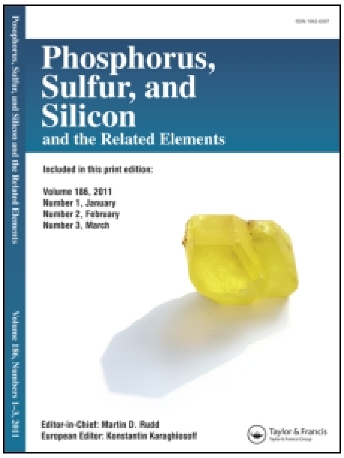

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Thermal Disproportionation of Diphenylphosphine Oxide and 10H-Phenoxaphosphine 10-Oxides

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THERMAL DISPROPORTIONATION OF DIPHENYLPHOSPHINE OXIDE AND 10H-PHENOXAPHOSPHINE 10-OXIDES

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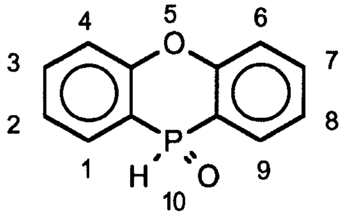
Abstract Diphenylphosphine oxide at 175° and 0.1 torr for one hour produced diphenylphosphinic anhydride and diphenylphosphine along with a small amount of tetraphenyldiphosphine. 10H-Phenoxaphosphine 10-oxides reacted similarly under these conditions except that the product ratios varied with ring substitution. At 100° and 0.1 torr 2,8-difluoro-10H-phenoxaphosphine 10-oxide reacted differently than at 175°, producing the diphosphine monoxide at the lower temperature. The products were identified by ^{31}P NMR spectroscopy.

A wide variety of ring-substituted 10H-phenoxaphosphine 10-oxides are available through hydrolysis of the corresponding 10-chloro-10H-phenoxaphosphines.[1-10] The chlorophosphines are usually produced by a well known Friedel-Crafts reaction between a substituted diphenyl ether and phosphorus trichloride. The secondary phosphine oxides are precursors to a potentially very large number of phosphorus-substituted compounds. Having observed the secondary phosphine oxides to be thermally unstable, we have undertaken the present work to identify the products of their thermal degradation. We have also analyzed the thermal degradation products of diphenylphosphine oxide.



10H-Phenoxaphosphine 10-Oxide

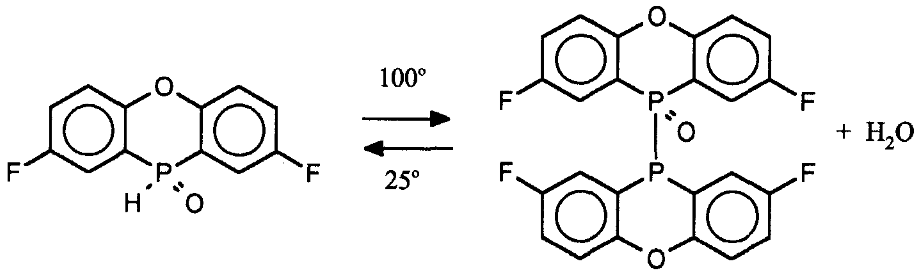
When diphenylphosphine oxide was heated at 0.1 torr and 175° for 1 hour, it produced several products which could be identified through their known ^{31}P NMR chemical shifts. Approximately half of the diphenylphosphine oxide remained unreacted. The main products were diphenylphosphinic anhydride and diphenyl phosphine along with a smaller amount of tetraphenyldiphosphine. The main overall reaction is thus represented by the following disproportionation reaction:

$$4\ Ar_2P(O)H \longrightarrow Ar_2P(O)OP(O)Ar_2 + 2\ Ar_2PH + H_2O$$

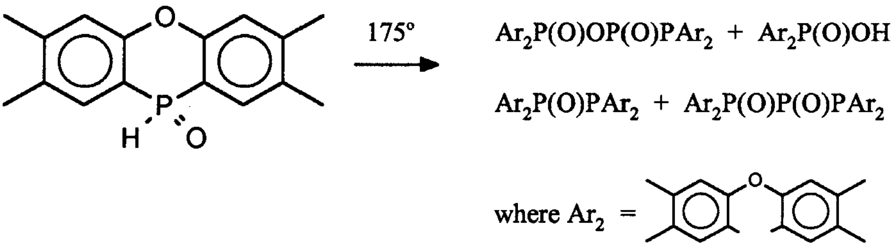
The diphosphine is presumably formed by reaction of the phosphine with starting material:

