measured by a Varian A-60A spectrometer on 10% (w/v) solutions in chloroform-*d*–carbon disulfide (1:1, v/v)[11] with tetramethylsilane (τ 10.00) as internal standard.

trans-**Hexahydro-1,3,5-benzotrioxepane (2) and *trans-syn-trans*-4,5:9,10-biscyclohexano-1,3,6,8-tetraoxacyclodecane (3)** were prepared according to the procedure of Brimacombe, *et al.*[1] The trioxepane **2** had bp 34–37° (0.02 mm) and n^{20}D 1.4659 (lit.[1] n^{20}D 1.4657). The tetraoxacyclodecane **3** had mp 164.5–165.5° (lit.[1] mp 166–167.5°).

(11) This mixed solvent system was used because it was suitable for low-temperature studies, which will be reported elsewhere at a later date.

meso- **(4) and *dl*-di-(*trans*-2-hydroxycyclohexyloxy)methane (5)** were prepared according to the procedure described by Head.[6] The *meso* compound **4** had mp 80–82° (lit.[6] mp 81–82°) and the *dl* modification **5** had mp 102.5–103.5° (lit.[6] mp 104–105°).

cis-anti-cis-**4,5:9,10-Biscyclohexano-1,3,6,8-tetraoxacyclodecane (8)** was prepared according to the procedure described by Brimacombe, *et al.*[1] It had mp 139–140° (lit.[1] mp 142–143°).

Acknowledgments. These investigations were supported by a grant (A4589) from the National Research Council of Canada. The authors wish to express their thanks to Dr. J. K. N. Jones and Dr. S. Wolfe for helpful discussions.

Stereochemistry of Some Reactions of Phospholane Derivatives[1]

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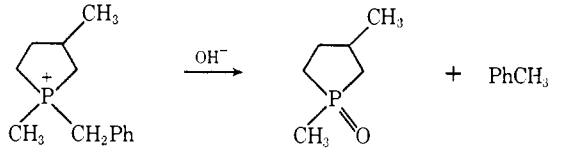
Abstract: The pure geometric isomers of 1-benzyl-1,3-dimethylphospholanium bromide (**1a** and **1b**) have been prepared and were subjected to treatment with aqueous sodium hydroxide. This resulted in the formation of the isomeric 1,3-dimethylphospholane 1-oxides (**2a** and **2b**) with complete retention of configuration. Arguments are presented favoring a stereospecific apical-equatorial displacement reaction. Reaction of **1a** and **1b** with sodium *n*-butoxide gave **2a** and **2b** with a high degree of retention but with detectable inversion. The pure oxides (**2a** and **2b**) yielded identical mixtures of these oxides when treated separately with concentrated hydrochloric acid. Pseudorotation of an intermediate phosphorane is suggested as being responsible for the formation of product mixtures. The oxide **2b** was observed to be reduced smoothly by phenylsilane to the corresponding phosphine (**4b**) with complete retention of configuration. Phosphines **4a** and **4b** are configurationally stable for long periods at 150°. Unlike **1**, 1,1-dimethylphospholanium bromide (**22a**) underwent slow cleavage with aqueous sodium hydroxide forming ring-opened product (**23**) as well as manifesting cleavage external to the ring (**22b**).

In a preliminary communication,[2] it was reported that both geometric isomers of 1-benzyl-1,3-dimethylphospholanium bromide (**1a** and **1b**) undergo cleavage with aqueous sodium hydroxide to produce exclusively toluene and the corresponding oxide (**2a** and **2b**) *with complete retention of configuration at the phosphorus atom.*

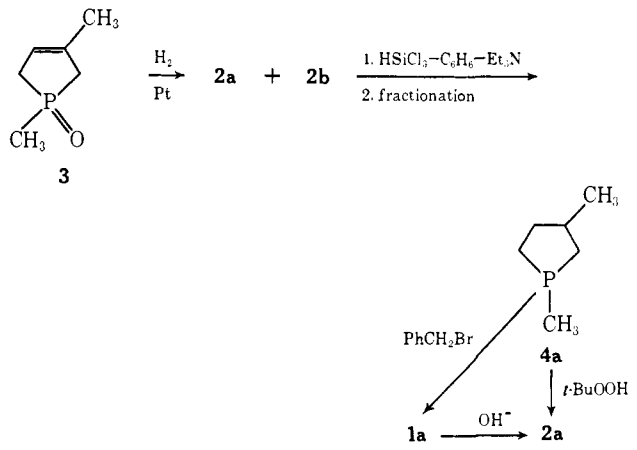


1a, mp 168.5–169.5° **2a**, mp 22°
b, mp 180–180.5° **b**, mp 72–73.5°

Although no definite assignment of the geometric configuration of the phosphonium salts has yet been made,[3] it was nevertheless possible to demonstrate the stereochemistry of the reaction in the following way. A mixture of **2a** and **2b** was prepared by catalytic reduction of 1,3-dimethyl-3-phospholene 1-oxide (**3**).[4] Reduction of the oxide mixture with trichlorosilane[5] produced a mixture of phosphines (**4a** and **4b**) which, after careful distillation, provided two fractions: pure **4a** and a mixture of the two phosphines enriched in **4b**. The configurational stability of **4** was evidenced by heating a mixture of **4a** and **4b** at various temperatures up to 150° for a 3-day period without any change occurring in the nmr spectrum when it was recorded again at room temperature.[6] Quaternization of **4a** with benzyl bromide yielded **1a**, which upon cleavage with aqueous sodium hydroxide yielded **2a**. The oxide **2a** was also produced by oxidation of **4a** with *t*-butyl hydroperoxide, a reaction known to occur with retention of configuration at phosphorus.[7] Isomer **1b**, obtained by quaternizing the

