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ALKYLOXY- AND SILYLOXY-DERIVATIVES OF P^V AND Sb^V

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Summary

The thermal decompositions of Ph_4POR ($R = CH_3$, $CH(CH_3)_2$, CH_2Ph) and Ph_4SbOCH_2Ph have been investigated. Previously suggested routes of intramolecular transfer whereby the valence of phosphorus and antimony is reduced, have been confirmed.

Ph_5P reacting with Ph_3SiOH produces unstable $Ph_3P(OSiPh_3)_2$ which decomposes to triphenylphosphine oxide and hexaphenyldisiloxane. A similar reaction of Ph_4POCH_2Ph with Ph_3SiOH (1/2) gave similar results. In the latter reaction a ratio of 1/1 results in unstable $Ph_3P(OCH_2Ph)OSiPh_3$ which decomposes to Ph_3PO and benzyloxytriphenylsilane. In similar reactions of Ph_5Sb and Ph_4SbOCH_2Ph with Ph_3SiOH stable $Ph_4SbOSiPh_3$ is produced.

Ph_3P reacts with $(CH_3)_3SiOOSi(CH_3)_3$ and $Ph_4SbOOGePh_3$ along an oxidizing—reducing route to give Ph_3PO, and $[(CH_3)_3Si]_2O$ and $Ph_4SbOGePh_3$, respectively.

Ph_5P reacting with $(CH_3)_3SiOOH$, Ph_3GeOOH and Ph_3SiOOH produces peroxides of the type Ph_4POOMR_3, which isomerize to unstable P^V compounds of the general formula $Ph_3P(OPh)(OMR_3)$ where M is an element of Group IV.

Methoxytetraphenylantimony was first obtained by reaction of Ph_4SbBr with sodium methylate and by alcoholization of pentaphenylantimony (PPA) [1]:

$$Ph_5Sb + CH_3OH \rightarrow Ph_4SbOCH_3 + PhH \quad (1)$$

This reaction is more convenient for synthesizing pure preparations. In previous work [2,3] we have shown that a phenyl group attached to Sb^V in eqn. 1 can be replaced not only by alcohols, but also by other compounds, having active hydrogen, such as, for instance, phenols and hydroperoxides. These reactions also apply to pentaphenylphosphorane (PPP):

$$Ph_5Z + ROH \rightarrow Ph_4ZOR + PhH \qquad (2)$$

$(Z = Sb, R = CH(CH_3)_2, Ph; Z = P, R = Ph)$

The thermal decomposition (150-180°C) of known Ph_4SbOCH_3 and of other compounds, obtained by us according to eqn. 2, is accompanied by a lowering of the valence of phosphorus and antimony by two possible intramolecular routes. The main route of decomposition for antimony compounds ($R = CH_3$, $CH(CH_3)_2$) is the formation of a carbonyl compound besides Ph_3Sb and benzene:

$$Ph_4SbOCH_3 \rightarrow Ph_3Sb + CH_2O + PhH \qquad (3)$$

$$Ph_4SbOCH(CH_3)_2 \rightarrow Ph_3Sb + CH_3C(O)CH_3 + PhH \qquad (4)$$

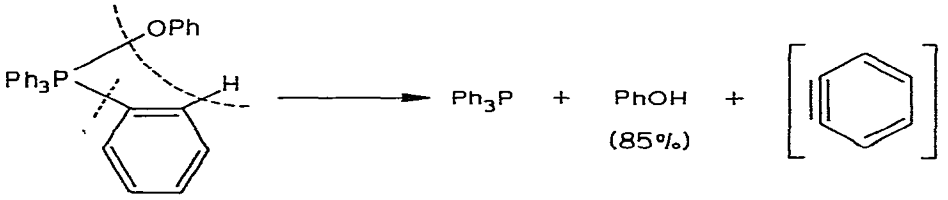
Ph_3Sb and alkyl(aryl)phenyl ether are formed by the second route. This is the main route for producing phenyloxytetraphenylantimony:

$$Ph_4SbOR \rightarrow Ph_3Sb + PhOR \qquad (5)$$

$(R = CH_3, CH(CH_3)_2, Ph)$

Thermal decomposition of Ph_4POPh (200°C) also leads to an ether and a trivalent phosphorus compound. However, the main route is the molecular transformation involving dissociation of an *ortho*-hydrogen atom from one of the phenyl groups attached to phosphorus, whereby Ph_3P, phenol and products of condensation of intermediate dehydrobenzene are formed. In the case of Ph_4POPh there is a similarity to the decomposition of PPP [4]:

$$Ph_4POPh \rightarrow Ph_3P + PhOPh \qquad (6)$$



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To confirm the above suggested routes, we prepared a series of new compounds of the type Ph_4ZOR according to eqn. 2, and subjected them to thermal decomposition. We thought it would be interesting to study the decomposition of monoalkoxy-derivatives of phosphorus with the same R as the antimony compounds investigated previously [2], and also to compare the decomposition of Sb and P analogues with other radicals.

From PPP and alcohols (methyl, isopropyl and benzyl) we obtained Ph_4POR (Ia, $R = CH_3$; Ib, $R = CH(CH_3)_2$; Ic, $R = CH_2Ph$). These are crystalline compounds with precise melting points which are very sensitive to air. On reaction with water or HCl in alcohol Ia-c are quantitatively transformed into triphenylphosphine oxide or tetraphenylphosphonium chloride:

$$Ph_4POR + H_2O \rightarrow [Ph_4POH] + ROH$$
$$\hookrightarrow Ph_3PO + PhH \qquad (8)$$

$$Ph_4POR + HCl \rightarrow Ph_4PCl + ROH \qquad (9)$$

On decomposition of Ia-c (180-190°C, not more than 1 h) the following compounds were obtained (yield, %): from Ia: triphenylphosphine (97), anisole (72), methanol (20), benzene (4); from Ib: triphenylphosphine (86), isopropyl phenyl ether (50), isopropanol (32), benzene (8); from Ic: triphenylphosphine (95), benzyl phenyl ether (91), benzaldehyde (7) and benzene (11).

