Peroxides of Elements other than Carbon. Part XVII.[1] The Reaction of Trialkylstibines and Trialkylbismuthines with t-Butyl Hydroperoxide and with Oxygen

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t-Butyl hydroperoxide reacts with trialkylstibines, R_3M, to give the corresponding stibine oxides, R_3MO, but with trialkylbismuthines to give products such as $RO{\cdot}OBu^t$, ROH, and ROR. Both reactions are thought to involve the intermediate metallonium ion $R_3\overset{\delta+}{M}OH$, which undergoes nucleophilic attack on H when M = Sb, and on R when M = Bi.

The autoxidation of the stibines and bismuthines involves a radical chain reaction, and gives products similar to those obtained with t-butyl hydroperoxide. It is suggested that an alkylperoxymetallic compound, $R_2MO{\cdot}OR$, is formed by homolytic alkylperoxydealkylation at the metal, followed by reduction of the peroxide by R_3M.

Two principal types of heterolytic reaction are recognised to occur between organometallic compounds and hydrogen peroxide or alkyl hydroperoxides. In the first type, exemplified by the reaction of trialkylboranes [equation (1)], a peroxy-anion nucleophilically attacks the metal centre, and an alkyl group then takes part in a nucleophilic 1,2-migration from the metal to oxygen.[2]

$$R_3B + \bar{O}{\cdot}OH \longrightarrow R_2\overset{R}{\underset{|}{B}}{-}O{-}OH \longrightarrow R_2B{\cdot}OR + \bar{O}H \qquad (1)$$

Under neutral conditions, there is evidence for an accompanying homolytic process.[3]

In the second type of reaction, exemplified by trialkylphosphines,[4] nucleophilic attack by the metal at a peroxide oxygen atom gives an hydroxy-metallonium ion, which is then deprotonated by the displaced oxy nucleophile, leaving the metal in a higher oxidation state [equation (2)].

$$R_3P{:} + \underset{H}{O{-}OH} \longrightarrow R_3\overset{+}{P}{-}OH + \bar{O}H \longrightarrow R_3PO + H_2O \qquad (2)$$

The two classes of metals which undergo these two types of reaction with hydroperoxides also react in different ways with molecular oxygen. Alkyl derivatives of the metals of Groups IB, IIB, and IIIB give the corresponding alkylperoxymetallic compounds [*e.g.* equation (3)], and the reactions are established to involve a homolytic chain with the propagation steps shown in equations (4) and (5).[5]

$$R_3B \xrightarrow{O_2} R_2BO{\cdot}OR \xrightarrow{O_2} RB(O{\cdot}OR)_2 \qquad (3)$$

$$R{\cdot} + O_2 \longrightarrow RO{\cdot}O{\cdot} \qquad (4)$$

$$ROO{\cdot} + BR_3 \longrightarrow RO{\cdot}O{\cdot}BR_2 + R{\cdot} \qquad (5)$$

Trialkylphosphines, on the other hand, react with oxygen to give the corresponding phosphine oxide and phosphinate ester in equal amount, together with phosphonates and phosphates as minor products [equation (6)].[6]

$$R_3P + O_2 \longrightarrow R_3PO + R_2P(:O){\cdot}OR + RP(:O)(OR)_2 + O{:}P(OR)_3 \qquad (6)$$

The following homolytic reactions were proposed to account for these products. The individual steps (8) and (9) have subsequently been established by e.s.r. spectroscopy.[7]

$$RO{\cdot}O{\cdot} + R_3P \longrightarrow RO{\cdot} + O{:}PR_3 \qquad (7)$$

$$RO{\cdot} + R_3P \longrightarrow RO{\cdot}PR_2 + R{\cdot} \qquad (8)$$

$$RO{\cdot} + R_3P \longrightarrow R{\cdot} + O{:}PR_3 \qquad (9)$$

Relatively little work has been carried out on the reaction of trialkylstibines or trialkylbismuthines with oxygen. Tripropyl- and tributyl-stibine were reported to react with air to give the compounds R_3SbO,Sb_2O_3

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[1] Part XVI, A. G. Davies and B. P. Roberts, *J. Chem. Soc.* (*B*), 1969, 317.

[2] A. G. Davies, 'Progress in Boron Chemistry,' vol. I, ed. H. Steinberg and A. L. McCloskey, Pergamon Press, Oxford, 1964, ch. 6.