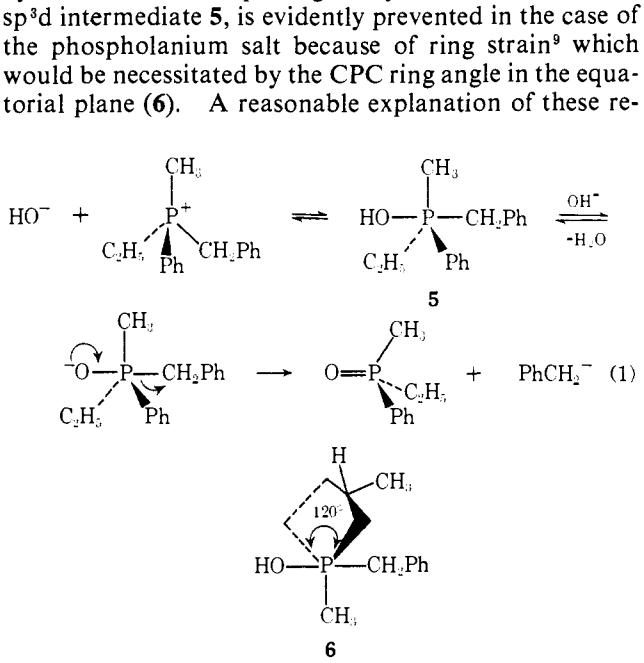
(1) This investigation was supported by National Institute of General Medical Sciences Special Research Fellowship 1-F3-GM-36,717-01 and in part by National Science Foundation Grant GP-7407.
(2) K. L. Marsi, *Chem. Commun.*, 846 (1968).
(3) The structure of **1b** is presently being determined by X-ray analysis by Dr. C. N. Caughlin, Montana State University.
(4) L. D. Quin, J. P. Gratz, and T. P. Barket, *J. Org. Chem.*, 33, 1034 (1968).
(5) (a) L. Horner and W. D. Balzer, *Tetrahedron Lett.*, 1157 (1965); (b) H. Fritsche, U. Hasserodt, and F. Korte, *Chem. Ber.*, 97, 1988 (1964); **98**, 171 (1965); S. E. Cremer and R. J. Chorvat, *J. Org. Chem.*, 32, 4066 (1967); S. E. Cremer, *Chem. Commun.*, 1132 (1968).
(6) By comparison, methyl-*n*-propylphenylphosphine racemized somewhat after 3-hr refluxing in toluene, showed about 20% racemization when distilled *in vacuo* [bp 86–88° (2.5–3.0 mm)], and was completely racemized during atmospheric distillation. See L. Horner, H. Fuchs, H. Winkler, and A. Rapp, *Tetrahedron Lett.*, 965 (1963). S. E. Cremer, R. J. Chorvat, C. H. Chang, and D. W. Davis, *ibid.*, 5799 (1968), have shown that 1,2,2,3,4,4-hexamethylphosphetane is stable to inversion at 162° for 4 days, but that the 1-phenyl and 1-*t*-butyl analogs undergo racemization at lower temperatures and possess activation energies quite similar to that of methyl-*n*-propylphenylphosphine. 1-Methyl-4-ethyl-4-phosphorinanol has also been shown to be configurationally stable [L. D. Quin and H. E. Shook, Jr., *ibid.*, 2193 (1965); see also H. E. Shook, Jr., and L. D. Quin, *J. Amer. Chem. Soc.*, **89**, 1841 (1967)].
(7) D. B. Denney and J. W. Hanifin, Jr., *Tetrahedron Lett.*, 2177 (1963).

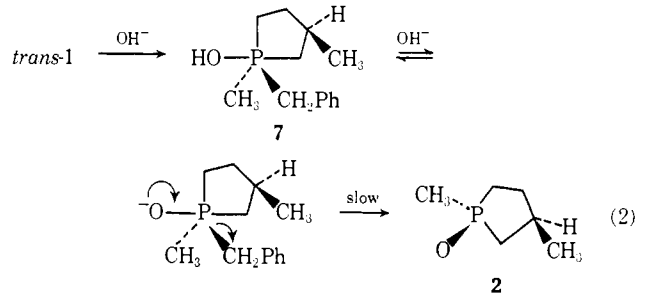
fraction enriched in **4b** and subsequent recrystallization of the resulting phosphonium salts, on base treatment gave **2b** which was shown to be identical with the oxide obtained by fractional crystallization of the mixture of **2a** and **2b**.



3

The observed stereochemistry suggests a somewhat different mechanism to be in operation than that proposed by McEwen[8] (eq 1) to account for inversion of configuration of phosphorus in the case of acyclic phosphonium salts. The attainment of linearity between hydroxide and the departing benzyl ion, as shown in the sp^3d intermediate **5**, is evidently prevented in the case of the phospholanium salt because of ring strain[9] which would be necessitated by the CPC ring angle in the equatorial plane (**6**). A reasonable explanation of these results lies in the proposal of the trigonal-bipyramidal intermediate **7**. This is illustrated for one enantiomer of the *trans*-dimethyl isomer (**1**) which could form **7** by the apical[10,11] introduction of hydroxide ion. Subsequent equatorial loss of the benzyl anion would lead to the oxide (**2**) with retention of configuration at phosphorus (eq 2). The implied third-order mechanism is entirely in accord with kinetic results obtained from a very similar cyclic phosphonium salt.[12] The possibility of pseudorotation **7** ⇌ **12** should be considered. This would





