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.

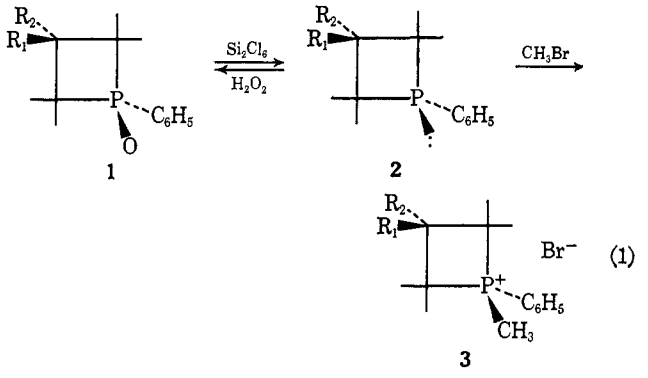
(3) K. Naumann, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7012 (1969).

(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).

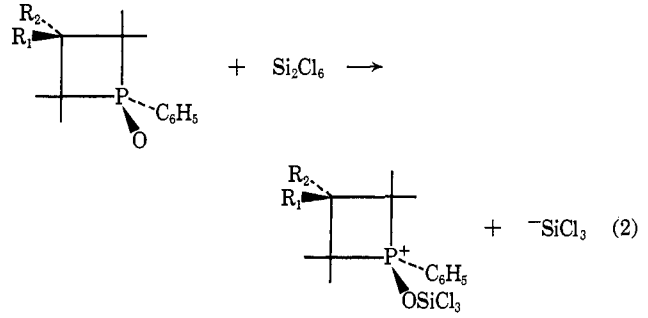
(6) L. Horner, *Pure Appl. Chem.*, **9**, 225 (1964).

(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



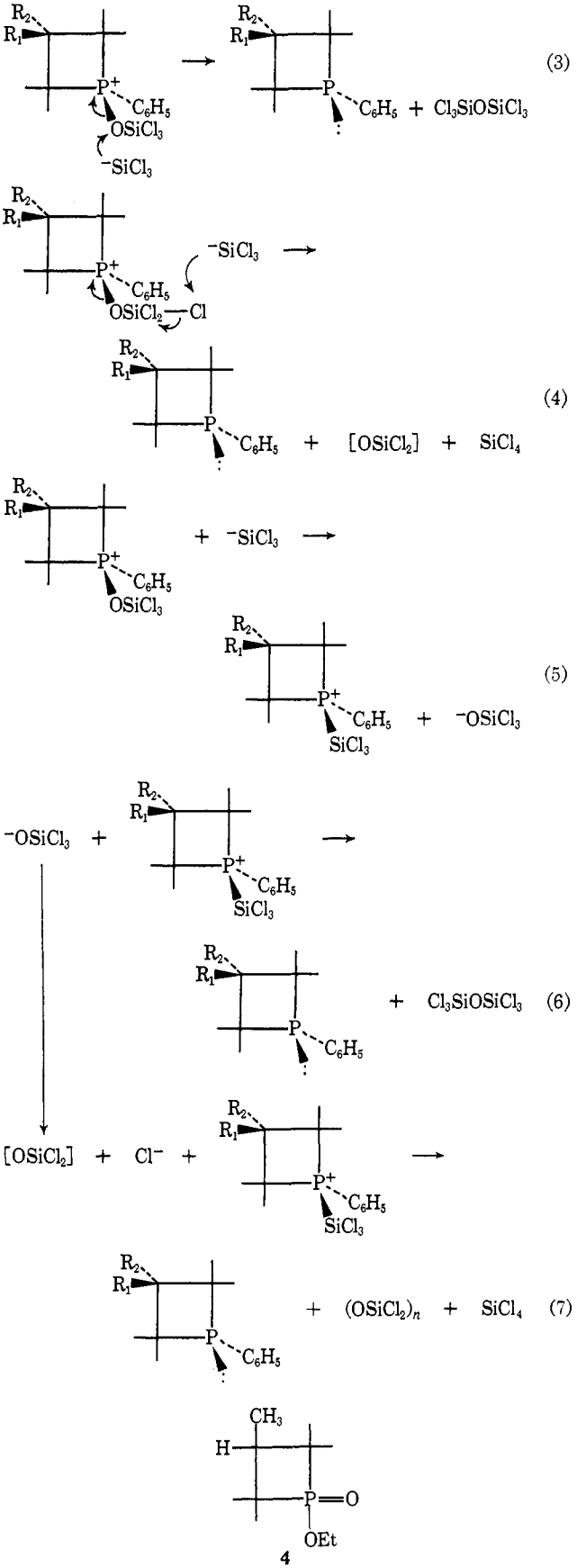
cis: $R_1 = H$; $R_2 = CH_3$
trans: $R_1 = CH_3$; $R_2 = H$

