stirring, for 12 hr. Solvent was removed in a rotary evaporator and the residue was recrystallized from methylene chloride–ethanol to give several crops of limonin. Solvent was removed from the mother liquors and the residue was chromatographed on acid-washed alumina. The content of the fractions was monitored by tlc using a 1:1 chloroform–ethyl acetate solvent system with Ehrlich's reagent to detect limonoids as described previously.[5] Those fractions containing a new nonpolar limonoid spot were combined, solvent was removed, and the residue was crystallized from methanol: mp 222–224°; ir (Nujol) ν 1758, 1718 (carbonyl), 1503, 879 (β-substituted furan), 904 cm^{-1} (exocyclic methylene); λ_{max} (EtOH) 215 mμ (ϵ 5200), 280 (16); R_f on tlc[10] 1.3 that of limonin; ORD in dioxane (c 0.15) at 22° $[\alpha]_{600}$ +27°, $[\alpha]_{370}$ +53°, $[\alpha]_{318}$ −107°, $[\alpha]_{281}$ +270°, $[\alpha]_{256}$ −340°, $[\alpha]_{246}$ +200° (last reading).

Anal. Calcd for $C_{26}H_{30}O_8$: C, 66.35; H, 6.42. Found: C, 65.8; H, 6.41.

Photolimonin II (4). Further work-up of the more polar fractions from the column by concentration gave several crops of impure limonin. Finally, solvent was removed and the residue was filtered through a short column of acid-washed alumina with chloroform to remove polar impurities. Solvent was removed from the eluents and the residue was crystallized from ethanol and then from chloroform–ethanol: mp 299–300° dec; ir (Nujol) ν 1753, 1698 (carbonyl), 1504, 879 cm^{-1} (β-substituted furan); λ_{max} (EtOH) 209, 283 mμ; R_f on tlc identical with that of limonin. Limonin and 4 could be resolved on silicic acid using a 1:1 benzene–nitromethane solvent system: ORD in dioxane (c 0.505) at 22° $[\alpha]_{600}$ −59.5°, $[\alpha]_{323}$ −1290°, $[\alpha]_{319}$ −1250°, $[\alpha]_{314}$ −1330°, $[\alpha]_{302}$ −690° (sh), $[\alpha]_{279}$ +615°, $[\alpha]_{260}$ −400° (last reading).

Anal. Calcd for $C_{26}H_{30}O_8$: C, 66.35; H, 6.42. Found: C, 65.8; H, 6.40.

Acknowledgment. The author is indebted to L. M. White for the analytical data, to Professor H. Mitsuhashi, Hokkaido University, for the ORD data, and to Dr. R. M. Horowitz for helpful discussions.

Registry No. 1, 1180-71-8; 2, 42867-82-3; 4, 42867-83-4.

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Phenylsilane Reduction of Phosphine Oxides with Complete Stereospecificity

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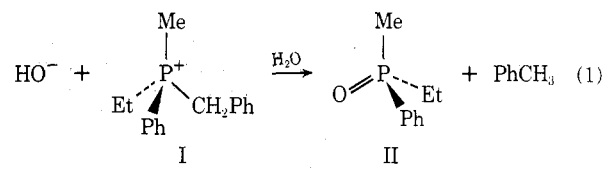
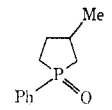
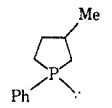
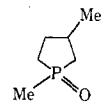
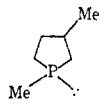
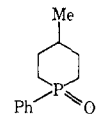
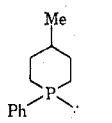
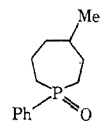
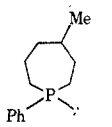
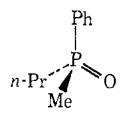
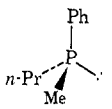
The resolution of racemic benzylethylmethylphenylphosphonium iodide into its enantiomers (I = R) by McEwen, *et al.*,[1] in 1959 made possible the first stereochemical studies of nucleophilic substitution reactions at phosphorus.[2] Since substitution of benzyl by hydroxyl occurs stereospecifically with inversion giving rise to optically pure phosphine oxide (II) from optically pure phosphonium salt (eq 1), the reaction provides access to optically active oxides for stereochemical studies.[3] Although attempts to prepare optically active phosphines by hydride reduction of optically active phosphine oxides produced only racemic mixtures,[4] Horner, a short time later, announced that cathodic reduction of optically active salts such as I yielded the corresponding phosphines with retention and high optical purity.[5] More recently, optically active phosphines have been successfully obtained from optically active oxides by amine-moderated reductions with trichlorosilane, which affords predominant retention or inversion of configuration depending upon the choice of amine.[6] One geometric isomer of 3-methyl-1-phenylphospholane 1-oxide (III) has been reduced with predominant inversion of configuration by use of hexachlorodisilane.[7]



