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PEROXIDES OF ELEMENTS OTHER THAN CARBON XIII*. THE PREPARATION OF SOME TRIALKYLTIN(IV) AND DIALKYLTIN(IV) PEROXIDES**

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SUMMARY

High yields of alkyl trialkyltin peroxides, $R_3Sn{-}O{-}OR'$, are obtained by azeotropic dehydration of mixtures of a trialkyltin oxide or hydroxide and an alkyl hydroperoxide. The corresponding reaction with dialkyltin oxides yields the diperoxydistannoxanes, $R'O{-}O{-}SnR_2{-}O{-}SnR_2{-}O{-}OR'$. The structures of these and related compounds are discussed.

DISCUSSION

Trialkyltin alkoxides have usually been prepared by treating trialkyltin chlorides with the appropriate sodium alkoxides. The trialkyltin alkyl peroxides ($R_3Sn{-}O{-}OR'$) were obtained by a similar reaction involving the sodium alkyl peroxide[2], or by treating a trialkyltin alkoxide with an alkyl hydroperoxide[3].

A more convenient preparation of the trialkyltin alkoxides was recently reported, in which a mixture of a bis(trialkyltin) oxide and an alcohol was subjected to azeotropic dehydration: this procedure is quick, the yields are high, and no transfer of the air-sensitive alkoxide is involved[4].

It therefore seemed probable that the azeotropic dehydration of mixtures of trialkyltin oxides or hydroxides, and alkyl hydroperoxides might provide a more convenient route to the alkyl trialkyltin peroxides (eqn. 1). A similar method has already been used for preparing alkyl triethyllead peroxides[5].

$$(R_3Sn)_2O + 2\,R'{-}O{-}OH \rightarrow 2\,R_3Sn{-}O{-}OR' + H_2O \qquad (1)$$

Triphenyltin tert-butyl peroxide and triphenyltin 2-phenyl-2-propyl peroxide were each obtained in 90% yield by azeotropic dehydration at room temperature of a mixture of bis(triphenyltin) oxide and an excess of the appropriate alkyl hydroperoxide in benzene. With bis(tributyltin) oxide a solvent was not necessary, and a quantitative yield of tributyltin tert-butyl peroxide was obtained simply by subjecting a mixture of the oxide and hydroperoxide to reduced pressure.

Trimethyltin hydroxide reacted with an equimolar amount of tert-butyl

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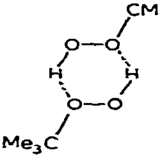
* For Part XII see ref. 1a.

** Some of the present work has been preliminarily reported[1b].

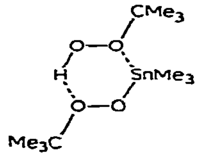
hydroperoxide in the presence of magnesium sulphate as a dehydrating agent, to give trimethyltin tert-butyl peroxide, but the use of an excess of the hydroperoxide gave a considerable amount of a complex with the composition $Me_3Sn{-}O{-}O{-}CMe_3 \cdot HO{-}O{-}CMe_3$. The free peroxide is a mobile liquid whereas the complex, which could also be synthesised from its components, is a crystalline solid, m.p. 28°, which can be recrystallised from pentane, and sublimed *in vacuo*.

From a study of the infrared spectrum, Walling and Heaton[6] suggested that tert-butyl hydroperoxide formed a hydrogen-bonded dimer (I), and we have found that trimethyltin tert-butyl peroxide is also partially associated (in benzene), presumably by coordinative bonding into dimers of the structure (III). The complex $Me_3Sn{-}O{-}O{-}CMe_3 \cdot HO{-}O{-}CMe_3$ might then involve both types of bonding, as illustrated in (II).

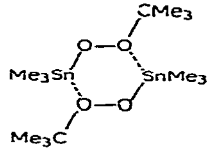
At 20° in dichloromethane solution (13%) the hydroxylic proton showed a sharp NMR signal 3.34 ppm downfield from the solvent, compared with 2.15 ppm in a solution containing the equivalent concentration of free hydroperoxide (3.3%). At −40° the signal for the complex hydroxyl shifted to 4.87 ppm downfield from dichloromethane and the signal broadened, then at −80° a sharp signal was obtained 6.03 ppm downfield from dichloromethane. This suggests that the complex is in equilibrium with free hydroperoxide at room temperature and that the association increases as the temperature is lowered.



