** was sulfurized by treatment with elemental sulfur (100 mg, 3.1 mmol) at room temperature for 15 hr. The reaction mixture was filtered and the solvent was removed under reduced pressure to yield crude phosphine sulfide. The crude product was chromatographed on silica gel, eluting with benzene to remove first, elemental sulfur, and then (+)-(*R*)-methylphenylpropylphosphine sulfide, **1** (40%), mp 58–78°, $[\alpha]D$ +12.9°, optical purity 58% (granted that sulfurization with elemental sulfur proceeded with complete retention[6]). Thus, the absolute rotation of **1** is calculated to be $[\alpha]D$ 22°. Repetition of the above sequence of reactions starting with 92% optically pure (+)-(*R*)-**10** gave methylphenylpropylphosphine (**2**), which yielded 83% optically pure (−)-**3** upon quaternization with benzyl bromide; resulfurization of this same phosphine afforded (−)-(*S*)-**1**, $[\alpha]D$ −16.3°. Using these data, the absolute rotation of **1** is calculated to be $[\alpha]D$ 20°. The pmr spectrum of **1** was consistent with its assigned structure and featured: PCH_3, d, τ 8.05, J_{PCH} = 13 Hz.

A solution of 58% optically pure (+)-(*R*)-**1** (65.2 mg, 0.33 mmol), $[\alpha]D$ +12.9°, in benzene (2 ml) was refluxed with Si_2Cl_6 (0.085 ml, *ca.* 0.5 mmol) for 6 hr. After alkaline hydrolysis and work-up of the reaction mixture as described above for methylphenylpropylphosphine oxide, the crude reduction product, **2**, was quaternized with excess benzyl bromide (see above) to give (54%) (+)-(*S*)-**3**, mp 182–195°, $[\alpha]D$ +23.1°, optical purity 63%.

Allylmethylphenylphosphine Sulfide (5). A solution of optically pure (+)-(*R*)-allylmethylphenylphosphine oxide[31] (2.75 g, 0.0153 mol), $[\alpha]D$ +21°, in benzene (65 ml) was refluxed with Si_2Cl_6 (2.66 ml, *ca.* 0.016 mol) for 1 hr. The reaction mixture was cooled to room temperature and elemental sulfur (0.98 g, *ca.* 0.031 mol) was added. After stirring for 12 hr, the reaction mixture was hydrolyzed by addition of water and the aqueous layer was extracted with ether. Removal of solvent under reduced pressure yielded crude phosphine sulfide, which was dissolved in ether and removed from the undissolved sulfur contaminant. Recrystallization from hexane–benzene (95:5) gave (−)-(*S*)-allylmethylphenylphosphine sulfide (**5**) (2.65 g, 88%) as long needles: mp 62–63°; $[\alpha]D$ −18.8°; pmr PCH_3, d, τ 8.03, J_{PCH} = 13 Hz; PCH_2CH=CH_2, m, τ *ca.* 6.8–7.3; PCH_2CH=CH_2, m, τ *ca.* 3.7–5.1; PC_6H_5, m, τ *ca.* 1.8–2.7.

Anal. Calcd for $C_{10}H_{13}PS$: C, 61.21; H, 6.68; P, 15.78; S, 16.34. Found: C, 61.03; H, 6.98; P, 15.78; S, 16.19.

A solution of (−)-**5** (100 mg, 0.51 mmol), $[\alpha]D$ −18.8°, in ether (50 ml) was stirred at *ca.* 5° with freshly prepared potassium azodicarboxylate (4.9 g, 0.025 mol), and glacial acetic acid (4 ml) was added slowly (3 hr). After addition, ether (50 ml) was added and the organic layer was washed three times with 50-ml portions of 1 *M* aqueous sodium hydroxide and twice with 50-ml portions of water, and dried (magnesium sulfate). Removal of solvent at reduced pressure gave a residue, which contained both **1** and unreduced **5**, as indicated by pmr analysis. This mixture was recycled through the diimide reduction process two more times, and the final product was chromatographed on silica gel, eluting with hexane, then hexane–ethyl acetate. The pmr spectrum of the white solid, which was obtained from the hexane–ethyl acetate eluate, was identical with that of authentic methylphenylpropylphosphine sulfide (**1**) and showed no vinyl absorption due to contamination by **5**. From the rotation of this sample of **1**, $[\alpha]D$ −16.3°, and the absolute rotation (22°) of **1** calculated above, the optical purity of this material is 74%. Assuming that conversion of the starting allylphosphine sulfide (**5**) to **1** is completely stereospecific, the optical purity of **5** with $[\alpha]D$ −18.8° is also 74% and therefore the absolute rotation of **5** is calculated to be $[\alpha]D$ 25°.