On the assumption that the mechanism for the reduction of **1** with Si_2Cl_6 parallels that proposed[3] for the reduction of acyclic phosphine oxides, the first step involves nucleophilic attack by oxygen on Si_2Cl_6 with formation of trichlorosiloxyphosphetanium and trichlorosilyl ions, as shown in eq 2.



In analogy to the mechanistic alternatives discussed[3] for the deoxygenation of quinuclidine N-oxide with Si_2Cl_6, subsequent steps may involve (a) attack of trichlorosilyl anion at oxygen with displacement of **2** (eq 3), or (b) attack at chlorine (fragmentation, eq 4), or (c) direct attack of trichlorosilyl anion at phosphorus and loss of trichlorosiloxy anion, with overall *retention* of configuration at phosphorus (eq 5), followed by displacement of phosphetane from silicon according to the scheme presented in eq 6 and 7.

A tentative decision between these mechanistic alternatives is possible on the basis of reaction kinetics. In a closely related reaction system, the base-catalyzed hydrolysis of the cyclic phosphinate **4**[8-10] takes place by attack on phosphorus[10] and proceeds at a rate which is *ca.* 10^5 times greater than that of the acyclic analog, ethyl di(*t*-butyl)phosphinate.[9] This rate acceleration, which apparently results from relief of angle strain in the intermediate phosphorane, may therefore be taken as a diagnostic of nucleophilic attack at phosphorus in phosphetane derivatives.[11] In contrast to ethyl di(*t*-butyl)phosphinate, ethyl diethylphosphinate, in which steric inhibition to nucleophilic attack is reduced, undergoes alkaline hydrolysis at a rate which is comparable



to that of **4**.[9,10] In the present work, it was found that both isomers of **1** were completely reduced under conditions (25°, 5 min, benzene) which were significantly milder than those required for the reduction even of *unbranched* acyclic analogs, such as methylphenyl-*n*-pro-

3-methyl groups;[5] the absolute assignments are tentative (S. E. Cremer, private communication).

(8) K. Bergesen, *Acta Chem. Scand.*, **21**, 1587 (1967).

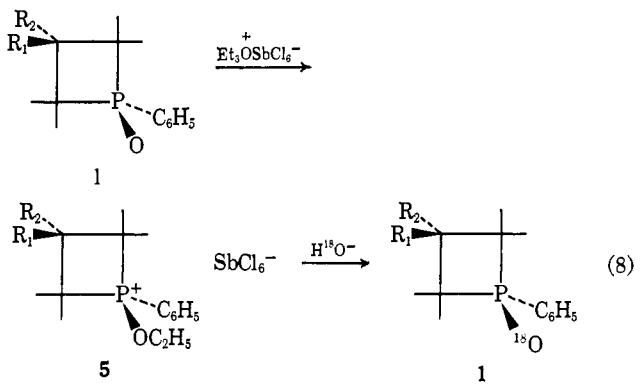
(9) W. Hawes and S. Trippett, *Chem. Commun.*, 577 (1968).