permit over-all apical introduction of nucleophile and apical departure of leaving group, similar to the McEwen mechanism[8] but with retention of configuration. Such a mechanism is consistent with the notion that in ionic reactions involving a trigonal-bipyramidal phosphorus atom, apical positions are favored by entering and leaving groups.[8,10] However, there are at least two arguments against this type of mechanism for the base decomposition of **1**. First, it is known that electronegative substituents attached to phosphorus exhibit a preference for apical positions in phosphoranes.[13] The facility with which such phosphoranes pseudorotate is determined to some extent by the number of electronegative substituents on phosphorus and by whether or not such substituents are deprived of their apical orientations in the resulting structures. In small ring systems, structures displaying 120° ring angles (*e.g.*, **6**) are evidently energetically unfavorable and are thought not to enter into the pseudorotation process.[10,14,15] For example, ^1H nmr investigations of **8** at −65° have shown it to be conformationally stable[16] but at −40° rapid positional exchange among methoxyl groups takes place. Compound **9** is conformationally stable to about 0°[17] and **10** shows no indication of positional change of the methoxyl group below its isomerization temperature of about 127°.[17] Furthermore, the methyl ester of propylphostonic acid (**11**) undergoes hydrolysis almost exclusively with ring cleavage,[10] whereas methyl ethylene phosphate gives 30% hydrolysis of the methyl ester group and 70% ring opening.[18] In the latter case, facile pseudorotation of a trigonal-bipyramidal intermediate has been proposed to account for the formation of near-statistical amounts of both products. The phostonic acid ester intermediate, on the other hand, has little freedom to pseudorotate because of restrictions imposed by the presence of the C–P ring bond. Thus by analogy, **7** would not be expected to pseudorotate

(8) W. E. McEwen, K. F. Kumli, A. Blade-Font, M. Zanger, and C. A. VanderWerf, *J. Amer. Chem. Soc.*, **86**, 2378 (1964).

(9) Molecular models show the ring angles of **6** to be significantly more strained than those of **7**. If the ring were assumed to be planar and the bond angles normal, the sum of the angles in **6** would be 558° as compared with 528° for **7**. The former ring structure deviates +18° from the sum of the angles of a pentagon and the latter −12°. As a first approximation then, it would seem reasonable that the CPC ring angle in the sp^3d intermediate would be 90°.

(10) E. A. Dennis and F. H. Westheimer, *J. Amer. Chem. Soc.*, **88**, 3432 (1966).

(11) The possibility of attack by hydroxide ion on the edge, rather than the face, of the tetrahedral phosphonium cation has been discussed earlier[8] and is considered unlikely since phosphine oxides of both inverted and retained configuration would be expected.

(12) G. Aksnes and K. Bergesen, *Acta Chem. Scand.*, **19**, 931 (1965).

(13) E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966); R. Schmutzler, *Advan. Fluorine Chem.*, **5**, 31 (1965); D. S. Payne, "Topics in Phosphorus Chemistry," Vol. 4, Interscience Publishers, New York, N. Y., 1967.

(14) F. H. Westheimer, *Accounts Chem. Res.*, 1, 70 (1968).

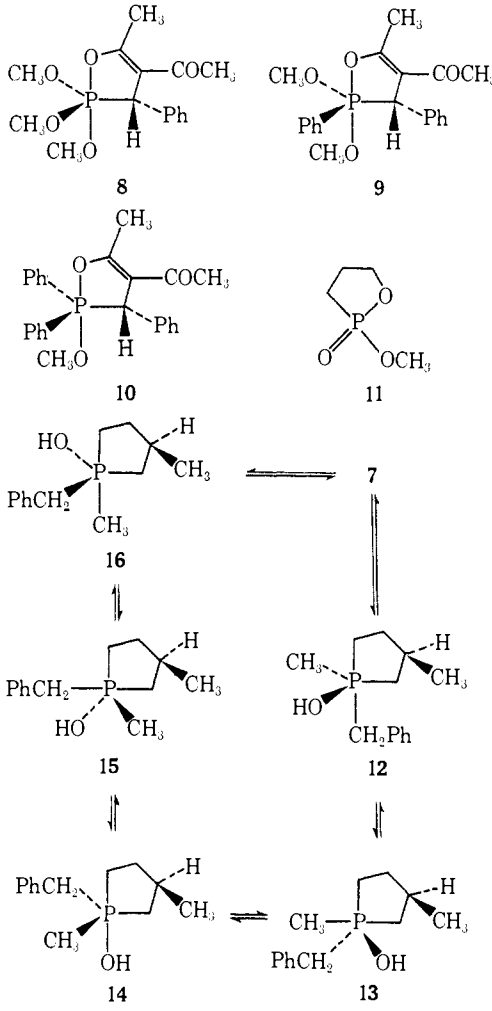
(15) F. Ramirez, *ibid.*, 1, 168 (1968).

(16) D. G. Gorenstein and F. H. Westheimer, *J. Amer. Chem. Soc.*, **89**, 2762 (1967).

(17) F. Ramirez, J. F. Pilot, O. P. Madan, and C. P. Smith, *ibid.*, **90**, 1275 (1968).

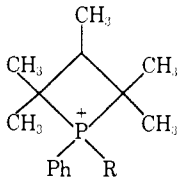
(18) F. Covitz and F. H. Westheimer, *ibid.*, **85**, 1773 (1963).

readily to **12**, or to any other structures for that matter. Secondly, if **7** ⇌ **12** did occur, it would seem unreasonable that further pseudorotations to structures **13**–**16**[19] should be inhibited, especially in view of evidence presented by Whitesides and Bunting which strongly suggests that apical–equatorial interchange and racemization share a common mechanism.[20] Since structures **7**, **12**, and **13** should produce the *trans* oxide and **14**–**16** the *cis* oxide, both **1a** and **1b** would be expected to lead to *mixtures* of the *cis* and *trans* oxides **2a** and **2b** if pseudorotation of **7** were operative.