In 1969 the use of phenylsilane to reduce one isomer of 1,3-dimethylphospholane 1-oxide (IV) with *complete* retention of configuration was noted by us.[8] Subsequently, other examples of the conversion of racemic cis and trans isomers of cyclic phosphine oxides to the corresponding phosphines with complete retention of configuration at phosphorus were demonstrated in our laboratories.[9-11] Since the synthetic utility of phenylsilane was not elaborated upon in previous publications[8-11] and since we have now shown that acyclic optically active phosphine oxides are subject to phenylsilane reduction giving rise to optically active phosphines, also with *complete* retention of configuration, we wish at this time to make more extensive comment on this very useful reagent. In fact, we believe it to be the reducing agent of choice when stereochemically pure phosphines are required from stereochemically pure phosphine oxides. This method of reduction is especially important because optically active phosphine oxides are now more generally and conveniently available than optically active phosphonium salts as a result of Mislow's procedure involving conversion of diastereomerically pure menthyl phosphinate esters to optically active phosphine oxides with Grignard reagents.[12] Too, the interest in phosphine–metal complexes in homogeneous catalysis and the possibilities of asymmetric synthesis using chiral phosphines in such complexes[13] add a further dimension of importance to this reductive technique. Yields surpass those of any other reductive method, averaging over 90%, and as far as we have been able to determine (Table I) the reaction is 100% stereospecific for the variety of oxides studied.

Table I
Examples of Phosphine Oxide Stereoisomers Reduced with Phenylsilane

Phosphine oxide (isomer of given mp)	Registry no.	Phosphine (isomer of given bp)	Registry no.	% yield of phosphine	Stereochemical proof
 III, mp 60–61°	34868-22-9	 49–51° (0.01 mm)	24901-29-9	92	*f*
 IV, mp 72–73.5°[b]	43140-03-0	 139° (760 mm)	21382-81-0	85	*f*
 mp 148–149°[c]	29782-17-0 (cis) 29782-18-1 (trans)	 76° (0.15 mm)	43140-04-1 (cis) 43140-05-2 (trans)	87	*f*
 mp 80–82°[d]	43140-06-3	 115° (0.05 mm)	43140-07-4	91	*g*
 mp 57–58°[e] [α]D +17.5° (benzene)	17170-48-8	 <70° (0.25 mm)	701-03-1	96	*h*

[a] *Cf.* ref 11. [b] *Cf.* ref 8. [c] *Cf.* ref 9. The other geometric isomer of mp 60–61° is also reduced to the phosphine with retention of configuration. [d] *Cf.* ref 10. This compound was 92% isomerically pure. [e] For preparation see ref 12b; reported[12b] rotation +17° (benzene). [f] The phosphines were stereospecifically reconverted to their oxides with *tert*-butyl hydroperoxide [D. B. Denney and J. W. Hanifin, Jr., *Tetrahedron Lett.*, 2177 (1963)]. [g] A stereochemical cycle was used (*cf.* ref 10). [h] The phosphine was quaternized with benzyl bromide (retention). The salt gave [α]D +37.9° (methanol) and is known to have the same configuration as the dextrorotatory oxide.[5]