The main products of decomposition, viz. triphenylphosphine, nonsymmetrical ethers and carbinols, are in accord with the above mentioned mode of decomposition of Ph_4POPh via two routes (eqns. 6 and 7). The P^{III} compound, Ph_3P, is produced quantitatively. However, in the decomposition of Ph_4POPh the ether is a side-product (yield of PhOPh 15%) [3], whereas in the decomposition of Ph_4POCH_3 and $Ph_4POCH(CH_3)_2$ the ether becomes predominant. These results agree with data recently published in ref. 5, where it was shown that compounds CH_3Ph_3POR, obtained from triphenylphosphinemethylene and the appropriate alcohol, decompose to produce methyldiphenylphosphine and alkyl phenyl ethers:

$$Ph_3P{=}CH_2 + ROH \rightleftharpoons CH_3Ph_3POR \qquad (10)$$

$$CH_3Ph_3POR \xrightarrow{\Delta} CH_3PPh_2 + PhOR \qquad (11)$$

$(R = CH_3, C_2H_5, CH(CH_3)_2)$

When Ph_4POPh [3] and Ia-b decompose a considerable amount of resinous material is obtained, which we attribute to the transformation of dehydrobenzene produced in reaction 7. Decomposition of Ic gave no resinous substance whatsoever. However, together with a high yield of benzyl phenyl ether a small amount of benzaldehyde (7%) was obtained. The latter arises from the decomposition of the initial compound according to the following reaction:

$$Ph_4POCH_2Ph \rightarrow Ph_3P + PhCHO + PhH \qquad (12)$$

Decomposition of Ia and Ib did not lead to carbonyl compounds. As has been mentioned above, production of such compounds was typical for the corresponding alkoxy-derivatives of antimony. In order to confirm this we prepared Ph_4SbOCH_2Ph from PPA and benzylcarbinol. This compound is stable when kept in air and reacts easily with HCl:

$$Ph_4SbOCH_2Ph + HCl \rightarrow Ph_4SbCl + PhCH_2OH \qquad (13)$$

It decomposes (180-190°C, 1 h) to give benzaldehyde quantitatively, besides Ph_3Sb and benzene:

$$Ph_4SbOCH_2Ph \rightarrow Ph_3Sb + PhCHO + PhH \qquad (14)$$

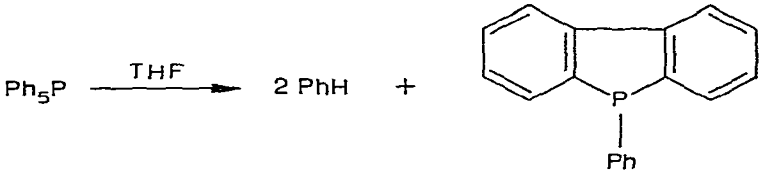
Bearing in mind the somewhat more acidic properties of silanols compared to those of carbinols [6], we decided to prepare the $Ph_4POSiPh_3$ compound by reaction 2. Until recently no information was available concerning the synthesis of such compounds, although the derivatives of phosphorus with P—O—Si bonds, such as dialkyl trialkylsilyl phosphites, $(RO)_2POSiR'_3$ [7], organosilylphosphinate, $R_2P(O)OSiR'_3$, phosphonate, $RP(O)[(OSiR'_3)]_2$, and phosphine oxides,

$(R_3SiO)_3P(O)$ [8], are well known and have been studied in detail.

The reaction of PPP with Ph_3SiOH with the initial components in the proportions 1/2 and 1/1 (THF, room temperature or brief heating at 60°C) did not give the expected results. With the proportion 1/2 the reaction mixture contained Ph_3PO and $(Ph_3Si)_2O$, as well as benzene, the yield of which was 2 moles per mole of initial PPP. Thus, unlike the reaction of PPP with carbinol or phenols, in the case of triphenylsilanol two phenyl groups are substituted; we suppose that in this case a disilyloxy-derivative of phosphorus is formed, but this is unstable and even at room temperature decomposes to phosphine oxide and siloxane:

$$Ph_5P + 2Ph_3SiOH \rightarrow [Ph_3P(OSiPh_3)_2] + 2PhH \qquad (15)$$
$$Ph_3PO + (Ph_3Si)_2O \leftarrow$$

This supposition is confirmed by the result of the reaction when the ratio is 1/1. The same products were obtained, i.e. benzene, $(Ph_3Si)_2O$ and Ph_3PO. However, the yield of the last compound was only 0.5 mole per mole of PPP. Furthermore, *P*-phenyldiphenylenephosphine was found, which might be accounted for by the decomposition of PPP. Indeed, in a THF solution at room temperature PPP decomposes in the same manner as in pyridine solution [4]:



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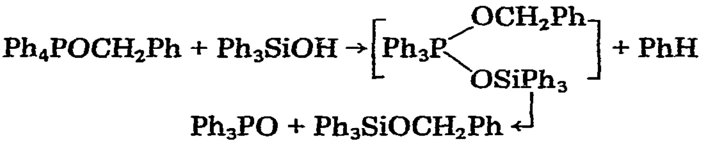
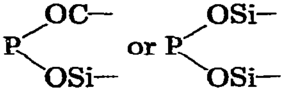
In separate experiments the presence of PPP that had not reacted with Ph_3SiOH (1/1) was proved by establishing the presence of its hydrolysis products. We decided to verify whether the phenyl group attached to phosphorus could be substituted by the Ph_3SiO-group in compounds which already have P—O—C bonds. For this purpose we carried out a reaction of Ph_3SiOH with Ph_4POCH_2Ph in conditions similar to those mentioned above. With a proportion of 1/1, 1 mole of benzene was formed per mole of initial product, but besides this a quantitative yield of Ph_3PO was obtained, as well as a previously undescribed triphenylsilyl benzyl ether. (For identification it was prepared from Ph_3SiCl and $PhCH_2ONa$.) Thus, the phenyl group in the initial compound is substituted and benzyloxy-(triphenylsilyloxy)triphenylphosphorane is produced, which decomposes to give the main products:



$$Ph_4POCH_2Ph + Ph_3SiOH \rightarrow \left[Ph_3P\begin{matrix}OCH_2Ph\\OSiPh_3\end{matrix}\right] + PhH \qquad (17)$$
$$Ph_3PO + Ph_3SiOCH_2Ph \leftarrow$$