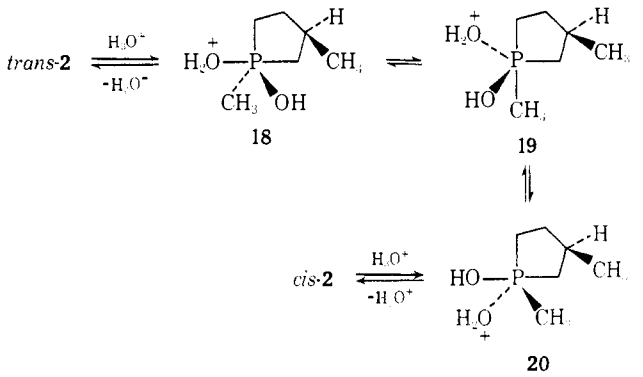
The recently reported alkaline cleavage of one isomer of structure **17a** with retention of configuration at phosphorus[21] may be rationalized in the same way as for **1**. However, it should be pointed out that the stereochemistry of the product may be thermodynamically rather than kinetically determined. It would be necessary to examine the behavior of the other geometric isomer in order to state conclusively that retention of configuration is a direct result of displacement of the benzyl ion by hydroxide ion.

On separate treatment with refluxing concentrated hydrochloric acid, both **2a** and **2b** were converted to identical mixtures of the oxides as determined by nmr analysis. Decomposition of pure **1a** and **1b** with sodium *n*-butoxide in *n*-butyl alcohol led to a kinetically determined mixture of **2a** and **2b**. In each case a high degree of retention was observed but with the accompaniment of a small but detectable amount of the oxide of inverted configuration. The results in the former case resemble quite closely the behavior of acylic phosphine oxides which undergo ready ^{18}O exchange[22] and —in the case of optically active oxides—complete racemization[22,23] under similar conditions. However, it should be noted that **17b** was recovered *unisomerized* after being refluxed with concentrated hydrochloric acid.

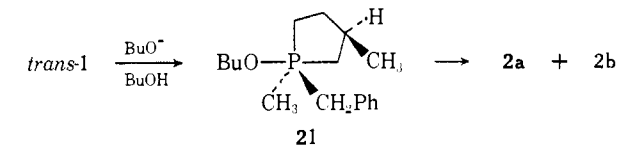


17a, R = CH_2Ph
b, R = O^-

Racemization of **2a** or **2b** may be explained by isomerization of the hydrated oxide *via* the common intermediate **19** to the attainment of equilibrium. Although **19** is energetically unfavorable with respect to **18** and **20**, its formation in minute amount is all that is required to cause eventual isomerization.



The sterochemical outcome of butoxide cleavage of **1a** and **1b** is somewhat analogous to that reported by Parisek and McEwen[24] who showed optically active methylethylphenylbenzylphosphonium iodide to form methylethylphenylphosphine oxide with net inversion but accompanied by extensive racemization. Our results are consonant with their mechanistic interpretation but with the qualification that pseudorotation of the proposed oxyphosphorane intermediate of the type **21** may account for some of the observed racemization.

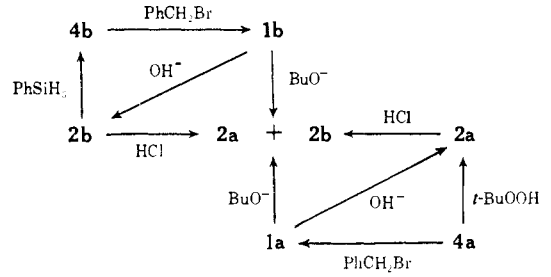


The difference between the phosphetane and phospholane behavior of the oxides in acid medium noted above may be attributable to the greater rigidity of the phosphetane ring and hence its greater reluctance to pseudorotate to give product mixtures.

(19) P. C. Lauterbur and F. Ramirez, *J. Amer. Chem. Soc.*, **90**, 6722 (1968).
(20) G. M. Whitesides and W. M. Bunting, *ibid.*, **89**, 6801 (1967).
(21) W. Hawes and S. Trippett, *Chem. Commun.*, 295 (1968).
(22) D. B. Denney and A. K. Tsolis, *J. Amer. Chem. Soc.*, **86**, 4486 (1964).
(23) L. Horner and H. Winkler, *Tetrahedron Lett.*, 3271 (1964).
(24) C. B. Parisek, W. E. McEwen, and C. A. VanderWerf, *J. Amer. Chem. Soc.*, **82**, 5503 (1960).

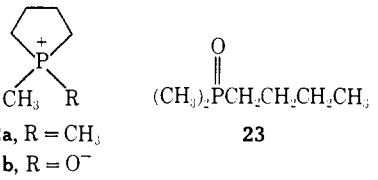
Since we were interested in obtaining pure **4b** (which could not be separated from a mixture of **4a** and **4b** by fractional distillation), phenylsilane reduction[25] of **2b** was examined as offering a possible route to **4b**. Trichlorosilane reduction of phosphine oxides is not completely stereospecific,[5a] provides only moderate yields of product, and suffers from the disadvantage that the procedure employs amines which are sometimes difficult to remove, especially in the purification of lower boiling phosphines. All of these objections appear to be overcome by the use of phenylsilane. Reduction of **2b** afforded **4b** in 95% yield *with complete configurational retention* as demonstrated by the fact that quaternization of **4b** with benzyl bromide yielded a phosphonium salt which was identical in every respect with **1b**. We are presently investigating the application of phenylsilane reduction in the synthesis of stereochemically pure acyclic phosphines, not now directly accessible from optically active phosphine oxides.[25a] Scheme I summarizes the stereochemistry of the reactions reported above.

