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 ([α]D −93°) according to the procedure of Mislow:[12b] oxide, [α]D +17.5° (benzene); lit.[12] [α]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: [α]D +37.9° (methanol); reported[5] [α]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.

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

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.

Table I
Product Distribution for Reactions of Tertiary Phosphines with Boron Trihalides

Registry no.[g]	Reaction	% $Ph_2P(O)OH$[f]	Other products (%)	Registry no.
43139-94-2	$Ph_2PCH_2OCH_3$[5] + BCl_3[c]	68	$Ph_2P(O)CH_2OCH_3$ (30)	4455-77-0
	$Ph_2PCH_2OCH_3$ + $BF_3 \cdot OEt_2$[d]	7	$Ph_2P(O)CH_2OCH_3$ (78)	
	$Ph_2PCH_2OCH_3$ + BBr_3[e]	28	$Ph_2P(O)CH_3$[b]	2129-89-7
13119-14-7	$Ph_2PCH_2SCH_3$[5] + BCl_3	85	$Ph_2P(O)CH_2SCH_3$ (11)	13119-15-8
	$Ph_2PCH_2SCH_3$ + $BF_3 \cdot OEt_2$	22	$Ph_2P(O)CH_2SCH_3$ (69)	
18629-57-7	Ph_2PCOCH_3[6] + BCl_3	77		
36838-04-7	Ph_2PCOPh[6] + BCl_3	87		
13119-19-2	$Ph_2PCH_2N(CH_3)_2$[5] + BCl_3	4		
607-01-2	$Ph_2PCH_2CH_3$[7] + BCl_3	0	$Ph_2P(O)CH_2CH_3$ (96)	1733-57-9
7650-91-1	Ph_2PCH_2Ph[7] + BCl_3	0	$Ph_2P(O)CH_2Ph$ (70)	2959-74-2
603-35-0	Ph_3P + BCl_3	0	$Ph_3P(O)$ (100)	791-28-6
794-39-8	$Ph_2PCH{=}CHPh$[8] + BCl_3	0	$Ph_2P(O)CH{=}CHPh$ (95)	795-47-1
7608-17-5	$Ph_2PC{\equiv}CPh$[8] + BCl_3	0	$Ph_2P(O)C{\equiv}CPh$ (97)	7608-18-6
5055-12-9	$Ph_2PCH_2CH_2OCH_2CH_3$[9] + BCl_3	0	$Ph_2PCH_2CH_2OH$ (91)	2360-04-5
4848-43-5	$Ph_2PCH_2CH_2NH_2$ + BCl_3	5		
24744-62-5	$Ph_2PCH_2CH(OCH_3)_2$[10] + BCl_3	8[a]		

[a] This reaction produced primarily dark-colored tar. [b] This product has also been obtained from the reaction of methoxymethyldiphenylphosphine with HBr.[11] [c] Registry no., 10294-34-5. [d] Registry no., 109-63-7. [e] Registry no., 10294-33-4. [f] Registry no., 1707-03-5. [g] Of tertiary phosphine.

One possible explanation of this reaction is that a quasi-phosphonium salt is formed which subsequently undergoes a basic hydrolysis similar to that of quaternary phosphonium compounds. However, when the reaction mixture is worked up with deoxygenated water, diphenylphosphine oxide is isolated, indicating that cleavage under acidic conditions can indeed occur.

Experimental Section

All reactions were carried out in a dry nitrogen atmosphere. Infrared spectra were made on a Perkin-Elmer Model 337 infrared spectrophotometer, nmr spectra were made on a Jeolco Model C-60H1 spectrophotometer, and all melting points are reported uncorrected.

Synthesis of Starting Compounds. All starting compounds except triphenylphosphine (Aldrich) and 2-aminoethyldiphenylphosphine were prepared by standard literature methods. The compounds were characterized by ir spectra, pmr spectra, and comparison of their physical properties with those reported in the literature.

2-Aminoethyldiphenylphosphine. Triphenylphosphine (26.2 g, 0.1 mol) was stirred with excess lithium (cut in small pieces) in tetrahydrofuran at room temperature for 3 hr, resulting in a dark red solution. 2-Bromoethylamine hydrobromide (18.5 g, 0.9 mol) was added to the solution with vigorous stirring. A mildly exothermic reaction ensued and the reaction mixture became colorless at the end of the addition. The solvent was removed at reduced pressure and the residue was vacuum distilled, yielding 11.0 g (53%) of 2-aminoethyldiphenylphosphine, bp 135–138° (0.04 mm) [lit.[12] bp 220° (9 mm)].

The pmr spectrum of a deuteriochloroform solution of this compound gave a singlet (NH) at δ 1.6 ppm, a multiplet (PCH_2–) at 2.2 ppm, a multiplet (NCH_2–) at 2.8 ppm, and a complex (aromatic protons) at 7.5 ppm in the ratio 2:2:2:5, respectively.

Reaction with Boron Trichloride. Method A. The starting phosphine was added slowly with stirring to excess liquid boron trichloride (Matheson) at 0°. The reaction mixture was allowed to warm to room temperature with the evaporation of the boron trichloride, and basic 3% hydrogen peroxide was added to the residue. The resulting aqueous mixture was extracted with $CHCl_3$ and any unreacted starting compound was isolated from the $CHCl_3$ phase as the corresponding phosphine oxide. Acidification of the aqueous phase with HCl resulted in the precipitation of diphenylphosphinic acid, mp 188–190° (lit.[13] mp 190–192°). The ir spectrum of this compound was identical with that of a sample of diphenylphosphinic acid prepared by treating chlorodiphenylphosphine with basic hydrogen peroxide.

Reaction with Boron Trichloride. Method B. Methoxymethyldiphenylphosphine (7.0 g, 0.03 mol) was added with stirring to excess liquid boron trichloride at 0°. The reaction mixture was allowed to warm to room temperature with the evaporation of the excess boron trichloride. Deoxygenated water was added to the residue and the aqueous mixture was extracted with chloroform. The chloroform extract was dried and stripped of the solvent, and the residue was vacuum distilled, yielding 2.0 g (33%) of diphenylphosphine oxide, bp 135–138° (0.4 mm), which crystalized upon standing (lit.[14] mp 53–56°). The ir spectrum of this compound showed strong absorbtion at 2275 (PH) and 1175 cm^{-1} (P=O).

Reaction with Boron Trifluoride Etherate. The phosphines were added to excess boron trifluoride etherate and the mixture was heated mildly (below reflux) for 2 hr. Basic 3% hydrogen peroxide was then added and the resulting mixture was extracted with $CHCl_3$. Unreacted starting material was isolated as the corresponding oxide from the $CHCl_3$ phase. Acidification of the aqueous phase resulted in the precipitation of diphenylphosphinic acid, whose structure was verified by comparison of its melting point and ir with those of an authentic sample.

Reaction of Boron Tribromide with Methoxymethyldiphenylphosphine. Methoxymethyldiphenylphosphine (4.4 g, 0.02 mol) was added slowly over a period of 0.5 hr to excess boron tribromide at 0°. A very exothermic reaction occurred. The reaction mixture was allowed to warm to room temperature, then cooled with an ice bath, and basic 3% hydrogen peroxide was added slowly. A very exothermic reaction occurred. The aqueous mixture was extracted with $CHCl_3$ and the aqueous phase was acidified, yielding 0.8 g (20%) of diphenylphosphinic acid.

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Registry No. 2-Bromoethylamine hydrobromide, 2576-47-8.

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