If Ph_4POCH_2Ph and Ph_3SiOH are taken in a proportion of 1/2, not only the phenyl group is substituted but the benzyloxy-group as well. In this case 1 mole of benzene is formed per mole of initial compound Ic, and quantitative yields of $(Ph_3Si)_2O$ and Ph_3PO are obtained. In this reaction, as in reaction 15, intermediate bis(triphenylsilyloxy)triphenylphosphorane is formed:

$$\mathrm{Ph_4POCH_2Ph + 2Ph_3SiOH \rightarrow [Ph_3P(OSiPh_3)_2] + PhH + PhCH_2OH} \qquad (18)$$
$$\mathrm{Ph_3PO + (Ph_3Si)_2O \leftarrow\!\rfloor}$$

Thus, phosphorus compounds in which, besides three P—C bonds, there are  $\mathrm{P{<}^{OC-}_{OSi-}}$ or $\mathrm{P{<}^{OSi-}_{OSi-}}$ groups are unstable and their decomposition leads to pentavalent phosphorus oxide compounds. Probably these circumstances may explain why in ref. 5 unexpected results were obtained when attempts were made to synthesize $\mathrm{(CH_3)_4POSi(CH_3)_3}$ from trimethylphosphinemethylene, $\mathrm{(CH_3)_3P{=}CH_2}$, and $\mathrm{(CH_3)_3SiOH}$ (—78°C), the adduct of the reaction (1/1) above 0°C decomposing to $\mathrm{(CH_3)_3PO}$, methane and $\mathrm{[(CH_3)_3Si]_2O}$, in stoichiometric yield.

In contrast to phosphorus, stable structures are known for the $\mathrm{Sb^V}$ derivatives $\mathrm{R_4SbOSiR'_3}$ and $\mathrm{R_3Sb(OSiR'_3)_2}$. For instance, the following compounds have been obtained and some of their properties described: $\mathrm{(CH_3)_4SbOSi(CH_3)_3}$, $\mathrm{Ph_4SbOSi(CH_3)_3}$, $\mathrm{(CH_3)_3Sb[OSi(CH_3)_3]_2}$, $\mathrm{Ph_3Sb[OSi(CH_3)_3]_2}$ [9,10] and $\mathrm{Ph_3Sb[OSiPh_3]_2}$ [11]. It has been reported that the chemical and thermal stability of these compounds increases as the number of phenyl groups increases. Thus, $\mathrm{Ph_3Sb[OSi(CH_3)_3]_2}$ begins to decompose, slowly liberating hexamethyldisiloxane, only at 280°C. We thought it would be interesting to prepare the compound $\mathrm{Ph_4SbOSiPh_3}$, in which all the substituents are phenyl groups and compare its decomposition with that of the analogous alkoxy-derivatives.

$\mathrm{Ph_4SbOSiPh_3}$ was synthesized from PPA and $\mathrm{Ph_3SiOH}$ by heating in THF to 90°C:

$$\mathrm{Ph_5Sb + Ph_3SiOH \rightarrow Ph_4SbOSiPh_3 + PhH} \qquad (19)$$

and also from triphenylsilanol by reaction with $\mathrm{Ph_4SbOCH_2Ph}$:

$$\mathrm{Ph_4SbOCH_2Ph + Ph_3SiOH \rightarrow Ph_4SbOSiPh_3 + PhCH_2OH} \qquad (20)$$

In both cases an excess of $\mathrm{Ph_3SiOH}$ did not lead to disilyloxy-derivatives as was the case in the reactions with phosphorus analogues. For the purpose of identification $\mathrm{Ph_4SbOSiPh_3}$ was prepared from sodium triphenylsilanolate and tetraphenylstibonium bromide in a solution of benzene or toluene:

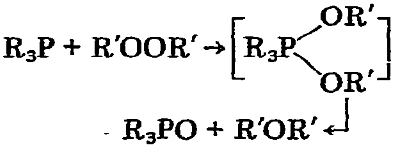
$$\mathrm{Ph_4SbBr + Ph_3SiONa \rightarrow Ph_4SbOSiPh_3 + NaBr} \qquad (21)$$

In contrast to alkoxy-derivatives, during the decomposition of $\mathrm{Ph_4SbOSiPh_3}$ (250-260°C, 1 h) the production of triphenylsilyl phenyl ether was not observed. Together with diphenyl (46%) and $\mathrm{Ph_3Sb}$ (45%) a product identified as $\mathrm{Ph_3Sb[OSiPh_3]_2}$ [11] of high fusibility and stable to air was obtained. Its formation may be explained by a disproportionation reaction taking place without change in the valence of antimony:

$$\mathrm{2Ph_4SbOSiPh_3 \rightarrow Ph_3Sb[OSiPh_3]_2 + Ph_5Sb} \qquad (22)$$
$$\mathrm{Ph_3Sb + Ph{-}Ph \leftarrow\!\rfloor}$$

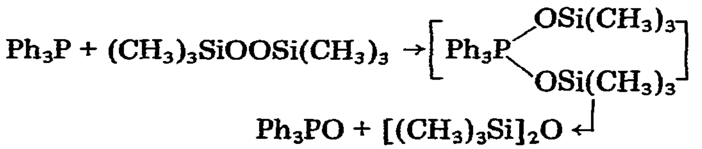
Under the conditions of the experiment PPA is converted to $\mathrm{Ph_3Sb}$ and diphenyl, in accord with ref. 12.

