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REACTIONS OF TRIPHENYLSTIBINE WITH tert-BUTYL- AND TRIPHENYL-SILYL HYDROPEROXIDES

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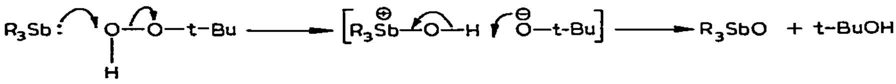
SUMMARY

Triphenylstilbene reacts with tert-butyl and cumyl hydroperoxides producing triphenylantimony oxide and the corresponding carbinols, the use of an initial reactant ratio of 3/1 producing oxide compounds of general formula $Ph_3Sb(OOR)_2$, where R = butyl, cumyl, in good yields.

The reaction of triphenylstibine with one equivalent of tert-butyl hydroperoxide followed by two equivalents of triphenylsilyl hydroperoxide produces a bi-elemental organic peroxide of formula $Ph_3Sb(OOSiPh_3)_2$ which liberates oxygen on thermal decomposition.

Reactions of triphenylstibine and triphenylphosphine with triphenylsilyl hydroperoxide (in a 1/1 ratio) gave hydroxy derivatives of antimony(V) or phosphorus(V) of the type $Ph_3M(OH)OSiPh_3$.

Reactions of organic derivatives of antimony(III) (organostibines) with hydroperoxide have not been investigated until recently despite the fact that the corresponding reactions with phosphorus are well known. In a recent publication Davies and co-workers[1] have shown that trialkylstibine, R_3Sb (R = Me, Et), reacts exothermically with tert-butyl hydroperoxide, quantitatively reducing the latter to a carbinol while the alkylstibine itself is oxidised to the corresponding antimony(V) alkyl oxide. No Sb–C bond cleavage occurs during this reaction and the authors assumed that the reaction mechanism is similar to that occurring during the oxidation of trialkylphosphines by hydroperoxides. Thus it was assumed that a nucleophilic attack by the organometallic compound on the peroxide oxygen occurs to give a hydroxymetallonium ion:



(1)

Deprotonation of this ion by the strongly nucleophilic tert-butyl oxy-anion produces trialkylantimony oxide and tert-butyl alcohol. In the presence of excess hydroperoxide, Ph_3SbO is then converted into the corresponding trialkylbis(tert-butylperoxy)-antimony:

$$R_3SbO + 2\ t\text{-}BuOOH \rightarrow R_3Sb(OO\text{-}t\text{-}Bu)_2 + H_2O \qquad (2)$$

In an independent study, we have studied the oxidation of triphenylstibine with tert-butyl, cumyl and triphenylsilyl hydroperoxides. Triphenylstibine reacted exothermically with an equivalent amount of tert-butyl hydroperoxide in benzene to give tert-butyl alcohol (0.95) and triphenylantimony oxide (0.94 mole per mole of hydroperoxide). When the initial ratio of reactants was $\frac{1}{3}$, the main product formed was triphenylbis(tert-butylperoxy) antimony, $Ph_3Sb[OOC(CH_3)_3]_2$, in 82% yield, together with tert-butanol and water. This latter peroxide was found to be identical to that prepared previously[2]. Similar reaction between triphenylstibine and cumyl hydroperoxide ($\frac{1}{3}$) produced triphenylbis(cumylperoxy)antimony (71% yield).

Reactions (1) and (2) may therefore provide a new and easier method of synthesizing not only alkyl-, but also phenyl-containing peroxides of the type $R_3Sb(OOR')_2$, materials which were first obtained by Rieche and co-workers from alkyl hydroperoxides and R_3SbX_2 (X = halogen or alkoxy group)[2].

We have used this method for the synthesis of the bielemental organo peroxide, $Ph_3Sb(OOSiPh_3)_2$. For this purpose the reaction of triphenylstibine with one equivalent of tert-butyl hydroperoxide was first undertaken and then two equivalents of triphenylsilyl hydroperoxide were quickly added to the reaction mixtures. In accordance with eqns. (1) and (2) a peroxy compound containing two triphenylsilylperoxy groups was obtained:

$$Ph_3Sb + t\text{-}BuOOH + 2\ Ph_3SiOOH \rightarrow Ph_3Sb(OOSiPh_3)_2 + t\text{-}BuOH + H_2O \qquad (3)$$

The yield of peroxide was 82%. The same peroxide, but in a smaller yield, (74%) was obtained by the reaction of triphenylantimony dihalide with triphenylsilyl hydroperoxide. We have proposed this latter reaction previously for the synthesis of the monoperoxide derivative, $Ph_4SbOOSiPh_3$.