A solution of 74% optically pure (−)-**5** (210 mg, 1.07 mmol), $[\alpha]D$ −18.8°, in benzene (5 ml) was refluxed with Si_2Cl_6 (0.28 ml, *ca.* 1.65 mmol) for 6 hr. After alkaline hydrolysis and work-up, as described above for **1**, the residual crude phosphine was purified by rapid distillation (kugelrohr) at reduced pressure, bp *ca.* 45° (0.1 mm), to yield (65%) allylmethylphenylphosphine (**4**) as a clear, colorless oil. A benzene solution containing a portion (80 mg, 0.45 mmol) of this phosphine was stirred with elemental sulfur (150 mg, 4.7 mmol) at room temperature for 12 hr. The reaction mixture was filtered and removal of solvent under reduced pressure yielded crude phosphine sulfide, which was dissolved in ether and removed from the undissolved sulfur contaminant. Evaporation of solvent gave a residue which was chromatographed on silica gel, eluting first with hexane to remove sulfur, then with benzene. The benzene eluate was treated with activated charcoal and yielded 45% of (−)-**1**, mp 60–62°, $[\alpha]D$ −17.7°, optical purity 70%. A second portion of the phosphine reduction product, which was assumed to be 70% optically pure (granted that resulfurization proceeded with complete stereospecificity), was quaternized with excess benzyl bromide, as described above for **2**, to yield (51%) (−)-(*R*)-allylbenzylmethylphenylphosphonium bromide (**6**) as a white crystalline solid: mp 134–137° (lit.[13] mp 127°); $[\alpha]D$ −17.0° (lit.[13] $[\alpha]D$ +15.7°). Assuming that quaternization proceeds with complete retention,[13] the absolute rotation of **6** is calculated to be $[\alpha]D$ 24°. The pmr spectrum of **6** exhibited PCH_3, d, τ 7.58, J_{PCH} = 13.5 Hz; PCH_2CH=CH_2, m, τ *ca.* 5.7–6.2; P$CH_2C_6H_5$, apparent doublet, τ 5.33, J_{PCH} = 15.5 Hz; PCH_2CH=CH_2, m, τ *ca.* 4.2–5.1; aromatic protons, m, τ *ca.* 1.8–3.1.

Hydrolysis of Optically Active Phosphonium Salts with Sodium Hydroxide. A. Ethoxymethyl-β-naphthylphenylphosphonium Nitrate[32] (7). A solution of optically pure (+)-(*S*)-methyl-β-naphthylphenylphosphine oxide,[18] **8** (200 mg, 0.75 mmol), $[\alpha]D$ +27° (chloroform), in dichloromethane (5 ml) was added to a solution of

(29) These differences have been rationalized in terms of differences in leaving group basicities.[28]

(30) 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% solutions 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 were measured on a Schmidt and Haensch visual polarimeter or on a Cary 60 spectropolarimeter. Determinations of ^{18}O content were made from mass spectra 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.

(31) A. W. Herriott and K. Mislow, *Tetrahedron Lett.*, 3013 (1968).