With the aid of ^{31}P and ^{1}H NMR a phosphorane structure for the intermediate products of attachment of alkyl peroxide to phosphines has been established [13]:



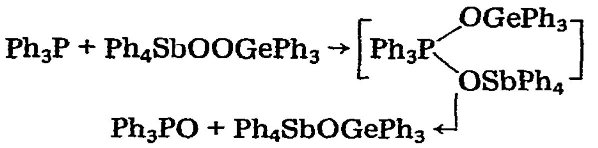
$$R_3P + R'OOR' \rightarrow \left[R_3P\begin{matrix}OR'\\OR'\end{matrix}\right] \rightarrow R_3PO + R'OR' \qquad (23)$$

Dialkoxyphosphoranes are compounds of low stability and decompose into the products usually obtained in this reaction, that is R_3PO and ethers. A similar reaction with disilyl peroxides might reveal a second route for obtaining disilyloxyderivatives of pentavalent phosphorus. Equimolar quantities of Ph_3P and trimethylsilyl peroxide in absolute ether reacted quickly under liberation of heat and precipitation of Ph_3PO (99%). In the solvent $[(CH_3)_3Si]_2O$ (82%) and $(CH_3)_3SiOH$ (8%) were found. These results are in accord with results of work carried out at the same time by other authors [14]. Thus, this peroxide reacts similarly to dialkyl peroxides:



$$Ph_3P + (CH_3)_3SiOOSi(CH_3)_3 \rightarrow \left[Ph_3P\begin{matrix}OSi(CH_3)_3\\OSi(CH_3)_3\end{matrix}\right] \rightarrow Ph_3PO + [(CH_3)_3Si]_2O \qquad (24)$$

Like the product of the reaction of PPP with Ph_3SiOH studied above (eqn. 15), the bis(trimethylsilyloxy)triphenylphosphorane formed is easily converted into oxide derivatives of silicon and phosphorus without the valence of the latter being changed. Another peroxide we investigated was a nonsymmetrical bielementorganic peroxide, $Ph_4SbOOGePh_3$, which is stable at room temperature [15]. Ph_3P reacted readily with this peroxide and two final products were obtained, namely Ph_3PO (97%) and $Ph_4SbOGePh_3$ (98%), which arose from the decomposition of the unstable P^V compound having P—O—Ge and P—O—Sb bonds:



$$Ph_3P + Ph_4SbOOGePh_3 \rightarrow \left[Ph_3P\begin{matrix}OGePh_3\\OSbPh_4\end{matrix}\right] \rightarrow Ph_3PO + Ph_4SbOGePh_3 \qquad (25)$$

To identify triphenylgermanyloxy(tetraphenyl)antimony it was synthesized from Ph_4SbBr and Ph_3GeOH in the presence of dry ammonia:

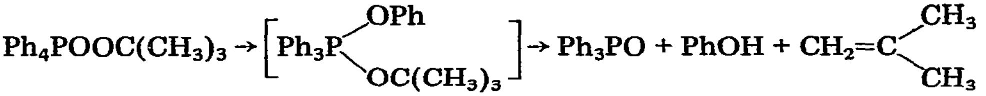
$$Ph_4SbBr + Ph_3GeOH \xrightarrow{NH_3} Ph_4SbOGePh_3 + HBr \qquad (26)$$

As already mentioned above, organic hydroperoxides are more acids than alcohols, and in reactions with PPP and PPA readily substitute one Ph-group for an alkylperoxy-group [3]:

$$Ph_5Z + R'OOH \rightarrow Ph_4ZOOR' + PhH \qquad (27)$$

$(Z = P;\ R' = C(CH_3)_3;\ Z = Sb;\ R' = C(CH_3)_3,\ C(CH_3)_2Ph)$

From PPA and tert-butyl and cumyl hydroperoxides in pyridine good yields are obtained of stable peroxides that are identical to peroxides obtained otherwise [16]. In the case of PPP [3] and $(CH_3)_3COOH$ the phosphorus peroxide formed is unstable at room temperature and isomerizes to a compound of phosphorane structure, which itself decomposes further:

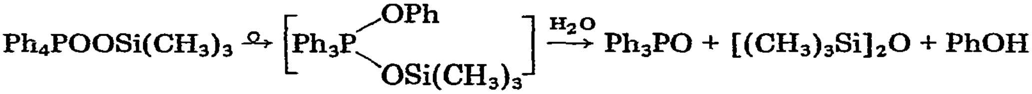


$$Ph_4POOC(CH_3)_3 \rightarrow \left[Ph_3P\begin{matrix}OPh\\OC(CH_3)_3\end{matrix}\right] \rightarrow Ph_3PO + PhOH + CH_2{=}C\begin{matrix}CH_3\\CH_3\end{matrix} \qquad (28)$$

It is also known that the peroxides of Group IVB elements possess a more mobile hydrogen atom than tertiary hydroperoxides [6,17]. Proceeding from their capabilities to association and basing our suppositions on spectroscopical, data the conformity of the acid properties of the following compounds has been established: $R_3COOH < R_3SiOOH$ ($R = CH_3, Ph$); $(CH_3)_3SiOOH < Ph_3SiOOH$ [6]; $Ph_3COOH < Ph_3GeOOH < Ph_3SiOOH$ [17].

We examined three hydroperoxides, namely $(CH_3)_3SiOOH$, Ph_3GeOOH and Ph_3SiOOH (the most acidic), supposing that on reaction with PPP they would produce bielementorganic peroxides of structure $Ph_4POOMPh_3$ (M = element of Group IV). When PPP reacted with $(CH_3)_3SiOOH$ (equivalent quantities of mixtures in ether and THF at —50°C and later at room temperature) the reaction mixture did not contain peroxide oxygen, and, moreover, benzene in 91% yield was revealed in the volatile portion. After mild hydrolysis of the residue, high yields of Ph_3PO, $[(CH_3)_3Si]_2O$ and phenol were obtained. From these findings it appears that as in the reaction with $(CH_3)_3COOH$ the reaction of PPP with trimethylsilyl hydroperoxide produces a peroxide, which easily regroups, the phenyl group migrating from phosphorus to oxygen:

$$Ph_5P + (CH_3)_3SiOOH \rightarrow [Ph_4POOSi(CH_3)_3] + PhH \qquad (29)$$



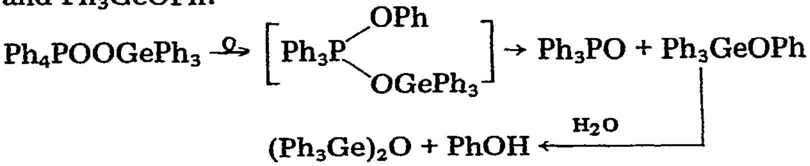
$$Ph_4POOSi(CH_3)_3 \xrightarrow{\Omega} \left[Ph_3P\begin{matrix}OPh\\OSi(CH_3)_3\end{matrix}\right] \xrightarrow{H_2O} Ph_3PO + [(CH_3)_3Si]_2O + PhOH \qquad (30)$$