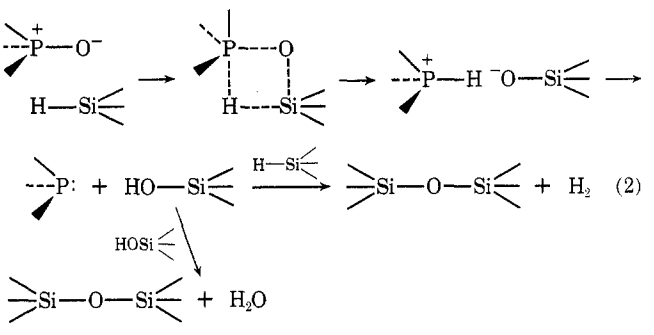
Phenylsilane was first used to reduce phosphine oxides to phosphines by Fritsche, *et al.*,[14] but its use was not noted again in the literature until our discovery of its stereochemical properties as a reducing agent.[8] In addition to superior yields and clean stereochemistry, there are many other advantages to its use. Phenylsilane is commercially available or may be made readily from phenyltrichlorosilane by lithium aluminum hydride reduction.[15] The reaction is normally carried out by mixing the phosphine oxide and phenylsilane together under nitrogen without a solvent and in a molar proportion of 3:2, respectively. Since phenylsilane is reasonably volatile (bp 120°) and siloxane polymers are nonvolatile, the resulting phosphine is obtained in high yield, usually in analytical purity, by simple vacuum distillation. If the phosphine and phenylsilane have similar boiling points, the ratio of phosphine oxide to phenylsilane may be increased to convert phenylsilane completely to polymeric material.

Unlike Horner's method,[5] which requires the construction of an electrochemical cell, no special equipment is needed. Furthermore, cathodic reduction requires the less accessible phosphonium salt enantiomers (usually as one of the halides) and is often complicated by anodic oxidation of bromide or iodide ion to the corresponding halogen which in turn may cause chemical oxidation of the phosphine.

Phenylsilane offers advantages over trichlorosilane[6] as a reducing agent since the later method employs the use of an amine which may be somewhat difficult to separate from the phosphine when the two have similar boiling points. Moreover, some racemization always accompanies the use of trichlorosilane and typical yields are only 50–60%.

Hexachlorodisilane does offer the advantage of reduction with inversion, if that stereochemical operation is required.[7] However, if a configurationally pure phosphine is desired, hexachlorodisilane may not be satisfactory since its use is attended by some stereomutation, attributed to the generation of silicon tetrachloride produced *in situ*.[7] Additionally, hexachlorodisilane is currently an expensive reagent. It might be noted that Mislow's method[12] for preparing optically active phosphine oxides can readily provide both *R* and *S* enantiomers; thus phenylsilane may be used to generate either enantiomeric phosphine.

Our observation that retention of configuration occurs, and that water and hydrogen gas are formed during the



(2)

course of the reduction, leads us to the preliminary belief that mechanism 2 may be operative.

Experimental Section

Typical Reaction of Phenylsilane with Phosphine Oxides. The phosphine oxide (10 mmol) and 6.7 mmol of freshly distilled phenylsilane[15] are added together in a 10-ml pear-shaped flask fitted with a small condenser. (The system is previously purged with nitrogen, and the condenser connected to a small nitrogen-filled balloon to maintain atmospheric pressure.) If the reaction does not commence spontaneously, the mixture is heated carefully with an oil bath. Heating is especially necessary if the oxide is a solid to effect solution of the oxide with phenylsilane. Initial slow evolution of hydrogen signals the onset of the reaction. The reaction may become quite vigorous and exothermic, especially with trialkylphosphine oxides; so it is best to have an ice bath available to control the reaction temperature if necessary. After spontaneous evolution of hydrogen subsides, the reaction is heated, usually for 1 hr longer, at 80–100°. Occasionally the contents of the flask form a porous, glass-like solid at this point. At other times an opalescent, viscous liquid is seen. The phosphine may be distilled from the reaction mixture either at atmospheric pressure or at reduced pressure depending upon its boiling point. During atmospheric distillations a small amount of water codistills with the phosphine. The water may be conveniently removed by azeotropic distillation with benzene or other low boiling azeotrope-forming solvents. The pot residue is a brittle, glass-like material which is easily dissolved with alcoholic potassium hydroxide.