[3] D. B. Bigley and D. W. Payling, *J. Chem. Soc.* (*B*), 1970, 1811; A. G. Davies and R. Tudor, *ibid.*, p. 1815.

[4] L. Horner and W. Jurgeleit, *Annalen*, 1955, **591**, 138.

[5] See ref. 1 and preceding papers.

[6] S. A. Buckler, *J. Amer. Chem. Soc.*, 1962, **84**, 3093.

[7] A. G. Davies and B. P. Roberts, *J. Organometallic Chem.*, 1969, **19**, P17; J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, 1969, **91**, 3944.

and R_3SbO,[8] but tribenzylstibine [9] and dimethylhalogenostibines [10] did not undergo carbon–metal bond cleavage and gave only the oxides $(PhCH_2)_3SbO$ and Me_2XSbO (X = Cl or Br) respectively.

Calingaert and his co-workers studied the autoxidation of triethylbismuthine.[11] Extensive cleavage of the alkyl–bismuth bonds occurred, and a solid was formed with the composition $Et_{0.6}BiO_{1.9}$ corresponding to a mixture of 77 mole % of EtOBiO and 23 mole % of Bi_2O_3. Diethyl peroxide, diethyl ether, ethanol, and gaseous hydrocarbons were also identified, and were thought to be formed by the breakdown of excited ether molecules [equation (10)].

$$[Et_2O]^* \longrightarrow Et_2O + Et_2O_2 + EtOH + C_2H_4 \qquad (10)$$

We report here a preliminary investigation of the reaction of trialkylstibines and trialkylbismuthines with t-butylhydroperoxide and with molecular oxygen. A novel peroxide reaction mechanism is postulated to account for the reactions of the bismuthines.

RESULTS

Trimethyl- and triethyl-stibine reacted vigorously with t-butyl hydroperoxide, reducing it essentially quantitatively to t-butyl alcohol, and being oxidised themselves to the corresponding stibine(v) oxide. No alkyl–metal bond cleavage could be detected [equation (11) R = Me or Et]. Further hydroperoxide then converted the stibine oxides into the trialkyldi(alkylperoxy)stibines [equation (12)] (see Table 1).

$$R_3Sb + Bu^tO{\cdot}OH \longrightarrow R_3SbO + Bu^tOH \qquad (11)$$

$$R_3SbO + 2Bu^tO{\cdot}OH \longrightarrow R_3Sb(O{\cdot}OBu^t)_2 + H_2O \qquad (12)$$

The reaction of trialkylbismuthines (R_3Bi) with t-butyl hydroperoxide was quite different. Trimethylbismuthine reacted mildly exothermically, and triethylbismuthine rather more vigorously. A solid was deposited, and g.l.c. analysis showed that the volatile products were t-butyl alcohol, the appropriate alcohols, alkyl t-butyl peroxides, and dialkyl ethers (ROH, $RO{\cdot}OBu^t$, and ROR respectively) and small amounts of alkanes and alkenes derived from the group R. Details are given in Table 1.

Attempts were made to detect free-radical intermediates in these reactions. When triethylbismuthine was treated with t-butyl hydroperoxide (2·58 mol.) in the presence of 2,2,6,6-tetramethyl-4-oxopiperidine 1-oxyl (0·033 mole) in an e.s.r. cavity, the amplitude of the triplet spectrum of the nitroxide decayed to zero during 42 min. The n.m.r. spectrum showed that under these conditions, no hydrocarbons were formed. Blank experiments showed that the nitroxide was stable to the other two reagents singly.

Similarly when t-butyl hydroperoxide (2×10^{-6} moles) was added to a benzene solution of triethylbismuthine (3×10^{-6} moles) and 2-methyl-2-nitrosopropane ($0{\cdot}65 \times 10^{-5}$ moles) the characteristic e.s.r. spectrum of ethyl t-butyl nitroxide (a_N 15·3 G, $a_{\beta H}$ 10·3 G) was immediately apparent, reaching a maximum intensity after 45 min. before slowly decaying. Trimethylbismuthine similarly gave rise to the spectrum of methyl t-butyl nitroxide after 43 min., increasing slightly after 145 min., but the signal was very weak, perhaps because the nitroxide decomposes rapidly. Blank experiments showed that all three reagents were needed to give rise to the radicals.