$$Ph_3SbCl_2 + 2\ Ph_3SiOOH \xrightarrow{Et_3N} Ph_3Sb(OOSiPh_3)_2 + 2\ HCl \qquad (4)$$

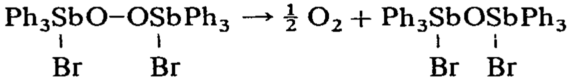
In a similar manner to tetraphenyl(triphenylsilylperoxy)antimony, $Ph_4SbOOSiPh_3$[3], in H_2SO_4 solution triphenylbis(triphenylsilylperoxy)antimony undergoes heterolytic scission of Sb–O and Si–O bonds producing H_2O_2 in quantitative yield.

$$Ph_3Sb(OOSiPh_3)_2 + 2\ H_2O + H_2SO_4 \rightarrow Ph_3SbSO_4 + 2\ Ph_3SiOH + H_2O_2 \qquad (5)$$

Unlike a monoperoxide, however, triphenylbis(triphenylsilylperoxy)antimony is relatively easily hydrolysed. If the material is held in contact with water for any length of time its reactivity noticably decreases and disappears completely after boiling in water for half an hour. The thermal decomposition of the diperoxide also proceeds in a different manner. It has been shown previously[3] that $Ph_4SbOOSiPh_3$ rearranges into a non-peroxy product on heating with the phenyl group migrating from the antimony atom to the oxygen:

$$Ph_4SbOOSiPh_3 \rightarrow Ph_3Sb(OPh)OSiPh_3 \rightarrow Ph_3SbO + Ph_3SiOPh \qquad (6)$$

The rearranged product is unstable and decomposes further to triphenylantimony oxide and a triphenylphenoxysilane. Under similar conditions (evacuated ampoules, 36 h, 100°) $Ph_3Sb(OOSiPh_3)_2$ decomposes to give a solid of high melting point and generates oxygen (0.84 mole per mole of initial peroxide). A similar decomposition has been described for $Ph_3Sb(Br)OOSb(Br)Ph_3$ peroxide, which on being heated for a short time in boiling benzene generated oxygen and was almost quantitatively converted to the oxide[4].



$$Ph_3\underset{\text{Br}}{\underset{|}{Sb}}O-O\underset{\text{Br}}{\underset{|}{Sb}}Ph_3 \longrightarrow \tfrac{1}{2}\,O_2 + Ph_3\underset{\text{Br}}{\underset{|}{Sb}}O\underset{\text{Br}}{\underset{|}{Sb}}Ph_3 \qquad (7)$$

In our experiments we have assumed that the diperoxide decomposes to produce compound (I) which possesses two Sb–O–Si bonds:

$$Ph_3Sb(OOSiPh_3)_2 \longrightarrow O_2 + \underset{\text{(I)}}{Ph_3Sb(OSiPh_3)_2} \qquad (8)$$

In order to identify compound (I) we have prepared this material by the following route:

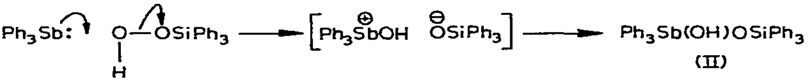
$$Ph_3SbCl_2 + 2\ Ph_3SiOH + 2\ NH_3 \longrightarrow Ph_3Sb(OSiPh_3)_2 + 2\ NH_4Cl \qquad (9)$$

Apparently, this reaction proceeds through the formation of an intermediate, $[Ph_3Sb{=}NH_2]^+Cl^-$, which then readily reacts with silanol. The product thus obtained (85% yield, m.p. 293°) was identical with compound (I), which was also confirmed by their reaction with HCl in alcohol. In both cases the compounds were converted to a mixture of Ph_3SbCl_2 and Ph_3SiOH in a quantitative ratio of $\frac{1}{2}$:

$$Ph_3Sb(OSiPh_3)_2 + 2\ HCl \longrightarrow Ph_3SbCl_2 + 2\ Ph_3SiOH \qquad (10)$$

It was interesting to investigate how triphenylsilyl hydroperoxide would oxidize triphenylstibine and triphenylphosphine, for if this peroxide is similar to tert-butyl hydroperoxide these organometallic compounds would be oxidised to the corresponding oxides of antimony(V) and phosphorus(V), while the hydroperoxide itself would be converted into triphenylsilanol.