(+)-(*R*)-Methylphenyl-*n*-propylphosphine Oxide. This compound was prepared by reaction of 2 *M* *n*-propylmagnesium bromide with (−)-$(S)_P$-methyl methylphenylphosphinate ($[\alpha]D$ −93°) according to the procedure of Mislow:[12b] oxide, $[\alpha]D$ +17.5° (benzene); lit.[12] $[\alpha]D$ +17° (benzene).

(+)-(*S*)-Benzylmethylphenyl-*n*-propylphosphonium Bromide. The optically active oxide from the above procedure was reduced with phenylsilane in the manner described. However, because of the reported thermal isomerization of optically active methylphenyl-*n*-propylphosphine,[5] the external bath temperature during the reduction process was kept below 80° and the reaction mixture was allowed to remain at this temperature for 3 hr. The phosphine was distilled (kugelrohr) below 70° (0.25 mm) and collected in a Dry Ice cooled receiver: yield 96% based on the oxide. The phosphine was dissolved in deoxygenated benzene and quaternized with twice the molar quantity of benzyl bromide. After the reaction mixture was allowed to stand overnight, the solvent and excess benzyl bromide were removed *in vacuo* and the resulting oily residue was triturated with ether, whereupon it immediately crystallized. The crystals were washed twice more with ether to furnish an 89% yield of phosphonium salt: $[\alpha]D$ +37.9° (methanol); reported[5] $[\alpha]D$ +36.8° (methanol).

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Registry No. Phenylsilane, 694-53-1; (+)-*S*-benzylmethylphenyl-*n*-propylphosphonium bromide, 5137-89-3.

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Carbon–Phosphorus Bond Cleavage in the Reaction of Tertiary Phosphines with Boron Trihalides

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The reaction of tris(*o*-methoxymethylphenyl)phosphine with boron trichloride has been reported to produce tris(*o*-chloromethylphenyl)phosphine.[2] The analogous reaction of methoxymethyldiphenylphosphine with boron trichloride was investigated in the course of some synthetic work. It was found that this reaction unexpectedly resulted in carbon–phosphorus bond cleavage to yield either diphenylphosphine oxide or diphenylphosphinic acid depending upon the method of work-up (eq 1). The addition of H_2O_2 to the reaction mixture was employed as a means to simplify the work-up in that diphenylphosphinic acid is more easily isolated than diphenylphosphine. Carbon–phosphorus bonds are of comparable strength to that of carbon–carbon bonds and only a few reactions are known, generally under basic conditions, which give rise to carbon–phosphorus bond breaking. The alkaline hydrolysis of quaternary phosphonium salts,[3] the reaction of tertiary phosphines with alkali metals,[4] and the Wittig reaction are examples of reactions of this type. There have been no reported reactions of organophosphorus compounds with any boron trihalide which resulted in carbon–phosphorus bond breaking. A study of the reaction of a series of tertiary phosphines with the boron trihalides was initiated.

$$Ph_2PCH_2OCH_3 + BCl_3 \xrightarrow{H_2O} Ph_2P(O)H \xrightarrow{H_2O_2} Ph_2P(O)OH \quad (1)$$

It was found that tertiary phosphines substituted with various electronegative functional groups on the carbon α to the phosphorus reacted with boron trichloride to give diphenylphosphinic acid in high yield. Phosphines substituted with similar functional groups on the β carbon gave much lower yields of the cleavage product. Phosphines containing only hydrocarbon substituents did not undergo phosphorus–carbon bond cleavage. These results are listed in Table I.

It is possible that bond cleavage was not a result of reaction with boron trichloride but a consequence of the reaction work-up with alkaline hydrogen peroxide. This possibility was eliminated by control experiments. The reaction of all the starting compounds with only basic hydrogen peroxide gave the corresponding tertiary phosphine oxides and no evidence of any cleavage product.

Boron trifluoride etherate also reacted with the same phosphines in a similar manner, but the resulting yields were generally much lower than that observed with boron trichloride. Boron tribromide reacted with methoxymethyldiphenylphosphine in the same manner. The reaction was very vigorous and extensive decomposition of the compound occurred, but about 20% of the cleavage product was isolated.