In a similar manner PPP reacts with Ph_3GeOOH in THF at room temperature to give the following products: benzene (87%), and after hydrolysis Ph_3PO (98%), $(Ph_3Ge)_2O$ (95%), phenol (90%). The same products, except benzene, in yields of 90, 95 and 71% respectively, were obtained when the above mentioned hydroperoxide reacted with Ph_4POCH_2Ph:

$$Ph_5P + Ph_3GeOOH \rightarrow [Ph_4POOGePh_3] + PhH \qquad (31)$$

$$Ph_4POCH_2Ph + Ph_3GeOOH \rightarrow [Ph_4POOGePh_3] + PhCH_2OH \qquad (32)$$

The regrouping also takes place with phenyl migrating from phosphorus to oxygen. The product resulting from the regrouping further decomposes into Ph_3PO and Ph_3GeOPh:

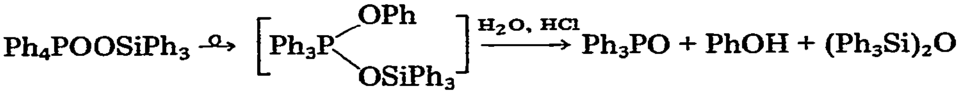


$$Ph_4POOGePh_3 \xrightarrow{\Omega} \left[Ph_3P\begin{matrix}OPh\\OGePh_3\end{matrix}\right] \rightarrow Ph_3PO + Ph_3GeOPh \qquad (33)$$

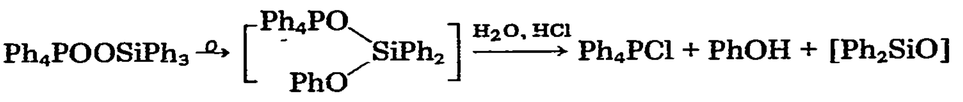
$$Ph_3GeOPh \xrightarrow{H_2O} (Ph_3Ge)_2O + PhOH$$

PPP also reacts with Ph_3SiOOH to produce a peroxide compound that regroups at room temperature, which is confirmed by the production of benzene (85%) and phenol (90%). However, in contrast to the peroxides investigated above (eqns. 30 and 33) the isomerical transformation occurs just as readily on the phosphorus atom as on the silicon atom. Heterolytic cleavage of the rearrangement product afforded approximately equal yields of a phosphonium salt (49.5%) and hexaphenyldisiloxane:

$$Ph_5P + Ph_3SiOH \rightarrow [Ph_4POOSiPh_3] + PhH \qquad (34)$$



$$Ph_4POOSiPh_3 \xrightarrow{\Omega} \left[Ph_3P\begin{matrix} OPh \\ OSiPh_3 \end{matrix} \right] \xrightarrow{H_2O,\ HCl} Ph_3PO + PhOH + (Ph_3Si)_2O \qquad (35)$$



$$Ph_4POOSiPh_3 \xrightarrow{\Omega} \left[\begin{matrix} Ph_4PO \\ PhO \end{matrix} SiPh_2 \right] \xrightarrow{H_2O,\ HCl} Ph_4PCl + PhOH + [Ph_2SiO] \qquad (36)$$

Experimental

All reactions were carried out under complete exclusion of water vapour, in vacuum, or in an atmosphere of dry air or inert gas. The amounts of liquid reaction products were determined by chromatographic analysis (GLC) using a "Tsvet-1" apparatus.

Methoxytetraphenylphosphorane

4.58 g (11.0×10^{-3} mol) of pentaphenylphosphorane (PPP) [12a] in 10 ml of absolute methanol in an evacuated and sealed ampoule was shaken for 10 h with the aid of a mechanical device at room temperature. Excess alcohol was condensed in a trap cooled by liquid nitrogen. In the condensate GLC analysis revealed: benzene (0.84 g, yield 95%). The solid residue, Ph_4POCH_3, was recrystallized in vacuum from hot cyclohexane, to give white crystals (2.55 g, yield 53%), m.p. 162°C. The compound is stable when kept in vacuum but is instantly hydrolyzed by the moisture in the air, quantitatively producing triphenylphosphine oxide. It dissolves readily in hot cyclohexane, less well in petroleum ether.

Isopropyloxytetraphenylphosphorane

3.75 g (9.0×10^{-3} mol) of PPP in 10 ml of absolute isopropanol was heated for 20 h at 50°C. In the liquid products GLC analysis gave benzene (0.42 g, yield 83%). The solid residue was recrystallized from cyclohexane in vacuum, to give 2.16 g (yield 65%) of yellow crystals of $Ph_4POCH(CH_3)_2$, m.p. 157°C. In air it is quantitatively transformed into Ph_3PO.

Ph_4POCH_3 and $Ph_4POCH(CH_3)_2$ react quantitatively with an excess of HCl in alcohol to produce tetraphenylphosphonium chloride.

Benzyloxytetraphenylphosphorane

Similarly to the preceding reaction 3.0 g PPP in 5 ml of benzyl alcohol (60 °C, 2 h) afforded benzene (0.5 g, yield 98%) and Ph_4POCH_2Ph (3.2 g, quantitative yield), m.p. 152-154°C (no change after recrystallization from cyclohexane in vacuum). Reaction of uncrystallized product with H_2O or HCl yielded quantitatively Ph_3PO or Ph_4PCl, respectively.

Thermal decomposition of alkoxy-derivatives of phosphorus

Alkoxy-derivatives of phosphorus were decomposed in an evacuated ampoule provided with a side-arm in which the liquid decomposition products were condensed.

Decomposition of methoxytetraphenylphosphorane

1.99 g of Ph_4POCH_3 was heated for 1 h at 170-180°C. GLC analysis of the products in the liquid gave (yield g, %): anisole (0.40, 72), methanol (0.03, 20) and benzene (0.02, 4). From the non-volatile portion Ph_3P (1.36 g, yield 97%), m.p. 76°C and 0.08 g of a resinous product were obtained.

Decomposition of isopropyloxytetraphenylphosphorane

Under similar conditions 1.6 g of $Ph_4POCH(CH_3)_2$ yielded: isopropyl phenyl ether (0.27 g, 50%), isopropanol (0.08 g, 32%), benzene (0.03 g, 8%), triphenylphosphine (0.97 g, 86%) and 0.21 g of resinous substance.