It was found that the reaction of equimolar amounts of Ph_3Sb and Ph_3SiOOH in benzene proceeded exothermically. But on carrying out the reaction at 5–6° only one product, $Ph_3Sb(OH)OSiPh_3$ (II), was produced, the structure of which was confirmed by elemental analysis and IR spectroscopy. The mechanism of this reaction may be visualised as follows. In a similar manner to the reaction involving tert-butyl hydroperoxide, Ph_3Sb attacks the peroxide oxygen of triphenylsilyl hydroperoxide which has a reduced electronic density due to $d\pi$–$p\pi$ conjugation. Further deprotonation does not occur however and a new SbOSi bond is formed:



(11)

(II)

If reaction (11) is undertaken without cooling, the resulting product (II) readily loses water and is converted to an oxide (III) in which respect it is similar to the compounds $R_3SbCl(OH)$ and $R_2SbCl_2(OH)$. These latter compounds, as is well known, have not been obtained in their pure state, because of the extraordinary readiness with which they are converted into the corresponding oxides, $(R_3SbCl)_2O$ and $(R_2SbCl_2)_2O$ (R = phenyl, benzyl)[5]:

$$2\,\mathrm{Ph_3Sb(OH)OSiPh_3} \rightarrow \underset{\text{(III)}}{\mathrm{(Ph_3SbOSiPh_3)_2O}} + \mathrm{H_2O} \qquad (12)$$

On treatment with HCl (III) is quantitatively converted into a mixture of Ph_3SbCl_2 (0.98 mole) and Ph_3SiOPH (0.97 mole per mole of initial (III)), indicating the complete breakage of the SbOSb and SbOSi bonds in contrast to glacial acetic acid which only destroys the SbOSb bond:

$$\mathrm{(Ph_3SbOSiPh_3)_2O} + 2\,\mathrm{CH_3COOH} \rightarrow 2\,\underset{\text{(IV)}}{\mathrm{Ph_3Sb(OSiPh_3)OCOCH_3}} + \mathrm{H_2O} \qquad (13)$$

During the latter reaction a monoacetic derivative is formed whose analyses correspond to (IV).

When triphenylphosphine was allowed to react with triphenylsilyl hydroperoxide in a 1/1 ratio it was again found that only one product was formed whose molecular weight and elemental analysis were in complete agreement with the formula $Ph_3P(OH)OSiPh_3$ (V). The structure of the compound was also confirmed by IR spectra:

$$\mathrm{Ph_3P} + \mathrm{Ph_3SiOOH} \rightarrow \underset{\text{(V)}}{\mathrm{Ph_3P(OH)OSiPh_3}} \qquad (14)$$

Thus, the reaction of triphenylphosphine with triphenylsilyl hydroperoxide is exactly similar to the reaction of the antimony analogue. Quaternary phosphonium hydroxide, $R_4P^+OH^-$, readily decomposes to R_3PO and hydrocarbons[6]. In contrast, however, the product (V) is rather stable. Thus, lengthy heating (130°, 15 h) had no effect on the material and similar results were obtained after extensive heating with HCl in a water/dioxane medium or with KOH (20%). Heterolytic decomposition of the material was only achieved after heating with a 30% solution of HCl in alcohol for 8 hours, when Ph_3PO (m.p. 143–146°) and a mixture of Ph_3SiOH and $(Ph_3Si)_2O$ were obtained in quantitative yield:

$$\begin{tikzcd}
\mathrm{Ph_3P(OH)OSiPh_3} + 2\,\mathrm{HCl} \arrow[r] & \mathrm{Ph_3SiOH} \arrow[d, "-\mathrm{H_2O}"'] & + & \mathrm{Ph_3PCl_2} \arrow[d, "+\mathrm{H_2O}"] & (15) \\
& \mathrm{(Ph_3Si)_2O} & & \mathrm{Ph_3PO} + 2\,\mathrm{HCl} &
\end{tikzcd}$$

EXPERIMENTAL

Reaction of triphenylstibine with tert-butyl hydroperoxide

tert-Butyl hydroperoxide (0.71 g, 0.0079 mole) was added dropwise to a solution of triphenylstibine (2.8g, 0.0079 mole) in benzene (30 ml) under nitrogen. The temperature of the mixture increased immediately to ca. 40–50°. Analysis by GLC showed that tert-butyl alcohol (0.55 g, 95% yield) was the only volatile product present. The solid residue after washing with ether was shown to be triphenylantimony oxide, m.p. 219° (94% yield). The product was identical with that previously described[7].

When triphenylstibine (4.92 g, 0.0139 mole), stirred and cooled to 5–6°, was treated with 3 molar equivalents of hydroperoxide (3.75 g, 0.0417 mole), tert-butyl alcohol (0.84 g, 82% yield), water and triphenylbis(tert-butylperoxy)antimony (6.7 g, 82% yield), (m.p. 99°, from petr. ether, lit.[2] 101–102°) were obtained.