The reactions of the organometallic compounds with oxygen were then investigated.

Trimethylstibine in benzene absorbed 1·13 mol. of oxygen in 35 min. after an induction period of 3 min. During the reaction, a white, water-soluble peroxidic solid separated. It liberated iodide from potassium iodide solution, but the colour of the iodide was rapidly destroyed leaving a pale yellow solution, and the peroxidic content could not be determined; all the organostibines which were studied showed this behaviour. The empirical composition is given in Table 1, but the product could not be fully characterised. Methanol was identified (g.l.c.) as the only volatile product.

TABLE 1

Products from the interaction of trialkylstibines and trialkylbismuthines with t-butyl hydroperoxide and with oxygen

R_3M	Oxidant	Products
Me_3Sb	1 $Bu^tO{\cdot}OH$	0·82 Me_3SbO, 1·00 Bu^tOH
	3 $Bu^tO{\cdot}OH$	0·96 $Me_3Sb(O{\cdot}OBu^t)_2$, 1·00 Bu^tOH
Et_3Sb	1 $Bu^tO{\cdot}OH$	0·93 Et_3SbO, 0·97 Bu^tOH
	3 $Bu^tO{\cdot}OH$	0·92 $Et_3Sb(O{\cdot}OBu^t)_2$, 0·97 Bu^tOH
Me_3Bi	3 $Bu^tO{\cdot}OH$	2·01 Bu^tOH, 0·85 MeOH, 0·29 MeOMe, 0·95 $MeO{\cdot}OBu^t$
Et_3Bi	3 $Bu^tO{\cdot}OH$	2·02 Bu^tOH, 0·59 EtOH, 0·06 EtOEt, 0·99 $EtO{\cdot}OBu^t$
Me_3Sb	1·13 O_2	$C_{1·3}H_{4·4}SbO_{2·5}$, 0·31 MeOH
Et_3Sb	1·32 O_2	$C_{2·3}H_{6·6}SbO_{2·5}$, 0·67 EtOH, 0·35 MeCHO
Me_3Bi	1·71 O_2	$C_{0·46}H_{1·68}BiO_{4·0}$, 0·21 MeOH, 0·33 MeOMe, 0·53 $(MeO)_2$
Et_3Bi	1·78 O_2	$C_{0·28}H_{0·63}BiO_{2·5}$, 0·29 EtOH, 0·08 EtOEt, 0·52 $(EtO)_2$ *
$Me_3Bi + Et_3Bi$	3·56 O_2	0·31 MeOMe, 0·18 $(MeO)_2$, 0·23 EtOH, 0·10 EtOEt * 0·41 $(EtO)_2$, 0·53 MeOEt, 0·25 $MeO{\cdot}OEt$
Me_2SbBr	0·48 O_2	$Me_2Sb(O)Br$
Et_2SbBr	0·65 O_2	$Et_2Sb(O)Br$, EtOH, MeCHO (traces)

* Small amounts of ethylene, ethane, and butane were also detected by g.l.c. Yields are quoted in moles of product per mole of reactant.

Galvinoxyl (0·06 mole %) inhibited the oxidation for 55 min. (see Figure 1), before the brown colour faded and the autoxidation commenced at the usual rate. Phenothiazine (0·05 mole %) gave an induction period of 75 min., before oxygen was absorbed very much more slowly.

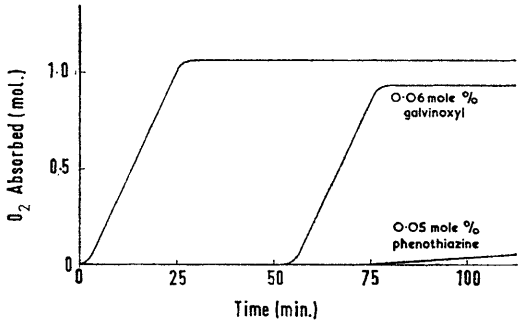


FIGURE 1 The autoxidation of trimethylstibine

[8] W. J. Jones and W. J. C. Dyke, *J. Chem. Soc.*, 1930, 1921.
[9] I. P. Tsukervanik and D. Smirnov, *Zhur. obshchei. Khim.*, 1937, **7**, 1527.
[10] G. T. Morgan and G. R. Davies, *Proc. Roy. Soc.*, 1926, *A*, **110**, 523.
[11] G. Calingaert, H. Soroos, and W. Hnizda, *J. Amer. Chem. Soc.*, 1942, **64**, 392.