(10) P. Haake, R. D. Cook, W. Schwarz, and D. R. McCoy, *Tetrahedron Lett.*, 5251 (1968).

(11) A similar rate enhancement is observed in the hydrolysis of silacyclobutanes (L. H. Sommer, O. F. Bennett, P. G. Campbell, and D. R. Weynenberg, *J. Am. Chem. Soc.*, **79**, 3295 (1957)).

pylphosphine oxide.[3] Reduction of a *branched* acyclic analog, *t*-butylmethylphenylphosphine oxide, predictably required substantially more vigorous conditions (80°, 3 hr, benzene).[12] These qualitative rate data, indicative of a large rate acceleration in the reduction of **1** relative to the acyclic model, may be taken to indicate that reduction of **1** by Si_2Cl_6 proceeds by attack on phosphorus, eq 5–7, rather than at chlorine or oxygen.

To show rigorously that attack of an external nucleophile on tetracoordinate phosphorus in a phosphetane derivative may proceed stereospecifically, with retention of configuration at phosphorus, a study of the base-catalyzed hydrolysis of *cis*- and *trans*-1-ethoxy-1-phenyl-2,2,3,4,4-pentamethylphosphetanium hexachloroantimonate (**5**) was undertaken (eq 8). *cis*-**5**, prepared by ethylation of *cis*-**1**, gave *cis*-**1** containing 4.83 ± 0.13 atom % ^{18}O/mole upon treatment with 0.5 *M* NaOH in 50% v/v H_2O–dioxane containing 4.98 ± 0.09 atom % ^{18}O/mole in the H_2O. That the incorporation of ^{18}O in the product was not due to exchange subsequent to displacement was demonstrated by a control experiment: when *cis*-**1** was subjected to the reaction conditions employed in the hydrolysis of **5**, no incorporation of ^{18}O from the $H_2{}^{18}O$ was observed. Similarly, ethylation of a mixture of **1** enriched in the *trans* isomer (*cis*:*trans* = 20:80), followed by alkaline hydrolysis of the produced **5**, yielded **1**, whose stereoisomeric composition was the same as that of the starting material. Retention of configuration in this displacement reaction contrasts with the inversion of configuration at phosphorus which was previously observed in the base-catalyzed hydrolysis of an acyclic alkoxyphosphonium salt.[13]



In a related study, Hawes and Trippett[14] found that the same isomer of **1** was obtained from a "homogeneous" sample of 1-benzyl-1-phenyl-2,2,3,4,4-pentamethylphosphetanium bromide (**6**), either by alkaline hydrolysis or by a Wittig olefin synthesis. Granted that the latter proceeds with retention of configuration at phosphorus,[15] Hawes and Trippett concluded that the alkaline hydrolysis of **6** proceeds with retention of configuration at phosphorus. However, since alkaline hydrolysis of *both* isomers of **6** affords the *same* mixture of **1**,[16] the reaction is stereoselective rather than stereospecific, indicative of equilibration at the intermediate phosphorane stage.[17]

The contrast in the stereochemical consequences of base-catalyzed hydrolysis of **5** and **6**, as well as the contrast in stereochemistry between the reactions of cyclic and acyclic phosphorus compounds described in this and preceding papers,[3,13] may be the result of differences in stabilities (and rates of interconversion) of intermediate phosphoranes. This point will be taken up in detail in the following paper.[18,19]

The isomers of **1** are not readily interconverted by aqueous sodium hydroxide or concentrated hydrochloric acid.[14] We find that stereomutation of **1** is readily effected by silicon tetrachloride in acetonitrile, to give an essentially equimolar mixture of isomers. Similarly, isomers of **2** are interconverted by silicon tetrachloride, and since silicon tetrachloride is also produced in the course of Si_2Cl_6 reductions of **1** (eq 7), extended contact time after reduction leads to stereomutation. These chemically induced stereomutations parallel the racemizations of optically active acyclic phosphines and phosphine oxides with silicon tetrachloride.[3]