Reaction of triphenylstibine with cumyl hydroperoxide (1/3)

In a similar manner, reaction of triphenylstibine (4.19 g, 0.0119 mole) and cumyl hydroperoxide (5.81 g, 0.0357 mole) on stirring for 2 h gave 5.46 g of pure triphenylbis(cumylperoxy)antimony (71% yield), m.p. 85° (lit.[2] 87°).

Reaction of triphenylstibine with tert-butyl and triphenylsilyl hydroperoxides

To triphenylstibine (1.82 g, 0.0051 mole) in benzene (15 ml) a solution of tert-butyl hydroperoxide (0.46 g, 0.0051 mole) in benzene (5 ml) was added in a dropwise manner while the mixture was cooled, and to the latter, after 5 to 10 min, a solution of triphenylsilyl hydroperoxide (3.02 g, 0.0103 mole) in benzene (15 ml) was added. The reaction mixture was stirred continuously for 2 h at room temperature while the water and carbinol formed was azeotropically distilled at reduced pressure from the reaction system. After complete removal of the solvent 3.96 g (82% yield) of triphenylbis(triphenylsilylperoxy)antimony was obtained. (m.p. 120° with decomposition). The peroxide readily dissolves in benzene and toluene, only slightly in ether and acetone and is insoluble in petroleum ether. It is capable of quantitatively reducing iodine from an acidic KI solution. (Found: Sb, 13.18; Si, 6.18; active O, 6.71, mol.wt. cryoscop. in benzene, 930. $C_{54}H_{45}O_4SbSi_2$ calcd.: Sb, 13.01; Si, 6.01; active O, 6.85%; mol.wt., 936). After keeping the product in water at room temperature for 24 and 60 h respectively, the peroxy content of the material was found to have decreased to corresponding values of 80 and 50%.

Reaction of triphenylantimony dichloride with triphenylsilyl hydroperoxide

A solution of triphenylantimony dichloride (1.69 g, 0.0039 mole in ether (100 ml) was mixed with a solution of triphenylsilyl hydroperoxide (2.32 g, 0.0079 mole) in ether (50 ml). The mixture was cooled to 0° and continuously stirred triethylamine (12 ml) was added. A white solid (triethylammonium chloride) separated immediately. After stirring for 30 min at reduced pressure the ether solvent was reduced to about 1/3 of its initial volume. The triphenylbis(triphenylsilylperoxy)antimony which separated out was washed with cold water as quickly as possible and dried in a vacuum to give 2.76 g (74% yield) of product. The melting point, and the percentages of Si, Sb and active O present in the product were found to be the same as for the substance described above.

Thermal decomposition of triphenylbis(triphenylsilylperoxy) antimony

The peroxide (0.96 g, 0.0010 mole) was heated for 30 h at 100° in an evacuated ampoule. After having previously connected the ampoule to a special apparatus for measuring oxygen the latter was opened when 19.40 ml of oxygen corresponding to 0.84 mole per mole of initial peroxide was determined. The solid formed, $Ph_3Sb(OSiPh_3)_2$ (0.85 g, m.p. 290°), was carefully washed with ether and treated with HCl in alcohol. From the resulting mixture triphenylsilanol (0.49 g, 96% yield), m.p. 148° (lit.[8] 151–153°) and triphenylantimony dichloride (0.44 g, 100% yield), m.p. 140–142° (lit.[9] 141–143°) were obtained.

Synthesis of triphenylbis(triphenylsilyloxy)antimony

A solution of triphenylantimony dichloride (1.36 g, 0.0032 mole) in ether (150 ml) was mixed with 1.78 g (0.0064 mole) of triphenylsilanol in 50 ml of ether. Dry ammonia was passed through the mixture for 15 min with stirring. After storing for 24 h $Ph_3Sb(OSiPh_3)_2$ was separated, carefully washed with water and a small amount of acetone and dried *in vacuo*. Yield 2.48 g (85%), m.p. 293° without depression when mixed with the product of the thermal decomposition of triphenylbis(triphenylperoxy)antimony. The compound was slightly soluble in ether and benzene. (Found: Sb, 13.20; Si, 5.95. $C_{54}H_{45}O_2SbSi_2$ calcd.: Sb, 13.51; Si, 6.20%.)