(I)



(II)

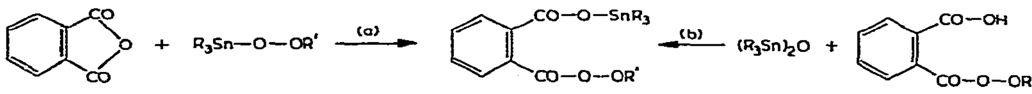


(III)

An analogous complex of the composition $[Et_3Sn{-}O{-}OH]_2 \cdot HO{-}OH$ has previously been reported; studies of its molecular weight showed that it dissociated in solution[7]. The formation of these compounds emphasises once again the basicity of an oxygen atom which is bonded to tin. The only comparable complexes of other metals which appear to have been reported[8] are the compounds $[PhCMe_2{-}O{-}O{-}Na \cdot HO{-}O{-}CMe_2Ph]_n$, where $n = 1$ or 2; again, the formation of these compounds was ascribed to the presence of a strong hydrogen bond.

The trialkyltin alkyl peroxides are stable at room temperature for at least some months, but are readily hydrolysed in air. In the infrared spectra they showed a band at 820–835 cm^{-1}, which can probably be ascribed to the O–O stretching vibration (*cf.* 877 cm^{-1} in H_2O_2[9], 850 cm^{-1} in $Me_3C{-}O{-}OH$, and 840 cm^{-1} in $PhCMe_2{-}O{-}OH$). The complex $Me_3Sn{-}O{-}O{-}CMe_3 \cdot HO{-}O{-}CMe_3$ showed two such bands at 835 and 845 cm^{-1}.

The tin alkyl peroxides react with phthalic anhydride to yield hydrolytically stable peroxyphthalates (eqn. 2a) which, when crystalline, serve as useful characteristic derivatives. The same peroxyphthalates are formed when a bis(trialkyltin) oxide reacts with 1-tert-butyl hydrogen 1-monoperoxyphthalate (eqn. 2b).



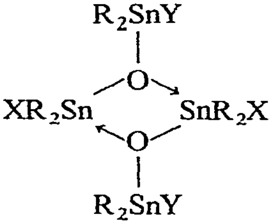
(2)

If dialkyltin oxides are treated with protic reagents, HX, a series of tin derivatives can be isolated, as shown in eqn. (3) (For refs. see ref. 10). Strong acids, such as hydrochloric or acetic acid, can be caused to react to completion to give the compound R_2SnX_2, but weak acids, such as phenols[11] or alcohols[12], usually take the reaction only to the stage of the distannoxanes, $R_4Sn_2X_2O$.

$$2\,R_2SnO \xrightarrow{HX} R_4Sn_2X(OH)O \xrightarrow{HX} R_4Sn_2X_2O \xrightarrow{HX} 2\,R_2SnX_2 \qquad (3)$$

The distannoxanes $R_4Sn_2X(OH)O$ and $R_4Sn_2X_2O$ can also be prepared by partially hydrolysing the compounds R_2SnX_2, and by treating R_2SnX_2 with the appropriate amount of R_2SnO. In non-polar solvents[10], and apparently in the crystal[13], these distannoxanes are usually dimeric, with the probable structures as shown in formula (IV) (Y=X or OH).

Some organoperoxytin compounds of these types have now been isolated.



	R	X	Y
(IVa)	Bu	O–O–tert-Bu	O–O–tert-Bu
(IVb)	Et	O–O–tert-Bu	O–O–tert-Bu
(IVc)	Bu	Cl	O–O–tert-Bu
(IVd)	Et	Cl	O–O–tert-Bu

When a mixture of dibutyltin oxide and tert-butyl hydroperoxide in benzene was subjected to azeotropic dehydration, 1,1,3,3-tetrabutyl-1,3-bis(tert-butylperoxy)-distannoxane was obtained as a crystalline solid which was dimeric in benzene, and hence has the probable structure (IVa). 1,1,3,3-Tetraethyl-1,3-bis(tert-butylperoxy)-distannoxane (IVb) was prepared similarly. The peroxydistannoxane (IVa) was also formed when the corresponding diacetoxydistannoxane (IV; R = Bu, X = Y = OAc) was treated with tert-butyl hydroperoxide in the presence of triethylamine, but attempts to stop the hydrolysis of dibutylbis(tert-butylperoxy)tin at the stage of the peroxydistannoxane (IVa) were unsuccessful, and only dibutyltin oxide was isolated.