Experimental Section[20]

Reduction of 1-Phenyl-2,2,3,4,4-pentamethylphosphetane 1-Oxides (1) with Si_2Cl_6. Mixtures of stereoisomers of **1**, which were enriched in either the *cis* or the *trans* isomer, were prepared[21] according to the method of Cremer and Chorvat.[5] Identification of *cis*- and *trans*-**1** was based on comparison of their pmr spectra with those reported[5,7] for these isomers, and the diastereomeric composition of **1** was determined by pmr integration (±5%). The general procedure used for reduction of **1** with Si_2Cl_6 was essentially the same as that described[3] for the reduction of optically active acyclic phosphine oxides with this same reagent. To obtain optimum yields of the phosphetane reduction product, all operations were carried out with rigorous exclusion of oxygen.[3]

A solution of **1** (0.944 g, 4 mmol), enriched in the *cis* isomer (*cis*:*trans* = 95:5), in benzene (20 ml) was stirred with Si_2Cl_6 (0.9 ml, *ca.* 5 mmol) at room temperature for 5 min, following the initially exothermic reaction which occurred on mixing. The homogeneous reaction mixture was cooled to 0° and was hydrolyzed by cautious addition of 30% aqueous sodium hydroxide (10 ml). Benzene (10 ml) was added and the organic layer was washed twice with 3-ml portions of water and dried (magnesium sulfate). Removal of solvent under reduced pressure gave the crude reduction product, which was purified by rapid distillation (kugelrohr) at reduced pressure, bp *ca.* 80° (0.1 mm), to yield (0.684 g, 78%) 1-phenyl-2,2,3,4,4-pentamethylphosphetane (**2**) as a clear, colorless oil. Quaternization of a portion of this sample of **2** (92 mg, 0.42 mmol) was carried out with a 20-fold excess of methyl bromide in benzene (2 ml) (*ca.* 25°, 6 hr). To avoid fractionation

(12) R. A. Lewis, K. Naumann, K. E. DeBruin, and K. Mislow, *Chem. Commun.*, 1010 (1969).

(13) G. Zon, K. E. DeBruin, K. Naumann, and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7023 (1969).

(14) W. Hawes and S. Trippett, *Chem. Commun.*, 295 (1968).

(15) A. Bladé-Font, C. A. VanderWerf, and W. E. McEwen, *J. Am. Chem. Soc.*, **82**, 2396 (1960).

(16) S. E. Cremer, R. J. Chorvat, and B. C. Trivedi, *Chem. Commun.*, 769 (1969).

(17) More recently, and after the present work was completed, it was shown that in the case of 1-benzyl-1-phenyl-2,2,3,3-tetramethylphosphetanium iodide (**7**), base-catalyzed hydrolysis does proceed with retention of configuration (J. R. Corfield, J. R. Shutt, and S. Trippett, *ibid.*, 789 (1969)). The difference in comportment of **6** and **7** toward hydrolysis may be attributed to steric effects, as will be discussed elsewhere (K. E. DeBruin and K. Mislow, *J. Amer. Chem. Soc.*, **92**, in press).

(18) K. E. DeBruin, K. Naumann, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7031 (1969).

(19) F. Ramirez, C. P. Smith, and J. F. Pilot, [*ibid.*, **90**, 6726 (1968)] have discussed an isomerization of four-membered cyclic oxyphosphoranes in terms of pseudorotation.

(20) 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 benzene, with tetramethylsilane as internal standard, except as noted. 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.