The autoxidation of triethylstibine in benzene or cyclohexane was very much faster; again a white, water-soluble solid was deposited, and ethanol and acetaldehyde were identified by g.l.c. Galvinoxyl inhibited the reaction; 2,2,6,6-tetramethyl-4-oxo-piperidine 1-oxyl and phenothiazine were less effective, but gave definite induction periods of less than 1 min. When the reaction was carried out in the presence of 2-methyl-2-nitrosopropane, the e.s.r. spectrum of ethyl t-butyl nitroxide and of di-t-butyl nitroxide became apparent. Details of the reactions are given in Table 1 and in Figure 2.

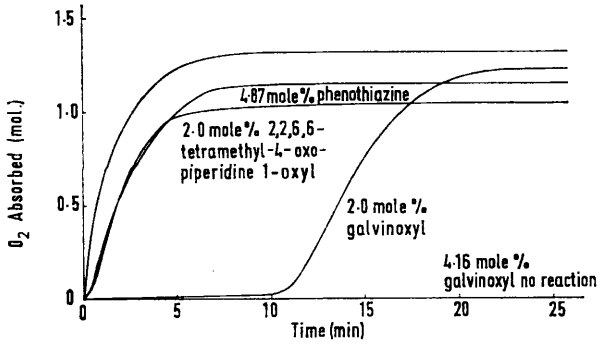


FIGURE 2 The autoxidation of triethylstibine

Dimethylphenylstibine slowly absorbed *ca.* 0·8 mol. of oxygen in 24 hr. to give a solid product and methanol. Diethylphenylstibine absorbed 1·1 mol. of oxygen in 14 min. giving ethanol (0·13 mol.) and a finely divided white solid. Galvinoxyl and the nitroxide showed the same inhibitory effect as they did with triethylstibine.

The autoxidation of the bismuthines was also subject to inhibition but the reaction products were different.

The autoxidation of trimethylbismuthine in benzene is illustrated in Figure 3. Galvinoxyl, phenothiazine, and

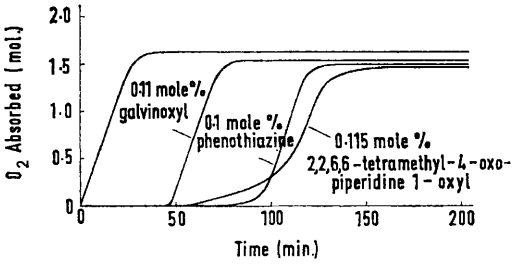


FIGURE 3 The autoxidation of trimethylbismuthine

2,2,6,6-tetramethyl-4-oxopiperidine 1-oxyl were all effective inhibitors. A pale yellow non-peroxidic solid separated during the reaction, and methanol, dimethyl ether, and methyl t-butyl peroxide were identified in solution (see Table 1). When the reaction was carried out in the presence of 2-methyl-2-nitrosopropane, no e.s.r. signal due to methyl t-butyl nitroxide was detected. To test whether a dialkyl peroxide might become involved in the reaction, the autoxidation was conducted in the presence of a molar equivalent of diethyl peroxide; the peroxide survived and was recovered.

The autoxidation, and its inhibition, of triethylbismuthine in benzene is illustrated in Figure 4. Again, a pale yellow solid was deposited during the reaction, and ethanol, diethyl ether, and diethyl peroxide were identified in the products by g.l.c. (see Table 1); this substantiates Calingaert's work, in which the reaction was carried out on the neat bismuthine at low temperature, and the products were identified by fractional distillation.[11]

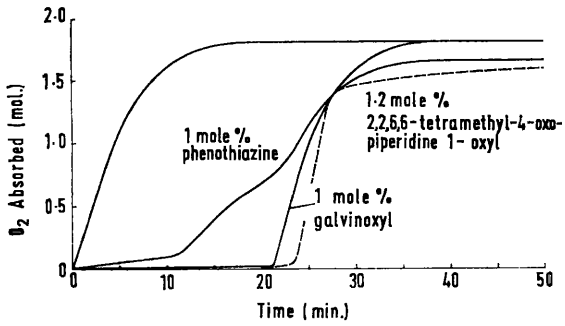


FIGURE 4 The autoxidation of triethylbismuthine

To check whether mixed dialkyl peroxides or ethers would be formed by the interbreeding of alkyl groups derived from two different bismuthines, equimolar amounts of trimethyl- and triethyl-bismuthine were autoxidised in mixture in benzene. The products are given in Table 1.