Decomposition of benzyloxytetraphenylphosphorane

Ph_4POCH_2Ph, obtained from 2.72 g (6.5×10^{-3} mol) of PPP, and 5 ml of benzyl alcohol were heated for 1 h at 190°C. In the condensate of the readily volatile decomposition products GLC analysis revealed (yield g, %): benzyl phenyl ether (0.80, 66), benzaldehyde (0.05, 7), benzene (0.06, 11). The residue in the ampoule was distilled with steam. Extraction of the distillate with ether afforded an additional quantity (0.30 g; 25%) of benzyl phenyl ether, m.p. 35-36 °C. The melting point was not depressed on mixing with pure substance. After distillation with steam the residue was recrystallized from ethanol to give 1.62 g of Ph_3P, m.p. 75°C (yield 95%).

Benzyloxytetraphenylantimony

3.00 g (5.9×10^{-3} mol) of pentaphenylantimony (PPA) in 10 ml of benzyl alcohol was heated in an evacuated sealed ampoule for 2 h at 90-95°C. Excess alcohol was removed under reduced pressure. Benzene (0.42 g, 98%) was found in the condensate. The residue was recrystallized from dry cyclohexane to give 2.24 g (yield 76%) of Ph_4SbOCH_2Ph, m.p. 138-142°C. The product is stable in air, dissolves readily in benzene, less readily in cyclohexane. Found: mol.wt. (cryoscopy, benzene) 518, $C_{31}H_{27}OSb$ calcd.: 537.

Reaction of benzyloxytetraphenylantimony with HCl

0.50 g of Ph_4SbOCH_2Ph and 3 ml of a saturated solution of HCl in ethyl alcohol at room temperature were allowed to stand for several hours. The ethyl and benzyl alcohol were distilled off with steam. A solution of KI was added to the hot filtrate of the still. Obtained: Ph_4SbI (0.51 g, 98%), m.p. 224°C. The m.p. of a mixture with pure Ph_4SbI [18] showed no depression.

Thermal decomposition of benzyloxytetraphenylantimony

2.34 g of Ph_4SbOCH_2Ph were heated for 1 h at 180-190°C. Found in the condensate of the liquid decomposition products: benzene (0.30 g, 87%) and benzaldehyde (0.34 g, 93%). The latter was identified as the 2,4-dinitrophenylhydrazine derivative (m.p. 232°C). The solid decomposition product was almost pure triphenylantimony (1.53 g, quantitative yield), m.p. 53°C (from alcohol).

Reaction of pentaphenylphosphorane with triphenylsilanol

(1). A mixture of 4.54 g (10.9×10^{-3} mol) of PPP and 6.00 g (21.8×10^{-3} mol) of Ph_3SiOH in 20 ml of THF was heated at 60°C for 15 min in an evacuated ampoule. GLC analysis of the condensate of the solvent gave: benzene (1.60 g, 20.5×10^{-3} mol, yield 94%). The residue was extracted with small portions of benzene to give Ph_3PO (3.01 g, 99%), m.p. 147°C. After recrystallization from benzene—cyclohexane, the m.p. was 152°C (lit. [19] 153.5°C). The product that was insoluble in benzene (5.7 g, 98%) melted after mixing with pure hexaphenyldisiloxane at 223°C (for $(Ph_3Si)_2O$ ref. 20 gives m.p. 227°C).

Similar results were obtained when the reaction was carried out at room temperature.

(2). A mixture of 4.54 g (10.9×10^{-3} mol) of PPP, 3.00 g (10.9×10^{-3} mol) of Ph_3SiOH and 20 ml of THF was heated at 60°C for 15 min. The solvent was evaporated. In the condensate benzene (0.93 g, 11.9×10^{-3} mol) was found. To the residue 15 ml of $CHCl_3$ was added and it was allowed to stand for 48 h in an atmosphere of dry nitrogen. The PPP that had not participated in the reaction was converted into Ph_4PCl. Excess $CHCl_3$ was distilled off with steam. KI was added to the aqueous filtrate. Obtained: Ph_4PI (1.86 g, 4.0×10^{-3} mol), m.p. 330°C (lit. [19] 333°C). After separating the phosphonium salt, the remainder afforded Ph_3PO (1.36 g, 5.0×10^{-3} mol), m.p. 152°C and $(Ph_3Si)_2O$ (2.86 g, 10.8×10^{-3} mol), m.p. 224°C.

Heating of the reaction mixture for more than 15 min or allowing it to stand at room temperature a prolonged time, gave besides the above mentioned products small quantities of *P*-phenyl-diphenylenephosphine, m.p. 90°C (from methanol). (lit. [12b], 90°C).

(3). A mixture of 3.83 g (9.2×10^{-3} mol) of Ph_3SiOH and 15 ml of THF was heated for 15 min at 60°C. Benzene (0.77 g, 10×10^{-3} mol) was found in the condensate of the solvent. Aqueous THF was added to the residue. After a period of 10-12 h the solvent was distilled off in vacuum. It contained 0.59 g (7.6×10^{-3} mol) of benzene. By conventional methods the remaining portion was separated into 2.5 g (9.0×10^{-3} mol) of Ph_3PO, m.p. 152°C and 2.35 g (4.4×10^{-3} mol) of $(Ph_3Si)_2O$, m.p. 223°C.

Decomposition of pentaphenylphosphorane in tetrahydrofuran

4.0 g (9.6×10^{-3} mol) of PPP in 20 ml of THF were placed in an evacuated ampoule and allowed to stand for several days at room temperature. GLC analysis of the condensate of the solvent revealed benzene (1.53 g, 19.5×10^{-3} mol). On recrystallization of the residue (3.01 g) from methanol 1.61 g (yield 60%) of pure *P*-phenyl-diphenylene-phosphine, m.p. 90°C, was obtained.