(21) We thank Dr. P. D. Henson for these preparations.

of stereoisomers, ether was used to precipitate and wash the product, 1,2,2,3,4,4-hexamethyl-1-phenylphosphetanium bromide, **3** (130 mg, 92%). Identification of *cis*- and *trans*-**3** was based on comparison of their pmr spectra (D_2O solvent) with the reported[5] spectra for these isomers. Pmr integration indicated that the diastereomeric composition of this sample of **3** was *cis*:*trans* = 95:5. Reoxidation of a second portion of **2** was effected by reaction with a tenfold molar excess of aqueous hydrogen peroxide at room temperature for 1 hr with benzene as solvent. The aqueous layer was separated and extracted three times with chloroform and the combined organic layers were dried (magnesium sulfate). Removal of solvent under reduced pressure afforded a residue, which was purified by sublimation at *ca.* 110° (0.1 mm) to give a quantitative yield of **1**, whose diastereomeric composition, as determined by pmr analysis, was essentially the same as that of the starting sample of **1**.

Repetition of the above reduction procedure starting with **1** enriched in the *trans* isomer (*cis*:*trans* = 20:80) led to isolation (70%) of **2**, which upon quaternization with methyl bromide afforded **3** in 86% yield. Pmr analysis of this sample of **3** indicated a stereoisomeric composition of *cis*:*trans* = 25:75. Reoxidation of **2**, as described above, afforded **1**, whose composition was the same as that of the starting sample of **1**.

It is noteworthy that essentially quantitative reduction of **1** with Si_2Cl_6 was effected even in diethyl ether solvent at *ca.* 0° for 10 min, as indicated by isolation of **3** in *ca.* 80% yield, after work-up and quaternization of **2**, as described above.

Base-Catalyzed Hydrolyses of 1-Ethoxy-1-phenyl-2,2,3,4,4-pentamethylphosphetanium Hexachloroantimonates (5). A solution of **1** (200 mg, 0.85 mmol), enriched in the *cis* isomer (*cis*:*trans* = 95:5), in dichloromethane (5 ml) was added to a solution of triethyloxonium hexachloroantimonate[22] (350 mg, 0.80 mmol) in dichloromethane (10 ml), and the mixture was stirred at room temperature for 10 hr. Addition of this reaction mixture to ether (100 ml) caused precipitation of **5** as a crystalline solid (350 mg, 72%), mp 200–201° dec. The pmr spectrum (acetone-d_6) of this material was consistent with that expected for **5** enriched in the *cis* isomer and featured $POCH_2CH_3$, doubled triplet, τ 8.60, J_{HCCH} = 7 Hz, J_{POCCH} = 0.7 Hz; $POCH_2CH_3$, apparent quintet, τ 5.71, J_{HCCH} = 7 Hz, J_{POCH} = 7 Hz.

Anal. Calcd for $C_{16}H_{26}POSbCl_6$: C, 32.04; H, 4.37; P, 5.16. Found: C, 32.37; H, 4.59; P, 5.22.

A solution (5 ml) of 0.5 *M* NaOH in 50% v/v H_2O–dioxane, containing 4.98 ± 0.09 atom % ^{18}O/mole in the water, was added to a mixture of dioxane (0.5 ml) and **5** (100 mg, 0.17 mmol), prepared as above, and the heterogeneous mixture was stirred at room temperature for 5 min. The reaction mixture was extracted with dichloromethane and the combined organic layers were dried (magnesium sulfate). Removal of solvent under reduced pressure gave **1**, whose stereoisomeric composition was the same (*cis*:*trans* = 95:5) as that of the starting material (**1**), and which contained 4.85 ± 0.13 atom % ^{18}O.

Treatment of the starting sample of **1** with aqueous base under exactly the same conditions used in the hydrolysis of **5** led to recovery of **1**, which showed no change in stereoisomeric composition and no incorporation of ^{18}O from $H_2{}^{18}O$.

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

A *cis*–*trans* mixture of **1** (200 mg, 0.85 mmol), which was enriched in the *trans* isomer (*cis*:*trans* = 20:80), was ethylated with triethyloxonium hexachloroantimonate as described above to give **5** (400 mg), mp 214° dec, in 83% yield. The pmr spectrum (acetone-d_6) of this sample of **5** featured $POCH_2CH_3$, doubled triplet, τ 8.62, J_{HCCH} = 7 Hz, J_{POCCH} = 0.7 Hz; $POCH_2CH_3$, apparent quintet, τ 4.25, J_{HCCH} = 7 Hz, J_{POCH} = 7 Hz.