Dimethylbromostibine and diethylbromostibine in benzene were also subjected to autoxidation. The two reactions proceeded at about the same rate, but the ethyl compound

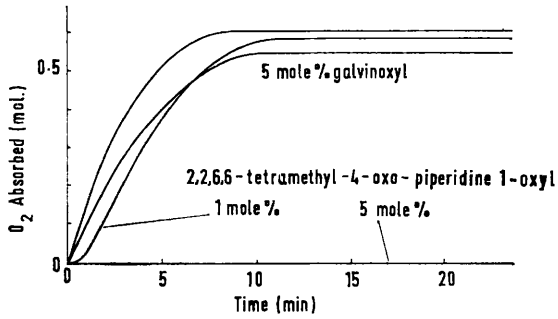
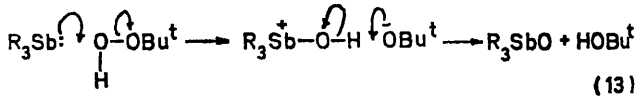


FIGURE 5 The autoxidation of diethylbromostibine

absorbed rather more than 0·5 mol. of oxygen, and some cleavage of the ethyl–antimony bonds was apparent. The effect of inhibitors on the autoxidation of diethylbromostibine is shown in Figure 5. No inhibition experiments were performed on dimethylbromostibine.

DISCUSSION

Oxidation by t-Butyl Hydroperoxide.—The oxidation of trialkystibines to the corresponding stibine(v) oxides by t-butyl hydroperoxide is analogous to the oxidation of trialkylphosphines [equation (2)], and in all probability proceeds by a similar mechanism, involving an S_N2 reaction by the antimony at an oxygen centre [equation (13)].



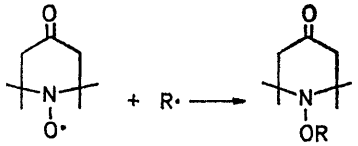
(13)

This reaction provides an easier preparation of the stibine oxides than that which has been used previously, which involves converting the trialkylstibine to the trialkyldibromostibine, then hydrolysing this on a basic

ion-exchange resin, and dehydrating the dihydroxide at 120°/1 mm.[12]

Further reaction of the stibine oxides with t-butyl hydroperoxide to give the peroxides $R_3Sb(O{\cdot}OBu^t)_2$ then involves nucleophilic substitution by the hydroperoxide at antimony. The overall reaction of a trialkylstibine with 3 molar equivalents of hydroperoxide provides a very easy new route to these peroxides, which have been prepared previously by Rieche and Dahlmann from the reaction of a variety of compounds of the general formula R_3SbX_2 with alkyl hydroperoxides.[13]

The reaction of trialkylbismuthines with t-butyl hydroperoxide is relatively complex. Bismuth(v) compounds of the type R_3BiO are apparently unknown, and the oxidation involves not a change in the oxidation state of the metal, but oxidative cleavage of the alkyl–bismuth bonds. The most surprising feature of the reaction is the fact that the products include the dialkyl peroxides, $RO{\cdot}OBu^t$, and the ethers, ROR. The small amounts of hydrocarbons which were detected are probably formed *via* the free radical R·, which can be trapped by 2,2,6,6-tetramethyl-4-oxopiperidine 1-oxyl, which is a specific scavenger for alkyl radicals by reaction (14). E.s.r. spectroscopy of the nitroxyl (I) which was produced [equation (15)] when the nitrosoalkane was used as a scavenger confirm the identity of the alkyl radical R· which was being trapped.