$$Ar_2PH + Ar_2P(O)H \longrightarrow Ar_2PPAr_2 + H_2O$$

We found that 10H-phenoxaphosphine 10-oxides generally did not decompose until a temperature of about 175° was reached. An exception was 2,8-difluoro-10H-phenoxaphosphine 10-oxide, which reacted at 100° to give primarily the diphosphine monoxide, identified by the doubled doublet in its proton-decoupled ^{31}P NMR spectrum. The NMR spectrum indicated conversion of most of the starting material to the diphosphine monoxide. At room temperature in $CDCl_3$ the reaction reversed, and after two days the starting material was almost completely regenerated.



At 175° 2,8-difluoro-10H-phenoxaphosphine 10-oxide reacted in the same way as diphenylphosphine oxide to produce the anyhydride, the phosphine, and a smaller amount of the diphosphine. When 2,3,7,8-tetramethyl-10H-phenoxaphosphine 10-oxide was heated to 175°, the phosphine and diphosphine apparently oxidized very rapidly, so that the observed products were the anhydride, the acid, the diphosphine monoxide, and the diphosphine dioxide.



$$\xrightarrow{175°} Ar_2P(O)OP(O)PAr_2 + Ar_2P(O)OH$$

$$Ar_2P(O)PAr_2 + Ar_2P(O)P(O)PAr_2$$

where Ar_2 =

Changes over time in the ^{31}P NMR spectrum indicated that the tetramethyl diphosphine dioxide then reacted with the phosphinic acid to produce more of the anhydride and the phosphine oxide.

$$Ar_2P(O)OH + Ar_2P(O)P(O)PAr_2 \longrightarrow Ar_2P(O)OP(O)PAr_2 + Ar_2P(O)H$$

The tendency of the tetramethyl phosphine and the tetramethyl diphosphine to oxidize more rapily than the corresponding difluoro compounds is consistent with previous observations in our laboratory that 2,3,7,8,10-pentamethyl-10H-phenoxaphosphine in chloroform autooxidizes at room temperature but that 2,8-difluoro-10-methyl-10H-phenoxaphosphine is relatively stable.[11]

The diphosphine produced on heating 2-chloro-8-methyl-10H-phenoxaphosphine 10-oxide at 180° proved to be a 50-50 mixture of the meso compound and the racemic form. Two peaks of equal intensity were seen in the ^{31}P NMR spectrum. The anhydride stereoisomers also gave two peaks of equal intensity. Integration of the peaks showed a 2:1 ratio of diphosphine to anhydride in this case in accordance with the following equation:

$$6\ Ar_2P(O)H \longrightarrow Ar_2P(O)OP(O)PAr_2 + 2\ Ar_2PPAr_2 + 3\ H_2O$$

Observed ^{31}P NMR results were as in Table I. The spectra were taken on a JEOL FX90Q spectrometer with $CDCl_3$ as solvent and 85% H_3PO_4 as external standard.

TABLE I ^{31}P NMR, ppm (J, Hz)

Parent Compound	Diphenyl phosphine	2,8-Difluoro-phenoxaphosphine	2-Chloro-8-methylphenoxaphosphine	2,3,7,8-Tetra-methylphenoxaphosphine
Derivative				
Ar_2PH	-41	-115		
Ar_2PPAr_2	-15	-45	-47.5, -48.1	
$Ar_2P(O)H$	22	-19	-19	-15
$Ar_2P(O)OP(O)Ar_2$	33	1	-0.5, -1.1	3
$Ar_2P(O)OH$		10		15
$Ar_2P(O)PAr_2$		-58, 15 (232)		-62.6, 16.7 (232)
$Ar_2P(O)P(O)Ar_2$				1

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