Scheme I



It was thought that investigation of the base cleavage reaction of **22a** might supply some worthwhile information about the behavior of the phospholanium ring system. Since benzyl or phenyl groups[26] are much more easily cleaved from phosphorus than alkyl groups, possible ring strain factors influencing ring fission could be obscured. This was found to be so. Work of Hays[27] indicates that phosphonium salts of the type $(CH_3)_2P^+R_2$, where R is a primary alkyl group other than methyl, would be expected to cleave in the ratio CH_4:RH of about 20:1 owing to differences in carbanion stability. Sodium hydroxide decomposition of **22a** results in the ratio **22b**:**23** of 3.5:1, an almost sixfold greater amount of ring cleavage than would be expected from carbanion stability alone. Ring cleavage can be readily explained on the basis of an intermediate of the type **7**, but the mechanism of formation of **22b** is at present unclear to us, and further work is now under way on the subject of base cleavage of aliphatic cyclic and acyclic phosphonium salts.

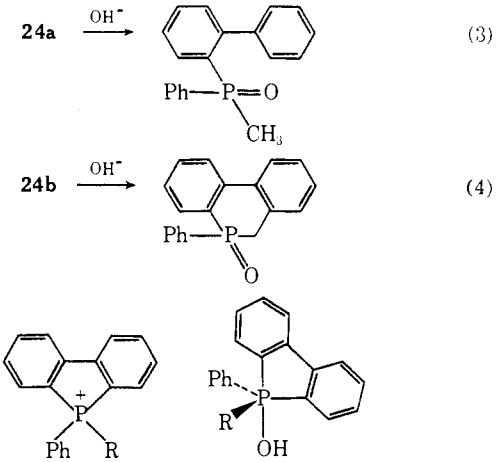
Compounds **24a** and **24b** have been subjected to alkaline hydrolysis[28,29] and as shown by eq 3 and 4 the heterocyclic ring bond was cleaved exclusively in both examples. From our results with **22a**, it seems likely



22a, R = CH_3
b, R = O^-

23

that the explanation for ring cleavage lies primarily in the more favorable stereochemistry of the intermediate **25** and not in the added stability of the substituted biphenyl anion as suggested.[29a] In **25** the CPC ring bonds are oriented apical equatorial, and displacement of the ring aryl group is permitted to occur in the more highly preferred diapical manner.[8,9]



24a, R = CH_3
b, R = CH_2I

25

Experimental Section

General. Melting points were determined on a Vanderkamp melting block in capillary tubes (sealed with silicone grease for hygroscopic materials) and are uncorrected; boiling points are also uncorrected. All ^1H nmr spectra were measured at 60 MHz with a Varian A-60 spectrometer, using tetramethylsilane as an internal standard unless otherwise noted. ^{31}P nmr spectra were determined on a Varian HA-100 spectrometer at 40.5 MHz and are expressed as parts per million from 85% H_3PO_4 used as an external standard. Vpc was carried out with an F & M 700 instrument utilizing helium as a carrier gas and employing a thermal conductivity cell. All operations involving trivalent phosphorus compounds were conducted in a nitrogen atmosphere. Moisture reactive halophosphines and very hygroscopic phosphine oxides were handled in a dry atmosphere. Methyldichlorophosphine was kindly supplied by the U. S. Army Chemical Research and Development Laboratories, Edgewood Arsenal, Md.

1,3-Dimethyl-3-phospholene 1-Oxide (3). This compound was prepared by the general procedure of Quin,[30] bp 86–88° (0.25 mm) (lit. 82–83° (0.5 mm)).

1,3-Dimethylphospholane 1-Oxide (Mixture of Isomers, 2). Oxide **3** (65.1 g) was dissolved in 150 ml of absolute methanol, the solution placed in a 500-ml pressure bottle, 0.25 g of PtO_2 added, and the mixture hydrogenated overnight at an initial pressure of 50 psi in a shaking Parr hydrogenator. After filtration of the catalyst and removal of the solvent by distillation, the residue was vacuum distilled to yield extremely hygroscopic product of bp 89–91° (0.55 mm) and mp 29–37.5° in 98.6% yield. The nmr spectra of the isomers **2a** and **2b** are reported below. Attempted vpc separation of the isomers on a variety of columns was unsuccessful.

(25) H. Fritsche, U. Hasserodt, and F. Korte, *Chem. Ber.*, **97**, 1993 (1964).

(25a) NOTE ADDED IN PROOF. K. Naumann, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 2788 (1969), have reported that Si_2Cl_6 and Si_3Cl_8 reduce optically active phosphine oxides with complete or nearly complete inversion of configuration. Cyclic phosphine oxides are reduced by Si_2Cl_6 with retention of configuration.

(26) G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 2342 (1929); K. D. Berlin and G. B. Butler, *Chem. Rev.*, **60**, 243 (1960).

(27) H. R. Hays and R. G. Laughlin, *J. Org. Chem.*, **32**, 1060 (1967).

(28) D. W. Allen, I. T. Millar, and F. G. Mann, *J. Chem. Soc., C*, 1869 (1967).

(29) D. W. Allen and I. T. Millar, *Chem. Ind.* (London), 2178 (1967).

(29a) NOTE ADDED IN PROOF. The importance of the stereochemistry of the phosphorane intermediate in product determination has since been recognized (D. W. Allen and J. T. Millar, *J. Chem. Soc., C*, 252 (1969); *ibid., B*, 263 (1969)).