The dichlorodistannoxane (IV; R=Bu, X=Y=Cl) underwent only partial substitution by tert-butyl hydroperoxide in the presence of triethylamine to give 1,1,3,3-tetrabutyl-1-(tert-butylperoxy)-3-chlorodistannoxane, probably with the dimeric structure (IVc), and the corresponding tetraethyl compound (IVd), was also obtained by azeotropic dehydration of a mixture of tert-butyl hydroperoxide and the appropriate chlorohydroxydistannoxane (IV; R=Bu or Et, X=Cl, Y=OH); a similar reaction with alcohols is known to give alkoxychlorodistannoxanes, (IV; X=Cl, Y=OR').

EXPERIMENTAL

Peroxidic oxygen was estimated iodometrically by Silbert and Swern's method[14]. Proton magnetic resonance spectra were recorded at 33.5° on a Perkin Elmer R10 spectrometer, and, at other temperatures on a Varian H 100 instrument. Molecular weights were determined at 25°, using a Mechrolab vapour pressure osmometer, Model 301 a.

Preparation of trialkyltin alkyl peroxides

(*a*). *Tributyltin tert-butyl peroxide.* A mixture of tert-butyl hydroperoxide (11.90 g containing 25% di-tert-butyl peroxide; 99 mmoles) and bis(tributyltin) oxide (19.08 g; 32 mmoles) was kept at 0.1 mm until all volatile compounds were removed, to yield tributyltin tert-butyl peroxide[2] (24.35 g; 64 mmoles); ν_{max} (neat) 835 cm^{-1}; τ (in CCl_4) 8.80 (CMe_3). (Found: active O^{14}, 4.40. $C_{16}H_{36}O_2Sn$ calcd.: O,4.23%.)

(*b*). *Triphenyltin tert-butyl peroxide.* Triphenyltin hydroxide (5.98 g, 16.3 mmoles) was converted to the oxide by azeotropic dehydration in benzene. tert-Butyl hydroperoxide (3.79 g, containing 41.5% of di-tert-butyl peroxide; 24.6 mmoles) was then added, and volatile compounds were removed at 0.1 mm. The residue was recrystallised from dry light petroleum (b.p. < 40°; 50 cc), yielding triphenyltin tert-butyl peroxide (6.41 g, 90%); m.p. 61–66° (lit.[3] 63–65°); ν_{max} (in nujol) 835 cm^{-1}. (Found: active O, 3.42. $C_{22}H_{24}O_2Sn$ calcd.: O, 3.65%.)

(*c*). *Triphenyltin 2-phenyl-2-propyl peroxide.* This compound was prepared in 89% yield by a similar method; m.p. 105–110° (lit.[3] 111–114°); ν_{max} (in nujol) 835 cm^{-1}, τ (in CCl_4) 8.51 (CMe_2). (Found: active O, 3.25. $C_{27}H_{26}O_2Sn$ calcd. 3.19%.) The peroxide content did not decrease during 5 months at room temperature.

(*d*). *Trimethyltin tert-butyl peroxide.* tert-Butyl hydroperoxide (4.0 g, containing 36.5% of di-tert-butyl peroxide; 28.2 mmoles) in benzene (10 cc) was added to a suspension of trimethyltin hydroxide (5.35 g, 29.6 mmoles) in benzene (15 cc). Anhydrous magnesium sulphate (6 g) was then added, and the mixture was stirred for 1 h. Next day, the mixture was filtered. The solvent was removed at 20 mm yielding the peroxide (5.77 g; active O found 5.8%) (lit.[3] b.p. 56°/12 mm) which was distilled at room temperature at 0.2 mm and collected at −10° (4.91 g, 61%); ν_{max} (neat) 835 cm^{-1}; τ (in CCl_4) 8.90 (CMe_3), 9.85 ($SnMe_3$) $J(^{119}Sn\text{–}H)$ 60.5 Hz, $J(^{117}Sn\text{–}H)$ 57.7 Hz. [Found: active O, 6.25; mol. wt. (by isothermal distillation in benzene), 338 (0.162 *M*), 362 (0.195 *M*). $C_7H_{18}O_2Sn$ calcd.: active O, 6.32%; mol. wt. 253 (Some white solid slowly separated from the benzene solution during the first 24 h, but the amount was too small to have a significant effect on the apparent molecular weight)].