(14)

$$Me_3C{\cdot}NO + R{\cdot} \longrightarrow Me_3C{-}N(O{\cdot}){-}R \quad (I) \qquad (15)$$

These inhibitors, however, appeared to have no effect on the formation of the compounds $RO{\cdot}OBu^t$, ROR, and ROH. The C–Bi bond is weak [$D(Me_2Bi{-}Me) = 44{\cdot}0$ kcal. mol.$^{-1}$; $D(Me_2Sb{-}Me) = 57{\cdot}0$ kcal. mol^{-1}],[14] and an S_H2 reaction by the t-butylperoxy- or alkoxy-radicals at carbon would be highly exothermic; we are reluctant, however, to postulate such a process in the absence of any precedent or corroborating evidence.

It appears more likely that the peroxide, ether, and alcohol are products of a heterolytic process. We suggest that the trialkylbismuthine nucleophilically attacks the β-oxygen atom of the hydroperoxide [*cf.* equation (13) for antimony]; the Bi^V state, however, is much less stable than Sb^V. Nucleophilic attack on the bismuthonium ion (II) therefore does not occur at the proton, but the powerfully nucleophilic t-butylperoxy-anion, which is formed in reaction (17) attacks at carbon, to give the dialkyl peroxide:

$$R_3Bi{:}\curvearrowright\ O(H){-}\overset{\curvearrowright}{O}Bu^t \longrightarrow \underset{(II)}{R_3\overset{+}{B}i{-}OH} + \bar{O}Bu^t \qquad (16)$$

$$Bu^t\bar{O} + Bu^tO{\cdot}OH \rightleftharpoons Bu^tOH + Bu^tO{\cdot}O^- \qquad (17)$$

$$Bu^tO{\cdot}O^- \curvearrowright\ R{-}\overset{\curvearrowright}{\overset{+}{B}}i(OH)R_2 \longrightarrow Bu^tO{\cdot}OR + R_2Bi{\cdot}OH \qquad (18)$$

The alcohol ROH might arise by a similar reaction of ŌH (from $R_2Bi{\cdot}OH$), and the ether, ROR, would, in turn, be formed by nucleophilic attack by RO^- from the alcohol.

The fact that compounds of the type $R_3Bi^VX_2$ are known where R is aryl or vinyl, but not alkyl[15] is consistent with this interpretation: the alkyl compounds decompose to Bi^{III} derivatives by the above mechanism, but nucleophilic attack on the aryl or vinyl group takes place much less readily. A similar decomposition mechanism, in which electrophilic alkylation is coupled with a drop in the oxidation state of the metal from n to $n - 2$, is recognised to occur for some other organometallics; for example, the general instability of the monoalkylthallium(III) compounds, $RTlX_2$, with respect to RX and Tl^IX, has recently been discussed in these terms.[16]

The traces of hydrocarbon products which are formed when radical scavengers are absent, probably arises through a parallel homolytic process involving molecule-induced homolysis [equation (19)] and which is a small fraction of the total reaction.

$$R_3Bi + O(H){-}OBu^t \longrightarrow R{-}BiR_2 \leftarrow O(H){-}OBu^t \longrightarrow R{\cdot} + R_2Bi{\cdot}OH + {\cdot}OBu^t \qquad (19)$$

Parallel heterolytic and homolytic processes have been observed previously in the reaction of trialkylboranes with neutral hydrogen peroxide[3] and with *N*-chlorodimethylamine.[17]

Autoxidation.—The effect of inhibitors on the autoxidation of trialkyl-stibines and -bismuthines establishes unequivocally that these reactions proceed by a radical chain mechanism. The effect of the nitroxyl scavenger suggests that, in all probability, an alkyl radical is a chain carrier. Reaction (20) can therefore be assumed.

$$R{\cdot} + O_2 \longrightarrow RO{\cdot}O{\cdot} \qquad (20)$$

Oxidative dealkylation of the metal could then take place by reactions (21)—(23).

$$RO{\cdot}O{\cdot} + MR_3 \longrightarrow \underset{(III)}{RO{\cdot}OMR_2} + R{\cdot} \qquad (21)$$

$$RO{\cdot}O{\cdot} + MR_3 \longrightarrow RO{\cdot} + OMR_3 \qquad (22)$$

$$RO{\cdot} + MR_3 \longrightarrow RO{\cdot}MR_2 + R{\cdot} \qquad (23)$$

Reaction (21), which produces an alkylperoxymetallic compound (III), is that which is now accepted for the