(30) L. D. Quin, J. P. Gratz, and T. P. Barket, *J. Org. Chem.*, **33**, 1034 (1968). The nmr spectrum is reported in this reference.

Anal. Calcd for $C_6H_{13}OP \cdot 0.25H_2O$: C, 52.73; H, 9.95. Found: C, 52.97; H, 9.90.

1,3-Dimethylphospholane (Mixture of Isomers, 4). To 47.5 g of the mixture of isomers (**2**) in 500 ml of benzene (previously dried over molecular sieves) was added 36.4 g of freshly distilled triethylamine (stored over solid KOH prior to distillation). The solution was cooled in an ice bath and 48.6 g of trichlorosilane in 200 ml of benzene added dropwise with stirring over a 1.5-hr period. A yellow sludge formed during the addition, and it was necessary to raise the stirrer in order to continue stirring. The mixture was refluxed gently for 16 hr, then cooled in an ice bath and 575 ml of 20% NaOH added dropwise with stirring and external ice cooling. After separating the organic layer, the aqueous layer was extracted with two 100-ml portions of benzene. The extracts were combined with the organic layer, dried over Na_2SO_4, concentrated, and simply distilled to yield 28.5 g of isomeric phosphines: bp 132–140° (760 mm). Separation of the isomers by vpc on a variety of columns was not successful.

1,3-Dimethylphospholane (Isomer 4a). The mixture of isomers (**4**), prepared by trichlorosilane reduction of 149 g of a mixture of **2a** and **2b** as described above, was distilled through a Nester–Faust annular spinning-band column at a reflux ratio of about 100:1. Eight fractions totalling 95.8 g were collected (bp 138.5–141°) and each checked by nmr. The ninth fraction (4.07 g) of bp 141° consisted of one isomer as shown by the presence of only one PCH_3 proton doublet; nmr (neat) δ 0.92 (d, 3, J = 3 Hz, PCH_3), 1.03 (d, 3, J = 6 Hz, $HCCH_3$), and 1.13–2.26 (m, 7, ring protons). The previous fractions showed additional peaks at δ 0.93 (d, J = 3 Hz, PCH_3) and 1.12 (d, J = 6 Hz, $HCCH_3$). ^{31}P nmr shifts for both isomers were identical at +33.8 ppm.

1,3-Dimethylphospholane 1-Oxide (Isomer 2a). To pure **4a** (0.692 g) in 4.07 g of benzene at 5° was added 0.865 g of 70% *t*-butyl hydroperoxide. The mixture was allowed to stand overnight and then concentrated and the residue distilled to yield **2a**, bp 98.5° (1.0 mm); mp 22°; nmr (C_6H_6) δ 0.90 (unresolved d, 3, J = 4 Hz, $HCCH_3$), 1.35 (d, J = 12.5 Hz, $P(O)CH_3$), and 0.97–2.02 (m, ring protons). The last two signals account for a total of ten protons; ^{31}P nmr = −63.3 ppm.

1,3-Dimethylphospholane 1-Oxide (Isomer 2b). The very hygroscopic mixture of isomers **2** (18.8 g) was dissolved in 134 g of hot, dry hexane and the solution allowed to cool to ambient temperature during which time crystals began forming. After subsequent cooling in an ice bath for 1 hr, the supernatant liquid was removed from the separated crystals under dry nitrogen pressure using a filter stick. A total of 18 similarly conducted crystallizations were required before about 2 g of pure **2b** was obtained, mp 72–73.5°; nmr (C_6H_6) δ 0.71 (d of d, 3, J = 6 Hz, $HCCH_3$, J = 0.9 Hz, $PCCCH_3$), 1.12 (d, J = 12.5 Hz, $P(O)CH_3$), and 1.50–2.15 (m, ring protons). The last two signals accounted for a total of ten protons; δ ^{31}P nmr = −62.6 ppm.

Anal. Calcd for $C_6H_{13}OP \cdot 0.25H_2O$: C, 52.73; H, 9.95. Found: C, 52.52; H, 9.93.

1-Benzyl-1,3-dimethylphospholanium Bromide (Isomer 1a). To 2.88 g of pure **4a** in 50 ml of benzene was added at 0° 7.82 g of benzyl bromide dissolved in 25 ml of benzene. The mixture was stored overnight in a refrigerator and 7.02 g of **1a** recovered, mp 168–168.5°; after three recrystallizations from 1:4 $CHCl_3$–EtOAc, **1a** melted at 168.5–169.5°. (With EtOH **1a** forms a 1:1 solvate.) Nmr in D_2O (with reference to exchanging H_2O signal): 2.79 ppm downfield (s, 5, C_6H_5); upfield signals at 0.85 (d, 2, J = 16 Hz, PCH_2Ph), 2.73 (d, 3, J = 14 Hz, PCH_3), 3.68 (d, 3, J = 5 Hz, $HCCH_3$), and 1.93–3.53 ppm (m, 7, ring protons); δ ^{31}P = −51.8 ppm.

Anal. Calcd for $C_{13}H_{20}BrP$: C, 54.37; H, 7.02. Found: C, 54.29; H, 7.24.

1-Benzyl-1,3-dimethylphospholanium Bromide (Isomer 1b). Fraction 2 (8.97 g) from the fractional distillation of the mixture of isomers (**4**) was dissolved in 75 ml of benzene and 19.6 g of benzyl bromide in 25 ml of benzene added dropwise with swirling and cooling in an ice bath. White crystals began separating immediately. After standing overnight, the solid was removed by filtration, washed with ether, and dried at 60° for 2 hr to yield 20.4 g of product, mp 162–168.5°. Fraction 3 (12.04 g) was treated similarly and gave 27.1 g of product of mp 161.5–168°. The two crops of crystals were combined and recrystallized 14 times from a 5:1 mixture of EtOH–EtOAc to a constant melting point of 180–180.5°. The 100-MHz nmr spectrum also confirmed the absence of any significant amount of **1a**. The benzyl protons of **1b** absorb slightly upfield from those of **1a**; δ ^{31}P = −51.8 ppm.