(32) In preliminary studies, an attempt was made to work with the tetrafluoroborate salt. Reaction of (+)-(*S*)-**8** with triethyloxonium tetrafluoroborate yielded an oil which gave, upon treatment with NaOH, 16% optically pure (+)-(*S*)-**8**.[33] Subsequent experiments showed that this oil consisted of approximately equal amounts of ethoxymethyl-β-naphthylphenylphosphonium tetrafluoroborate, which yielded (−)-(*R*)-**8** upon treatment with alkali, and a BF_3 adduct of (+)-(*S*)-**8**, which underwent base-catalyzed hydrolysis with retention of configuration to (+)-(*S*)-**8**. The BF_3 adduct could have arisen from reaction of **8** with BF_3, produced by decomposition of triethyloxonium tetrafluoroborate, or from decomposition of the ethoxyphosphonium salt. An independent experiment showed that ethoxytriphenylphosphonium tetrafluoroborate decomposes upon heating at its melting point to a white solid which shows no melting point depression when mixed with an authentic sample of a BF_3 adduct of triphenylphosphine oxide. A similar adduct of **8** and $SbCl_5$ was formed, but to a much smaller extent (*ca.* 10–20%), when triethyloxonium hexachloroantimonate was used as the alkylating agent. Treatment with silver nitrate decomposed the adduct to phosphine oxide.

(33) We thank Dr. R. Scartazzini for these experiments.

triethyloxonium hexachloroantimonate[34] (350 mg, 0.8 mmol) in dichloromethane (5 ml), and the mixture was stirred at room temperature for 2 hr. The reaction mixture was then added to a solution of silver nitrate (0.76 g, 0.0045 mol) in methanol (50 ml), causing immediate formation of a white precipitate. This heterogeneous mixture was stirred for 10 min and was filtered. Removal of solvent under reduced pressure afforded the crude (−)-(*S*)-phosphonium nitrate (**7**) as a yellow oil, $[\alpha]_D$ −15 ± 3°, which had been purified by extracting three times with 50-ml portions of ether, to remove (by decantation) any phosphine oxide (**8**) which was produced by treatment with methanolic silver nitrate.[32] The pmr spectrum of **7**[35] exhibited PCH_3, d, τ 7.28, J_{PCH} = 13 Hz; $POCH_2CH_3$, apparent quintet, τ 5.62, J_{POCH} = 7 Hz, J_{HCCH} = 7 Hz; $POCH_2CH_3$, t, τ 8.48, J_{HCCH} = 7 Hz; PC_6H_5, m, τ *ca.* 1.5–2.5.

A solution (10 ml) of 0.5 *M* sodium hydroxide in 50% v/v aqueous dioxane, containing 5.11 ± 0.10 atom % ^{18}O/mole in the water, was added to freshly prepared[35] (−)-(*S*)-**7**, and the mixture was stirred at room temperature for 5 min. The reaction mixture was extracted three times with 50-ml portions of dichloromethane and the combined organic layers were dried (magnesium sulfate). Removal of solvent under reduced pressure afforded the phosphine oxide, **8**, as a white crystalline solid, which was purified by sublimation (130°, 0.1 mm) to yield (150 mg, 75%) optically pure (−)-(*R*)-**8**, mp 145–146°, $[\alpha]_D$ −27° (chloroform), which contained 5.02 ± 0.24 atom % ^{18}O/mole.

When (+)-(*S*)-**8** was subjected to exactly the same conditions used in the hydrolysis, no incorporation of ^{18}O from the $H_2{}^{18}O$ was found.

B. Ethylmercaptomethylphenylpropylphosphonium Hexachloroantimonate (9). A solution of 74% optically pure (−)-(*S*)-methylphenylpropylphosphine sulfide, **1** (100 mg, 0.5 mmol), $[\alpha]_D$ −16.3°, in dichloromethane (2 ml) was added to a solution of triethyloxonium hexachloroantimonate (220 mg, 0.5 mmol) in dichloromethane (10 ml), and the mixture was stirred at room temperature for 1 hr. Addition of this reaction mixture to ether (100 ml) caused precipitation of a white crystalline material, which was identified as (−)-(*S*)-ethylmercaptomethylphenylpropylphosphonium hexachloroantimonate, **9** (250 mg, 89%): mp 107–109°; $[\alpha]_D$ −14.9° (acetone); optical purity 74%, assuming that ethylation proceeded with complete stereospecificity and with retention of configuration. The pmr spectrum (acetone-d_6) of **9** was consistent with its assigned structure and featured PCH_3, d, τ 7.32, J_{PCH} = 13 Hz.