[12] G. Long, G. O. Doak, and L. D. Freedman, *J. Amer. Chem. Soc.*, **1964**, **86**, 209.
[13] A. Rieche, J. Dahlmann, and D. List, *Annalen*, 1964, **678**, 167; D.B.P. 1,158,975.
[14] L. H. Long, *Pure and Appl. Chem.*, 1961, **2**, 61.
[15] P. G. Harrison, *Organometallic Chem. Rev.*, 1970, **5**, 183.
[16] M. D. Johnson, *Chem. Comm.*, 1970, 1037.
[17] A. G. Davies, S. C. W. Hook, and B. P. Roberts, *J. Organometallic Chem.*, 1970, **23**, C11.

organic compounds of many other metals; it gains support from the demonstration by e.s.r. that the similar reaction of alkoxyl radicals [equation (23)] takes place when t-butoxyl radicals are generated in the presence of trialkylstibines or trialkylbismuthines.[7] For the stibines, where the +(v) oxidation state is readily accessible (as it is in the phosphines), reaction (21) may be in competition with reaction (22), which might be followed by the alkoxydealkylation (23).

The products which are isolated are principally those resulting from the interaction of the initially formed peroxides (III) with the organometallic compounds, and resemble closely the products which were identified from the reactions of t-butyl hydroperoxide with the trialkylbismuthines (see Table 1). Calingaert reported [11] that, on one occasion, autoxidation of triethylbismuthine at −60° to −50° gave an unstable compound which decomposed vigorously on warming; it was suggested that this compound was a peroxide of the structure $Et_3Bi{\cdot}O{\cdot}O$.

The insoluble solids which separated during the autoxidation reactions appear to be polymeric metal oxides containing an average of one or less than one alkyl group per metal atom. Their compositions are not reproducible probably because the degree of oxidative dealkylation depends on the stage in the reaction at which the partially oxidised material separates from solution.

The autoxidation of the dialkylbromostibines also follows a homolytic chain process, but the metal is not dealkylated. The electronegative bromine stabilises the Sb^V oxidation state, and the autoxidation probably proceeds by a mechanism similar to that which has been proposed for phosphites, [equations (24)—(26)].[18] Reactions of this type may be important during the later stages of the autoxidation of both trialkylstibines and trialkylbismuthines.

$$R^{\cdot} + O_2 \longrightarrow RO{\cdot}O^{\cdot} \quad (24)$$

$$ROO^{\cdot} + R_2BrSb \longrightarrow RO^{\cdot} + R_2BrSbO \quad (25)$$

$$RO^{\cdot} + R_2BrSb \longrightarrow R^{\cdot} + R_2BrSbO \quad (26)$$

EXPERIMENTAL

Preparation of Compounds.—Trimethylstibine [b.p. 76—77°, 67% yield; lit.,[19] b.p. 78·5°, τ(CCl_4) 9·25], triethylstibine [b.p. 161°, 77% yield; lit.,[20] b.p. 161°, τ (CCl_4) 8·79—8·89, $J/\delta = 10$], trimethylbismuthine [b.p. 107°, 50% yield; lit.,[20] b.p. 107°, τ 8·99], and triethylbismuthine [b.p. 36°/0·5 mm., 78% yield; lit.,[21] b.p. 48°/1 mm., τ (CCl_4) 8·3—8·35, $J/\delta \longrightarrow \infty$] were prepared by treating the appropriate metal trichloride with an alkylmagnesium halide.

Addition of bromine to the trialkylstibine gave the dibromotrialkylstibines, which gave the bromodialkylstibines on pyrolysis. These reacted with phenylmagnesium bromide in ether to give the dialkylphenylstibines. Details of these compounds are given in Table 2.

Reactions with t-Butyl Hydroperoxide.—Trimethylstibine. t-Butyl hydroperoxide (0·141 g.) was injected through a self-sealing rubber serum cap into a solution of trimethylstibine (0·261 g., 3 mol.) in benzene (5 ml.) under nitrogen. The temperature of the mixture rose immediately to *ca.* 50°. Analysis by g.l.c. showed that t-butyl alcohol was the only volatile solute present. Trimethylstibine oxide was recovered from the solution in 82% yield, m.p. 180°, τ [in D_2O as $Me_3Sb(OH)_2$] 8·41 (Found: C, 19·5; H, 4·9; Sb, 65·9. Calc. for C_3H_9OSb: C, 19·7; H, 4·9; Sb, 66·1%). This was identical with the material prepared by Long, Doak, and Freedman's method.[12]