During 4 months, a crystalline solid separated (0.36 g, 7%) which was filtered off and washed with pentane: τ (in $CDCl_3$) 9.91 (MeSn), $J(^{119}Sn\text{–}H)$ 61 Hz, $J(^{117}Sn\text{–}H)$ 58 Hz, 9.1 (Me_3C); relative intensities 2.85/1. (Found: active O 2.48%.) The peroxide content of the filtrate was unchanged. These data would be compatible with complexes of the composition $(Me_3Sn)_2O \cdot Me_3Sn\text{-}O\text{–}O\text{–}$tert-Bu, or $(Me_3SnOH)_2 \cdot Me_3Sn\text{–}O\text{–}O\text{–}$tert-Bu, but attempts to synthesis these from the components were unsuccessful.

(*e*). *Trimethyltin tert-butyl peroxide tert-butyl hydroperoxide.* If reaction (*d*) is carried out using an excess of the hydroperoxide, products with a high peroxide content are obtained. The above complex separates as long needles, m.p. 28°, and can be recrystallised from light petroleum. The same compound was isolated in 66% yield when trimethyltin tert-butyl peroxide and tert-butyl hydroperoxide were mixed in equimolar amounts, and the product was sublimed at 0.2 mm at room temperature. (Found: active O, 9.25. $C_{11}H_{28}O_4Sn$ calcd.: 9.30%.) ν_{max} (neat) 3200 (OH), 835 and 845 cm^{-1}; τ (in CCl_4 at 33°) 9.55 (Me_3Sn), $J(^{119}Sn\text{–}H)$ 59.7 Hz, $J(^{117}Sn\text{–}H)$ 57.2 Hz, 8.6 (Me_3C), 0.5 (OH); relative areas, found 21/9.3/1, calcd. 18/9/1.

The resonance signal of the OH group of the free hydroperoxide, and of the complex, in dichloromethane was studied as a function of temperature.

(*i*). tert-Butyl hydroperoxide (3.3% w/w). Temperature, δ (ppm from CH_2Cl_2): 20°, −2.15; 0°, −2.32; −20°, −2.54; −40°, −2.90; −60°, −3.44; −80°, −4.08.

(*ii*). Complex (13% w/w). Temperature, δ (ppm from CH_2Cl_2), width of peak at half height (Hz): 20°, −3.34, 6; 0°, −3.71, 8; −20°, −4.23, 24; −40°, −4.87, 55; −60°, −5.48, 30; −80°, −6.03, 13.

(*iii*). Complex (26% w/w). Temperature, δ, width: −56°, −5.40, –; −74°, −6.15, 58; −80°, −6.38, 30; −82°, −6.42; –.

Reaction of trialkyltin alkyl peroxides with phthalic anhydride

(*a*). Phthalic anhydride (0.255 g, 1.72 mmoles) dissolved when it was shaken for 20 min with a solution of tributyltin tert-butyl peroxide (0.651 g, 1.72 mmoles) in dry carbon tetrachloride (6 cc). The solvent was removed at reduced pressure, and the residue was recrystallised from pentane at −80°, giving 1-tert-butyl tributyltin 1-monoperphthalate (0.77 g, 85%); m.p. 40–41°, ν_{max} 1745, 1645 (C=O) cm^{-1}. (Found: C, 54.7; H, 7.8; active O, 2.95. $C_{24}H_{40}O_5Sn$ calcd.: C, 54.7; H, 7.7; active O, 3.04%.)