Anal. Calcd for $C_{12}H_{20}PSSbCl_6$: C, 25.66; H, 3.59; P, 5.51. Found: C, 25.37; H, 3.84; P, 5.31.

A solution of 74% optically pure (−)-(*S*)-**9** (210 mg, 0.36 mmol), $[\alpha]_D$ −14.9° (acetone), in dioxane (0.5 ml) was treated with a solution (50 ml) of 0.5 *M* sodium hydroxide in 50% v/v aqueous dioxane at room temperature for 5 min. The heterogeneous reaction mixture was extracted three times with 50-ml portions of dichloromethane and the combined organic layers were dried (magnesium sulfate). Removal of solvent afforded a slightly yellow oil, which was purified by rapid distillation (kugelrohr) at reduced pressure, bp *ca.* 95° (0.1 mm), to yield (+)-(*R*)-methylphenylpropylphosphine oxide, **10** (57 mg, 88%), $[\alpha]_D$ +15.0°, optical purity[23] 75%.

(34) H. Meerwein, *Org. Syn.*, **46**, 113 (1966); H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and G. Willfang, *J. Prakt. Chem.*, **154**, 83 (1939).

(35) It was observed by pmr that (−)-(*S*)-7 decomposes with a half-life of *ca.* 30 min at 40° in $CHCl_3$, to give (+)-(*S*)-8 (retention) and an unidentified ethylated product (possibly ethyl nitrate). However, 7 is optically and chemically more stable in methanol solution, with a half-life for decomposition of greater than 5 days.

Stereochemistry of Nucleophilic Displacement at Phosphorus in Some Phosphetanium Salts[1]

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Abstract: Hexachlorodisilane reduction of phosphetane oxides and base-catalyzed hydrolysis of alkoxyphosphetanium salts both proceed with complete retention of configuration at phosphorus. Mechanistic alternatives are discussed. Stereomutation at phosphorus is observed on treatment of phosphetanes and phosphetane oxides with silicon tetrachloride.

It has been shown[3] that reduction of acyclic phosphine oxides with hexachlorodisilane (Si_2Cl_6) proceeds with inversion of configuration at phosphorus. Previously, the same stereochemical course had been observed[4] for reductions with trichlorosilane in the presence of triethylamine ($HSiCl_3$–Et_3N), and it was subsequently suggested[3] that here perchloropolysilanes may also function as reactive intermediates. Since Cremer and Chorvat[5] showed that reduction of both *cis*- and *trans*-1-phenyl-2,2,3,4,4-pentamethylphosphetane 1-oxides (**1**) with $HSiCl_3$–Et_3N proceeds with *retention* of configuration at phosphorus, it was of interest to determine whether the parallel in stereochemical directions observed for Si_2Cl_6 and $HSiCl_3$–Et_3N reductions of acyclic phosphine oxides would also be maintained in reductions of **1**. Our findings are given below.

Reduction of *cis*- or *trans*-**1** with Si_2Cl_6 proceeds with essentially complete *retention* of configuration at phosphorus, to give *cis*- or *trans*-1-phenyl-2,2,3,4,4-pentamethylphosphetane (**2**), respectively. The stereochemical direction for the deoxygenation was established by two routes: hydrogen peroxide reoxidation of **2** to **1**, and quaternization of **2** with methyl bromide to *cis*- and *trans*-1,2,2,3,4,4-hexamethyl-1-phenylphosphetanium bromide (**3**), respectively (eq 1). Both conversions are known to proceed with retention of configuration.[6,7]

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

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

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

(7) The analyses of these compounds, on which claims for stereospecificity are based, are conveniently carried out by pmr.[5] The prefixes *cis* and *trans* refer to the relationship between the 1-phenyl and