Anal. Calcd for $C_{13}H_{20}BrP$: C, 54.37; H, 7.02. Found: C, 54.61; H, 6.90.

Reaction of 1a and 1b with Sodium Hydroxide. Ten milliliters of 1.00 *N* NaOH was pipetted into a 25-ml flask containing 1.00 g of either **1a** or **1b** and the resulting solution heated at reflux for 19 hr. Early clouding of the reaction mixture indicated that the reaction was probably complete within 1 hr. Salt **1a** appeared to be more reactive than **1b**. Toluene and water were removed by azeotropic distillation with benzene, and the resulting benzene solution was decanted from the precipitated inorganic material, concentrated, and distilled. Salt **1a** gave 0.33 g of **2a**, bp 96° (1.5 mm), mp 22°. The nmr spectrum of this oxide was identical with that of the oxidation product of **4a**. Salt **1b** yielded 0.34 g of **2b**, bp 96° (1.5 mm), mp 70–71°. The nmr spectrum of this oxide was identical with that of the oxide obtained by repeated crystallization of **2**. Vpc analysis showed toluene and the respective oxides, **2a** and **2b**, to be the only products of this reaction.

Reaction of 1a and 1b with Sodium *n*-Butoxide. To 25 ml of dry *n*-butyl alcohol containing 0.080 g of reacted sodium was added 1.00 g of either **1a** or **1b**. The resulting solution was heated for 5 hr at reflux temperature. A precipitate began forming within the first few minutes of heating. After concentrating the mixture resulting from the decomposition of **1b**, the residue was distilled to yield 0.405 g of product, bp 77° (0.25 mm) and mp 70–71°. The nmr spectrum of the distillate showed considerable predominance of **2b** over **2a**. Vpc analysis of the reaction mixture detected only *n*-butyl ether, toluene, and **2**. The product from the reaction of **1a** with sodium *n*-butoxide was worked up in the same manner and shown by nmr analysis to consist primarily of **2a** but with a small amount of **2b** present; the melting point was 24°.

Acid-Catalyzed Isomerization of 2a and 2b. Compounds **2a** and **2b** were treated separately but identically as follows: to 0.75 g of the oxide was added 4.0 ml of concentrated HCl. The resulting slightly yellowish solution was boiled for 2 hr, cooled in an ice bath, and neutralized with saturated Na_2CO_3; most of the water was removed by distillation, and last amounts of water were azeotropically distilled with benzene. The benzene solutions were examined by nmr and the spectra of the oxide mixtures showed in detail the same nmr pattern as the synthetic mixture **2**, except for differences in percentage composition. The oxides were recovered by distillation in 75% yield, bp 87° (0.45 mm).

Reduction of 2b with Phenylsilane. Oxide **2b** (0.740 g) was placed in a 15-ml, round-bottomed flask previously purged with nitrogen and 0.430 g of phenylsilane[31] was added. The mixture was heated slightly until a homogeneous mixture was effected, whereupon a brisk reaction occurred with effervescence. The mixture was then allowed to stand at ambient temperature for 0.5 hr and then the phosphine distilled off at atmospheric pressure. To the distillate was added 1.92 g of benzyl bromide in 10 ml of benzene and the solution allowed to stand overnight. The crystals were removed and washed with benzene to yield 1.21 g of material, mp 178–179° without further recrystallization. This product was shown to be identical with **1b** by a mixture melting point. The absence of any detectable amount of **1a** was demonstrated by nmr spectroscopy.

1-Methyl-3-phospholene 1-Oxide. This hygroscopic material was prepared in 54.5% yield by the general procedure of Quin;[30] bp 116° (0.82 mm) (lit.[4] 59° (0.16 mm)); nmr (neat) δ 1.58 (d, 3, J = 13 Hz, $P(O)CH_3$), 2.38 (m, 4, PCH_2), and 5.90 (d, 2, J = 27 Hz, $=CH$).

1-Methylphospholane 1-Oxide (22b). 1-Methyl-3-phospholene 1-oxide (35.8 g) was reduced catalytically in a Parr hydrogenator with Adam's catalyst in 200 ml of EtOH at an initial pressure of 50 psi. After concentration, the dark brown residue was distilled giving 35.2 g of **22b**, bp 93–94° (0.65 mm); nmr (neat) δ 1.52 (d, J = 13.5 Hz, $P(O)CH_3$) and 1.65 (m, CH_2); δ ^{31}P nmr = −61.9 ppm.

Anal. Calcd for $C_5H_{11}OP$: C, 50.84; H, 9.39. Found: C, 51.04; H, 9.39.

1,1-Dimethylphospholanium Bromide (22a). Compound **22b** (15.63 g) was reduced with phenylsilane in the same way as **2b**. 1-Methylphospholane, bp 123° (760 mm), was obtained in 95.5% yield. The distillate, 12.8 g, was added to a cold solution of 71.2 g of CH_3Br in 100 ml of benzene. The mixture was allowed to stand overnight and 21.7 g of white, hygroscopic solid obtained which

(31) R. A. Benkeser, H. Lanesman, and D. J. Foster, *J. Amer. Chem. Soc.*, 74, 648 (1952). It was found that if the reaction mixture was not extracted with water prior to distillation of phenylsilane, vigorous decomposition ensued during the distillation process.

decomposed at temperatures over 350°; nmr in D_2O (ppm upfield from exchanging H_2O signal): 2.53 (d, J = 14 Hz, PCH_3), 2.31 (s), and 1.93–2.83 (m).