Reaction of benzyloxytetraphenylphosphorane with triphenylsilanol

(1). To Ph_4POCH_2Ph, obtained from 2.7 g (6.5×10^{-3} mol) of PPP, 1.81 g (6.5×10^{-3} mol) of Ph_3SiOH dissolved in THF was added in vacuum. After 24 h the solvent was removed in vacuum. GLC analysis gave: benzene (0.48 g, 94%). The residue was treated with warm pentane. Ph_3SiOCH_2Ph, 2.25 g (95%), m.p. 81°C, was obtained from the filtrate. Mixing with authentic product gave no depression of the m.p. The portion insoluble in pentane (1.8 g, 98%) was Ph_3PO, m.p. 150°C.

(2). Ph_4POCH_2Ph was prepared from 3.7 g (8.8×10^{-3} mol) of PPP and 10 ml of benzyl alcohol. After removing excess alcohol a solution of 4.81 g (17.6×10^{-3} mol) of triphenylsilanol in THF (15 ml) was added in vacuum. The reaction mixture was allowed to stand in vacuum for 24 h. The solvent was removed at reduced pressure. Found in the solvent: benzene (0.64 g, 95%). Obtained from the residue: 2.2 g (91%) of Ph_3PO, m.p. 151°C and 4.61 g (99%) of $(Ph_3Si)_2O$, m.p. 225°C.

Synthesis of benzyloxytriphenylsilane

3.0 g of Ph_3SiCl and the calculated amount of $PhCH_2ONa$ in benzyl alcohol (50 ml) were boiled for 28 h. The solvent was removed in vacuum. With pentane Ph_3SiOCH_2Ph was extracted from the residue. Obtained: 3.1 g (85%) of crystalline substance, m.p. 83-84°C (from pentane). (Found: C, 81.48; H, 5.75; Si, 7.18; mol.wt. 360. $C_{25}H_{22}OSi$, calcd.: C, 81.90; H, 6.01; Si, 7.66%; mol.wt. 366.)

Synthesis of triphenylsilyloxytetraphenylantimony

(1). A mixture of 3.70 g (7.3×10^{-3} mol) of PPA and 2.00 g (7.3×10^{-3} mol) of Ph_3SiOH in 20 ml of THF was heated in a sealed ampoule for 2-3 h at 90°C. Benzene (0.54 g, 95%) was found in the condensate of the solvent. The solid residue was recrystallized in vacuum from dry cyclohexane. Obtained: 2.50 g (yield 80%) of $Ph_4SbOSiPh_3$, m.p. 215-220°C. The compound dissolves readily in benzene, THF, carbon tetrachloride, moderately in cyclohexane, does not dissolve in hot petroleum ether. (Found: Sb, 17.53; Si, 4.04; mol.wt. (cryoscopy in benzene) 722. $C_{42}H_{35}OSbSi$, calcd.: Sb, 17.26; Si, 3.98%; mol.wt. 705.)

(2). Ph_3SiOH and metallic sodium were placed in a flask connected to a reflux condenser and a calcium chloride tube and boiled for 5 h in benzene. The solution was filtered, and the concentration of Ph_3SiONa in the filtrate was determined by titration with a standard solution of HCl. A calculated amount of Ph_4SbBr was added, and the precipitated NaBr was filtered off. Benzene was removed at reduced pressure, The solid residue was recrystallized from a petroleum ether—benzene mixture. A product with m.p. 215-220°C was obtained, which according to elementary analysis was identical to the product obtained from PPA and Ph_3SiOH. Yield 70%.

(3). To a solution of Ph_4SbOCH_2Ph prepared from 3.00 g (5.5×10^{-3} mol) of PPA and 10 ml of benzyl alcohol a solution of Ph_3SiOH (3.10 g, 10.0×10^{-3} mol) in 20 ml of THF was added in vacuum. The mixture was heated for several hours at 95-100°C. The liquid products were removed under reduced pressure. The residue was dissolved in a small quantity of ether. Obtained from the filtrate: 1.53 g (5.4×10^{-3} mol) of Ph_3SiOH, m.p. 148°C which had not participated in the reaction. The portion insoluble in ether was $Ph_4SbOSiPh_3$, m.p. 222°C, yield 3.81 g (97%).

Reaction of triphenylsilyloxytetraphenylantimony with HCl

10-15 ml of a saturated solution of HCl in alcohol was added to 3.86 g of $Ph_4SbOSiPh_3$ and allowed to stand for several hours. Excess alcohol was distilled off with steam, the residue in the still was filtered while hot, and KI was added to the filtrate to precipitate Ph_4SbI (3.01 g, 99%), m.p. 224°C. The residue insoluble in water, after recrystallization from a mixture of petroleum ether and benzene, melted at 152°C. The melting point of a mixed sample with pure Ph_3SiOH was the same. Yield 1.50 g (99%).

Shaking of a benzene solution of $Ph_3SbOSiPh_3$ with an excess of 0.1 *N* HCl at room temperature gave similar results.

Thermal decomposition of triphenylsilyloxytetraphenylantimony

3.40 g of $Ph_4SbOSiPh_3$ was heated for 1 h at 250-260°C. In the condensate benzene (0.042 g, 11%) and diphenyl (0.34 g, 45%) were found. The greater part of the contents of the ampoule was dissolved in a small amount of sulphurous ether. Obtained from the extract: Ph_3Sb (0.76 g, 44.5%), m.p. 53°C. The portion that was insoluble in ether (2.1 g, 50%) melted at 310-312°C (from benzene). The compound is identical with $Ph_3Sb(OSiPh_3)_2$ described in ref. 11. (Found: Sb, 13.60; Si, 5.95. $C_{54}H_{45}O_2SbSi_2$ calcd.: Sb, 13.51; Si, 6.20%.) Treatment of $Ph_3Sb(OSiPh_3)_2$ (1.70 g) with HCl in alcohol, afforded quantitatively: Ph_3SiOH (1.00 g), m.p. 149°C (lit. [20] 151-153°C) and Ph_3SbCl_2 (0.88 g), m.p. 140°C (lit. [18] 141-143°C).

Reaction of triphenylphosphine with trimethylsilyl peroxide

To a solution of 3.35 g (9.27×10^{-3} mol) of Ph_3P in 20 ml of ether a solution of 2.28 g (9.27×10^{-3} mol) of trimethylsilyl peroxide in 5 ml of ether was gradually added. The temperature of the mixture increased noticeably. After a short time (15 min) needle-like crystals precipitated. GLC analysis of the condensate gave the following products: $[(CH_3)_3Si]_2O$, (1.85 g, 82%) and $(CH_3)_3SiOH$ (0.19 g, 8.25%). The crystalline product (3.5 g, 99%) was pure Ph_3PO, m.p. 151-153°C.