Reaction of triphenylstibine with triphenylsilyl hydroperoxide

Method A. A solution of triphenylsilyl hydroperoxide (0.61 g, 0.0021 mole) in benzene (10 ml) was added dropwise with stirring and cooling (5–6°) under argon to a solution of triphenylstibine (0.74 g, 0.0021 mole) in the same quantity of benzene. The reaction mixture was allowed to stand overnight at 0°. The solvent was then removed when 1.29 g (95% yield) of $Ph_3Sb(OH)OSiPh_3$, m.p. 318°, was obtained. This material dissolved readily in benzene and THF but was insoluble in most other organic solvents. (Found: Si, 4.41; mol. wt. cryoscop. in benzene, 634. $C_{36}H_{31}O_2SiSb$ calcd.: Si, 4.35%; mol. wt., 645). The IR spectrum of the compound exhibited absorption maxima at 440–460, 988 and 1115 cm^{-1} respectively, characteristic of Sb–C, Sb–O–Si and Si–C bonds. Absorptions corresponding to the OH group could not be observed in spectra taken on solutions of the material in oil or benzene, and only in THF solution were such absorptions observed at 3030–3220 cm^{-1}, indicating intense intra-, and possibly, intermolecular actions.

Method B. To a solution of triphenylstibine (1.36 g, 0.0038 mole) in benzene (10 ml) under argon a solution of triphenylsilyl hydroperoxide (1.22 g, 0.0038 mole) was added. The mixture was heated strongly when a fine white crystalline solid, $(Ph_3SbOSiPh_3)_2O$, separated. The presence of water in the condensate of the solvents was detected by Fischer's method. The oxide obtained was washed several times with benzene and then with ether when 2.41 g (98% yield) was recovered. The substance did not melt below 320° and was insoluble in benzene, THF, ether, alcohol, bromoform and other organic solvents. (Found: Sb, 18.57; Si, 4.53. $C_{72}H_{60}O_3Sb_2Si_2$ calcd.: Sb, 19.12; Si, 4.41%.)

Heterolytical cleavage of bis[(triphenylsilyloxy)triphenylantimony]oxide, $(Ph_3SbOSiPh_3)_2O$

Method A. The product (0.66 g) was heated in the presence of alcohol containing excess HCl until it dissolved completely. The solvent was removed and the solid residue (0.72 g), was separated into Ph_3SbCl_2 (0.45 g, 97% yield, m.p. 141°) and Ph_3SiOH (0.27 g, 98% yield, m.p. 148°) by fractional crystallization from alcohol.

Method B. $(Ph_3SbOSiPh_3)_2O$ (1.52 g) was dissolved in glacial acetic acid by moderate heating (1–2 min, 30°). The volatile products were distilled off at reduced pressure and the residual $Ph_3Sb(OSiPh_3)OCOCH_3$ (1.50 g, 96% yield, m.p. 318°) washed with alcohol then with hexane and dried *in vacuo*. The product was readily soluble in benzene and ether. The acetate group was determined by titration with NaOH. (Found: Sb, 17.77; Si, 4.06; CH_3COO, 8.70; mol. wt., 676. $C_{38}H_{33}O_3SbSi$ calcd.: Sb, 17.75; Si, 4.07; CH_3COO, 8.59%; mol. wt., 687.)

When the monoacetate was treated with NaOH solution a product (m.p. 312°) was obtained. Its IR spectrum was found to be identical with the spectrum of $Ph_3Sb(OH)OSiPh_3$. Reaction with HCl produced an equimolar mixture of Ph_3SbCl_2 and Ph_3SiOH which were separated by conventional methods.

Reaction of triphenylphosphine with triphenylsilyl hydroperoxide

Triphenylsilyl hydroperoxide (1.80 g, 0.0062 mole) was treated with triphenylphosphine (1.63 g, 0.0062 mole) in ether (30 ml) under nitrogen using similar conditions to those described above, the temperature of the mixture increasing to 40–50°. After standing at room temperature for 24 h a crystalline solid $Ph_3P(OH)OSiPh_3$ separated (3.00 g, quantitative yield), m.p. 121–123° (washed with ether). The compound was readily soluble in benzene, moderately soluble in ether and insoluble in petroleum ether. (Found: C, 78.48; H, 6.00; Si, 5.15; mol. wt., 536. $C_{36}H_{31}O_2PSi$ calcd.: C, 78.00; H, 5.60; Si, 5.06%; mol. wt., 555.) The IR spectrum exhibited bands in the part of the spectrum corresponding to vibrations of P–Ph and Si–Ph bonds and also in that part of the spectrum associated with the OH group (3330–3400 cm^{-1}). A further band at 900 cm^{-1} was also present which was absent in the IR spectra of the initial substances and which, according to previous authors[10], may be ascribed to the SiOP groups.

The compound underwent heterolytical cleavage with HCl in a similar manner to the corresponding antimony derivatives.

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