Anal. Calcd for $C_6H_{14}BrP$: C, 36.57; H, 7.16. Found: C, 36.97; H, 7.35.

Dimethyl-*n*-butylphosphine Oxide (23). *n*-Butyldichlorophosphine, bp 92–99° (79 mm) (lit.[32] 58–60° (22 mm)), prepared by a literature method,[32] was made to react with methylmagnesium bromide[33] to yield dimethyl-*n*-butylphosphine, bp 56–60° (72 mm) (lit.[33] 69–70° (100 mm)). The latter phosphine (29.7 g) was dissolved in 250 ml of CH_2Cl_2 and 32.5 g of *t*-butyl hydroperoxide was added with vigorous stirring to the solution at −20°. After concentration, the residue was distilled to give **23**, a low melting, hygroscopic solid, in 95% yield, bp 70–73° (0.25 mm); nmr (CH_2Cl_2) δ 1.05 (d, J = 14.5 Hz CCH_3), 1.38 (d, J = 12.5 Hz, P(O)CH_3), and 0.72–1.89 (m, CH_2); δ ^{31}P nmr = −38.3 ppm.

(32) R. B. Fox, *J. Amer. Chem. Soc.*, **72**, 4147 (1950).

(33) G. Kamai and L. A. Khismatullina, *Zh. Obshch. Khim.*, **26**, 3426 (1956); *Chem. Abstr.*, **51**, 9512 (1957).

Anal. Calcd for $C_6H_{15}OP \cdot 0.5H_2O$: C, 50.32; H, 11.26. Found: C, 50.50; H, 11.36.

Reaction of 22a with Sodium Hydroxide. To 5.91 g of **22a** was added 30 ml of 2 *M* NaOH and the mixture refluxed until no further change in gas volume was evident (about 4 days). Benzene was added, the water removed by azeotropic distillation, the solution concentrated, and the residue distilled and collected as one fraction. This was examined by ^{31}P nmr and the phosphorus signals shown to be identical with those of authentic **22b** and **23**. Integration of the signals gave a ratio of **22b**/**23** of 3.5:1. A second run was performed under identical conditions, and an aliquot was titrated with standard acid showing the reaction to have proceeded 99 ± 1% to completion.

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Stereochemistry of Asymmetric Silicon. XII. Reactions of Silicon–Oxygen and Silicon–Nitrogen Compounds with Boron Halides[1,2]

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Abstract: The stereochemistry of the reactions of a variety of optically active alkoxysilanes and aminosilanes with boron halides has been studied. For these reactions, which yield the halosilane, the simplest and most obvious mechanistic possibility would be a four-center mechanism and this has been previously proposed by other authors. We have found that most of the reactions proceed with *inversion* of configuration. (The major exception is BCl_3 plus R_3Si^*OR'.) Thus, clearly, the general mechanistic situation is not the one previously assumed and the present paper discusses new mechanistic possibilities for these interesting reactions of asymmetric silicon with strong Lewis acids.

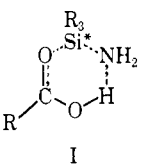
Although the dynamic stereochemistry of reactions of silicon–oxygen[4] and silicon–nitrogen bonds[5] with a wide variety of reagents is known, a systematic study of the factors affecting stereochemical path with strong aprotic acids as reagents has not yet been reported.

The boron halides are strong Lewis acids and, in contrast to HX, BX_3 would not be expected to very rapidly yield halide ion subsequent to coordination with a nitrogen or oxygen function. Thus, the boron halides posed an extremely interesting mechanistic question concerning whether, after coordination, the lesser ionic character of the boron–halogen bond relative to the hydrogen–halide bond would lead to retention of configuration *via* a four-center S_Ni–Si transition state. This question arises because the reaction of aminosilanes with hydrogen halides such as HCl usually proceeds with inversion of configuration whereas an acid of decreased strength such as benzoic changes the stereochemistry to predominant *retention of* configuration[5] with $R_3Si^*NH_2$.

For the inversion reactions of aminosilanes with HCl our preferred mechanism was formulated as in (1).

$$R_3Si^*NR'_2 + HCl \underset{}{\overset{\text{pentane}}{\rightleftharpoons}} \underbrace{R_3Si^*\overset{+}{N}HR'_2\,Cl^-}_{\text{ion pair}} \xrightarrow{HCl} \left[Cl\cdots Si\cdots \overset{H}{\underset{R'_2}{N}}\cdots HCl\right] \longrightarrow ClSi^*R_3 + R'_2NH_2^+Cl^- \quad (1)$$

In the reaction of $R_3Si^*NH_2$ with benzoic acid compared to HCl, the combination of lowered acidity of the reagent and low steric requirements of the $-NH_2$ group changed the predominant stereochemistry from 91% inversion of configuration with HCl to 79% retention with benzoic acid and the transition state for this latter retention reaction was formulated according to I. Evidence



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(1) For the preceding paper in this series, see: L. H. Sommer and J. McLick, *J. Am. Chem. Soc.*, **91** 2001 (1969).

(2) We are grateful for generous support of this work by Dow Corning Corporation.

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(4) For the most recent paper in this series dealing with this subject and for references to earlier papers, see: L. H. Sommer and H. Fujimoto, *J. Am. Chem. Soc.*, **90**, 982 (1968).

(5) L. H. Sommer and J. D. Citron, *ibid.*, **89**, 5797 (1967).