Anal. Calcd for $C_{16}H_{26}POSbCl_6$: C, 32.04; H, 4.37; P, 5.16. Found: C, 32.51; H, 4.55; P, 5.20.

The base-catalyzed hydrolysis of this sample of **5** was carried out as described above, using ordinary water, and gave **1**, whose composition was the same as that of the starting material (*cis*:*trans* = 20:80).

Stereomutation after Reduction of Stereoisomeric 1-Phenyl-2,2,3,4,4-pentamethylphosphetane 1-Oxides (1) with Si_2Cl_6. A solution of **1** (0.944 g, 4 mmol), enriched in the *cis* isomer (*cis*:*trans* = 95:5), in benzene (25 ml) was stirred with Si_2Cl_6 (0.68 ml, 4 mmol) at room temperature. Aliquots were removed at various time intervals and were quenched by addition to 30% aqueous sodium hydroxide. Work-up and quaternization of the reduction product, **2**, with excess methyl bromide were carried out as described above and afforded **3** in 80–90% yields. Pmr analysis of these samples of **3** indicated that as the length of contact time after reduction increased, there was a steady decrease in the amount of *cis*-**3**, and after *ca.* 6 hr an equilibrium mixture of **3** was obtained in which the *cis*:*trans* ratio was 40:60. Repetition of this experiment starting with **1**, enriched in the *trans* isomer (*cis*:*trans* = 10:90), afforded this same equilibrium mixture of **3** (*cis*:*trans* = 40:60) after *ca.* 6 hr.

Stereomutation of Stereoisomeric 1-Phenyl-2,2,3,4,4-pentamethylphosphetanes (2) with Silicon Tetrachloride. A solution of **2** (0.456 g, 2.1 mmol), enriched in the *cis* isomer (*cis*:*trans* = 95:5), in benzene (10 ml) was stirred with silicon tetrachloride (0.25 ml, *ca.* 2 mmol) at room temperature. Aliquots were removed at various time intervals and were quenched by addition to 30% aqueous sodium hydroxide. Work-up and quaternization of recovered **2** with methyl bromide, as described above, led to **3** in 70–90% yields. Pmr analysis of these samples of **3** revealed a steady decrease in the amount of the *cis* isomer, and that after *ca.* 50 hr an equilibrium mixture of **3** was obtained in which the *cis*:*trans* ratio was 40:60. Repetition of this reaction starting with **2** enriched in the *trans* isomer (*cis*:*trans* = 25:75) led to isolation of the same equilibrium mixture of **3** (*cis*:*trans* = 40:60) after *ca.* 50 hr. The composition of the equilibrium mixture is the same as that reported[5] for the thermal stereomutation of **2**.

Stereomutation of Stereoisomeric 1-Phenyl-2,2,3,4,4-pentamethylphosphetane 1-Oxide (1) with Silicon Tetrachloride. A solution of **1** (0.143 g, 6.1 mmol), enriched in the *cis* isomer (*cis*:*trans* = 95:5), in acetonitrile (0.5 ml) was stirred with silicon tetrachloride (1.5 ml, 1.4 mmol) at room temperature for 12 hr. The reaction mixture was cooled to 0° and was hydrolyzed with 30% aqueous sodium hydroxide (1 ml). The aqueous layer was extracted with chloroform and the combined organic layers were dried (magnesium sulfate). Removal of solvent under reduced pressure afforded crude phosphetane oxide, which was purified by sublimation (see above) to give recovered **1** with a *cis*:*trans* composition of 65:35. Repetition of this reaction starting with **1** enriched in the *trans* isomer (*cis*:*trans* = 20:80) resulted in the recovery of **1** with *cis*:*trans* = 60:40.