Reaction of triphenylphosphine with triphenylgermanylperoxytetraphenylantimony

A mixture of 0.51 g (1.96×10^{-3} mol) of Ph_3P and 1.51 g (1.96×10^{-3} mol) of $Ph_4SbOOGePh_3$ in equal amounts (30 ml) of ether and THF was allowed to stand (15-20 h) at room temperature in argon. The reaction mixture did not contain peroxide oxygen. After removing the solvent in vacuum the residue was washed with alcohol. The filtrate yielded Ph_3PO (0.52 g, 98%), m.p. 144°C. The portion that was insoluble in alcohol had m.p. 184°C. The IR spectrum was the same as that of $Ph_4SbOGePh_3$, obtained by another method. Obtained: 1.47 g of substance (yield 99%).

Synthesis of triphenylgermanyloxytetraphenylantimony

Ph_4SbBr, 1.59 g (3.12×10^{-3} mol) in 150 ml of ether was placed in a flask provided with a stirrer and an arm for introducing ammonia, and 1.00 g (3.12×10^{-3} mol) of Ph_3GeOH in 100 ml of ether was added. While mixing a current of dry ammonia was passed through the solution for 15 min. The precipitated

NH_4Br was filtered off and the solvent was removed from the filtrate under reduced pressure. The solid residue was thoroughly washed with a small amount of ether and hexane. Obtained: 2.0 g (yield 85%) of $Ph_4SbOGePh_3$, m.p. 189-191°C. The product is stable in air, moderately soluble in ether and CH_2Cl_2, readily soluble in benzene, toluene and acetone, insoluble in hexane. The IR spectrum has an intense absorption band in the region 790 cm^{-1}, corresponding to vibrations of the Sb—O—Ge bonds. On reaction with HCl it is quantitatively converted into a mixture of Ph_4SbCl, m.p. 200-202°C (lit. [18] 205°C) and $(Ph_3Ge)_2O$, m.p. 178-180°C (lit. [21] 183-184°C).

Reaction of pentaphenylphosphorane with trimethylsilyl hydroperoxide

2.30 g (5.0×10^{-3} mol) of PPP in 50 ml of THF was placed in a three-necked flask fitted with a stirrer, a thermometer and drying tubes. The solution was cooled to —50°C and a solution of 0.53 g (5.0×10^{-3} mol) of trimethylsilyl hydroperoxide [22] in 50 ml of ether was slowly added. The reaction mixture was stirred for 3 h at —50°C after which the temperature was gradually raised to room temperature. The solvent and the liquid products were distilled off in vacuum. Found in the condensate: benzene (0.36 g, 90%) and $[(CH_3)_3Si]_2O$ (0.74 g, 99%). The residue was distilled with steam. Obtained: phenol, which was identified as tribromophenol (0.91 g, 73%), m.p. 92-93°C, and Ph_3PO (0.90 g, 86%), m.p. 150-152°C.

Reaction of pentaphenylphosphorane with triphenylgermyl hydroperoxide

A mixture of 1.37 g (3.3×10^{-3} mol) of PPP and 1.01 g (3.1×10^{-3} mol) of Ph_3GeOOH [23] in 50 ml of THF was allowed to stand for 24-48 h in an atmosphere of dry argon at room temperature until peroxide oxygen had completely disappeared. Found in the condensate of the solvent: benzene (0.21 g, 90%). The residue was washed with moist acetone and then with alcohol. Obtained: $(Ph_3Ge)_2O$ (0.92 g, 98%), m.p. 181°C. The alcohol filtrate was distilled with steam. Found in the condensate: phenol, which was identified as tribromophenol (0.89 g, 90%), m.p. 92°C. Obtained from the still residue: Ph_3PO (0.79 g, 95%), m.p. 152°C.

Reaction of benzyloxytetraphenylphosphorane with triphenylgermyl hydroperoxide

To a solution of Ph_4POCH_2Ph, obtained from 2.0 g PPP, in 10 ml of benzene 1.53 g of Ph_3GeOOH in 10 ml of benzene was added in small amounts in vacuum. The ampoule was cooled, filled with dry argon, sealed and allowed to stand overnight. The solvent was removed in vacuum. The residue, a dense viscous mass, did not contain peroxide oxygen. Distillation with steam gave phenol. Obtained: $C_6H_2Br_3OH$ (0.99 g, 70%), m.p. 92°C. The still residue was filtered. On treatment of the filtrate with KI Ph_4PI (0.14 g, 7%), m.p. 331°C precipitated. The solid residue was distilled with steam, washed with acetone and then with benzene. Obtained: $(Ph_3Ge)_2O$ (1.35 g, 95%), m.p. 180°C and from the filtrate Ph_3PO (1.01 g, 90%), m.p. 152°C, which was not depressed on mixing with pure oxide.

Reaction of pentaphenylphosphorane with triphenylsilyl hydroperoxide

The reaction was carried out under conditions similar to the reaction with Ph_3GeOOH. The THF (10 ml) solution of PPP (2.14 g, 5.14×10^{-3} mol) was added to an equal volume of Ph_3SiOOH [23] (1.5 g, 5.14×10^{-3} mol). After 40-50 h GLC analysis of the condensate of the liquid products gave benzene (0.34 g, 85%). The residue was treated with HCl in alcohol and distilled with steam. Found in the distillation products: phenol (1.53 g $C_6H_2Br_3OH$, 90%, m.p. 94-95°C). On addition of KI to the aqueous filtrate, Ph_4PI (1.18 g, 49.5%), m.p. 330-333°C, precipitated. After distillation in the usual manner, the residue yielded Ph_3PO (0.63 g, 44%), m.p. 149-150°C, $(Ph_3Si)_2O$ (0.63 g, 46%), m.p. 220-224°C and 0.45 g of viscous product not containing phosphorus. The IR spectrum of this product showed absorption bands which were attributed to Si—O and Si—C bonds.

Reactions carried out at 0°C gave similar results.

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