The same compound was obtained by treating 1-tert-butyl hydrogen 1-monoperphthalate (0.933 g, 3.85 mmoles) in ether (10 cc) with bis(tributyltin) oxide (1.166 g, 1.96 mmoles). Volatile material was removed at reduced pressure, and the product was isolated by the above procedure, in 88% yield.

(*b*). Triphenyltin tert-butyl peroxide similarly reacted with phthalic anhydride to give 1-tert-butyl triphenyltin 1-monoperphthalate; m.p. 18–22°; ν_{max} 1765, 1645 (C=O) cm^{-1}. (Found: active O, 3.05. $C_{30}H_{28}O_5Sn$ calcd.: active O, 2.75%).

(*c*). A similar reaction with triphenyltin 2-phenyl-2-propyl hydroperoxide gave only non-peroxidic products, presumably resulting from the redox rearrangement in the cumylperoxy group.

Preparation of tetraalkyldistannoxy alkyl peroxides

(*a*). *1,1,3,3-Tetrabutyl-1,3-bis(tert-butylperoxy)distannoxane.* (*i*). A mixture of tert-butyl hydroperoxide (1.3 g, containing 31% of di-tert-butyl peroxide; 14.5 mmoles) and dibutyltin oxide (2.5 g, 10 mmoles) was heated under reflux under a Dean and Stark water trap; more hydroperoxide was added to make good that which collected in the trap. When all the oxide had dissolved, the solvent was removed under reduced pressure, and the residue was recrystallised from hexane to give the distannoxane (IVa); m.p. 78–79°. [Found: C, 43.6; H, 8.5; active O, 5.15; mol.wt. (in C_6H_6), 1300 (1.3% w/v), 1328 (2.8%), 1458 (7.5%). $(C_{24}H_{54}O_5Sn_2)_2$ calcd.: C, 43.7; H, 8.2; active O, 4.85%; mol.wt., 1320.]

(*ii*). (*a*). Triethylamine (2cc) was added to a mixture of 1,1,3,3-tetrabutyl-1,3-diacetoxydistannoxane (1.3 g) and tert-butyl hydroperoxide (2 cc) in benzene (10 cc). Crystals of triethylammonium acetate (0.51 g) separated and were filtered off. The filtrate yielded the peroxydistannoxane (IVa); m.p. 78–79°. (Found: active O, 4.5%.)

(*b*). *1,1,3,3-Tetraethyl-1,3-bis(tert-butylperoxy)distannoxane.* Similarly, tert-butyl hydroperoxide reacted with diethyltin oxide in benzene to give the distannoxane (IVb); m.p. 135–143° (from hexane). (Found: active O, 6.1. $C_{16}H_{38}O_5Sn_2$ calcd.: active O, 5.8%.)

(*c*). *1,1,3,3-Tetrabutyl-1-chloro-3-(tert-butylperoxy)distannoxane.* (*i*). 1,1,3,3-Tetrabutyl-1,3-dichlorodistannoxane was treated with tert-butyl hydroperoxide and triethylamine by the method described in reaction (*aii*) yielding the chloroperoxydistannoxane (IVc); m.p. 57–67°. (Found: C, 39.7; H, 7.6; Cl, 5.95; active O, 2.65. $C_{20}H_{45}ClO_3Sn_2$ calcd.: C, 39.9; H, 9.0; Cl, 5.85; active O, 2.65%.)

(*ii*). 1,1,3,3-Tetrabutyl-1-chloro-3-hydroxydistannoxane was mixed with tert-butyl hydroperoxide and subjected to azeotropic dehydration as in reaction (*ai*), yielding the chloroperoxydistannoxane; m.p. 57–67°.

(*d*). *1,1,3,3-Tetraethyl-1-chloro-3-(tert-butylperoxy)distannoxane.* 1,1,3,3-Tetraethyl-1-chloro-3-hydroxydistannoxane and tert-butyl hydroperoxide were azeotropically dehydrated as in reaction (*cii*), yielding the chloroperoxydistannoxane, (IVd); m.p. 125–126°. (Found: Cl, 7.7; active O,3.43. $C_{12}H_{29}ClO_3Sn$ calcd.: Cl, 7.2; active O, 3.24%.)

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