TABLE 2

Organoantimony compounds

Compd.	B.p. (mm.)	Yield (%)	Found (%) C	H	Hal	Reqd. (%) C	H	Hal	τ
Me_3SbBr_2	m.p. 195° [e]	72	11·1	2·9	49·1	11·0	2·8	48·9	*f*
Et_3SbBr_2	111 (0·1)	62	19·6	4·4	43·3	19·6	4·1	43·3	*g*
Me_2SbBr [a]	43 (2·8) [d]	85	10·1	2·8	34·4	10·4	2·6	35·0	
Et_2SbBr [b]	56 (1·7)	63	18·4	4·0	26·9	18·5	3·9	27·0	
Me_2PhSb	96 (12) [e]	26	42·1	4·7	52·7	42·0	4·8	53·2	*h*
Et_2PhSb	87 (0·1)	96	46·4	5·9	46·6	46·8	5·8	47·4	*i*

[a] From pyrolysis at 210°/90—100 mm. [b] From pyrolysis at 170—180°/400—410 mm. Lit. values: [e] 192—193° [12]; [d] 107°/90 mm.[22]; [e] 95°/10 mm.[23]. τ Values: [f] 8·10 (in D_2O); [g] 8·45 (t, CH_3), 7·22 (q, CH_2) J 8 Hz (in D_2O); [h] 2·50—3·10 (Ph), 9·10 (CH_3) (in CCl_4); [i] 8·2—9·0 $J/\delta = 0·5$ (in CCl_4), 2·40—3·0 (Ph).

When the stibine was treated under the same conditions with 3 molar equivalents of the hydroperoxide, water and a white solid immediately separated. The solid was purified by sublimation at 40—50°/0·1 mm., yielding bis-(t-butylperoxy)trimethylstibine (86% yield) m.p. 79—80° (lit.,[13] 82—84°), τ 8·48 (Me) and 8·87 (Bu^t) (Found: C, 38·2; H, 7·4; Sb, 34·9; active O, 18·8. Calc. for $C_{11}H_{27}O_4Sb$: C, 38·3; H, 7·9; Sb, 35·3; active O, 18·6%).

Triethylstibine. Under similar conditions, triethylstibine reacted with 1 molar equiv. of t-butyl hydroperoxide to give *triethylstibine oxide* as a white amorphous powder which was thoroughly washed with ice-cold pentane; 93% yield, m.p. 167—168° (Found: C, 32·5; H, 6·6; Sb, 53·9. $C_6H_{15}OSb$ requires C, 32·1; H, 6·7; Sb, 54·1%). This was identical with the material obtained by hydrolysing dibromotriethylstibine on an Amberlite 1R4B (OH) ion exchange resin, and then dehydrating the dihydroxide at 120°/0·1 mm. for 2 hr., followed by sublimation at 150°/0·04 mm. (52% yield).

In the air, the oxide was hydrolysed back to the *dihydroxide*, which is a viscous oil (Found: C, 29·6; H, 6·9; Sb, 49·8. $C_6H_{17}O_2Sb$ requires C, 29·7; H, 7·0; Sb, 50·0%).

When the stibine was treated with 3 molar equivalents of the hydroperoxide, *bis-(t-butylperoxy)triethylstibine* was obtained as a pale yellow liquid (92% yield) which could not be distilled; τ 7·8—8·8 (complex C_2H_5), 8·87 (Bu^t) (Found: C, 43·5; H, 8·6; Sb, 31·6. $C_{14}H_{33}O_4Sb$ requires C, 43·5; H, 8·6; Sb, 31·4%).

Trimethylbismuthine. t-Butyl hydroperoxide (0·453 g., 3 mol.) was injected into a solution of trimethylbismuthine

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(1·675 g.) in benzene (5 c.c.) under nitrogen. A mildly exothermic reaction occurred, and a pale yellow solid was deposited during 40 min. After 24 hr., the volatile products were analysed by g.l.c., giving the results recorded in Table 1.

Triethylbismuthine. The same procedure was used as above.

Autoxidation Reactions.—The apparatus used was similar to that described previously, except that aliquots of standard solutions of the organometallic reagent were injected into the solvent in the flask by means of a calibrated syringe passing through a self-sealing rubber cap. The results are given in Table 1.

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