472. *Peroxides of Elements other than Carbon. Part VIII.*[1] *Organoperoxides of Tin.*

By D. L. Alleston and Alwyn G. Davies.

A number of mono- and di-organoperoxytin(IV) compounds, $R'_{4-n}Sn(O{\cdot}OR)_n$, where $n = 1$ or 2, have been prepared by the nucleophilic reaction of alkyl hydroperoxides with organotin(IV) compounds: tri- and tetra-peroxy-analogues ($n = 3$ or 4) were obtained in solution, but could not be purified. The corresponding acyl peroxides and the symmetrical peroxide $Ph_3Sn{\cdot}O{\cdot}O{\cdot}SnPh_3$ decompose by a reaction involving, at least in part, oxidative dealkylation of the tin.

Previous papers in this series have described the preparation of organoperoxides (I) of silicon[2] and of germanium[3] by reactions involving the nucleophilic substitution of a peroxidic reagent at the metal M (equation 1).

$$n\mathrm{RO{\cdot}OH} + \mathrm{R'_{4-n}MX_4} \longrightarrow \underset{\text{(I)}}{\mathrm{R'_{4-n}M(O{\cdot}OR)_n}} + [n\mathrm{HX}] \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

This paper describes the preparation of some peroxytin derivatives (I; M = Sn) by a similar process. Rieche and Bertz have meanwhile described in a preliminary report [4a] and in a patent [4b] the preparation of a number of monoperoxytin compounds by the reaction shown in equation (1) where $n = 1$, M = Sn, and X = halide or alkoxide.

We have prepared trialkylalkylperoxytin compounds by a number of different methods. First, they can be obtained by treating an alcoholic solution of the sodium salt of a hydroperoxide with a solution of the trialkyltin chloride or bromide (Rieche and Bertz's method). Sodium chloride is precipitated and the peroxide can be recovered from the solution: the peroxide is very readily hydrolysed, however, and if the salt is very finely divided and the filtration is slow, it is expedient to distil the peroxide directly from the salt. By this procedure, triethyl-t-butylperoxytin and tributyl-t-butylperoxytin were obtained as colourless high-boiling liquids. Ammonia is a convenient base for causing the reaction between hydroperoxides and silicon[2] or germanium[3] halides, but under the same conditions triethyltin bromide gave only the ammine $Et_3SnBr,2NH_3$.

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[1] Part VII, Davies, Hare, and White, *J.*, 1961, 341.

[2] Part I, Buncel and Davies, *J.*, 1958, 1550.

[3] Part VI, Davies and Hall, *J.*, 1959, 3835.

[4] Rieche and Bertz, (*a*) *Angew. Chem.*, 1958, **70**, 507; (*b*) G.P. 1,081,891.

The monoperoxy-compounds are more conveniently obtained by reaction between the hydroperoxide and the trialkylmethoxytin, the only by-product then being methanol. Tributyl(decahydro-9-naphthylperoxy)tin and decahydro-9-naphthylperoxytriphenyltin were prepared by this method; crude tributyl-(1-methyl-1-phenylethylperoxy)tin decomposed on distillation.

The trialkyltin cyanides have the same advantage of a volatile by-product, but are less reactive than the methoxides. No reaction occurred between tributyltin cyanide and t-butyl hydroperoxide at 60—75°, but gas was evolved smoothly in the presence of polystyrenesulphonic acid. After a second similar treatment, tributyl-t-butylperoxytin was obtained.

Finally, we have also obtained tributyl-t-butylperoxytin by treating tributyltin hydride with 2 mol. of t-butyl hydroperoxide in decalin. No hydrogen is liberated: the first mol. of hydroperoxide is reduced according to reaction (2), and the water separates as a suspension. The second mol. of hydroperoxide then produces the peroxytin compound by reaction (3).

$$\mathrm{Bu_3SnH + Bu^tO{\cdot}OH \longrightarrow Bu_3Sn{\cdot}OBu^t + H_2O} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$\mathrm{Bu_3Sn{\cdot}OBu^t + Bu^tO{\cdot}OH \longrightarrow Bu_3Sn{\cdot}O{\cdot}OBu^t + Bu^tOH} \quad . \; . \; . \; . \; . \; . \quad (3)$$

We also tried to prepare tributyl-(1,2,3,4-tetrahydro-1-naphthylperoxy)tin by treating bistributyltin oxide in ether with 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide in a desiccator containing phosphoric oxide. The products, after distillation at 110°(bath)/0·001 mm., had about one-quarter of the expected peroxide content, and contained much 1,2,3,4-tetrahydro-1-oxonaphthalene. Rieche and Bertz obtained tripropyl-(1,2,3,4-tetrahydro-1-naphthylperoxy)tin, which decomposed at 100—110°, by treating the methoxytin compound with the hydroperoxide.[4b]

Attempts were then made to extend these reactions to the preparation of di-, tri-, and tetra-alkylperoxides of tin (I; $n = 2$—4). Two factors rendered this progressively more difficult as the number of alkylperoxy-substituents was increased. First, the compounds become much less volatile and more thermally labile than the monoperoxides, and often cannot be distilled below their decomposition temperatures; secondly, they are much more readily hydrolysed and are thus difficult to purify by crystallisation at low temperature. Hence, although all these peroxides can apparently be prepared in solution, we have not been able to isolate the pure tri- and tetra-peroxides.

Dibutyldi-t-butylperoxytin was prepared by treating dimethyltin dichloride in methanol successively with sodium methoxide and t-butyl hydroperoxide. Under the same conditions, butyltri-t-butylperoxytin and butyltri-(1-methyl-1-phenylethylperoxy)tin were obtained in solution, but partial hydrolysis occurred during the isolation procedure. Butyltin trihydride reacted very vigorously with an excess of t-butyl hydroperoxide; the peroxide was reduced according to reaction (4), but the water which is liberated precluded the possibility of isolating the tin triperoxide.

$$\mathrm{BuSnH_3 + 3Bu^tO{\cdot}OH \longrightarrow BuSn(OBu^t)_3 + 3H_2O} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

Tin tetrachloride reacted with sodium t-butyl peroxide in methanol to give what was apparently crude tetra-t-butylperoxytin, but this compound decomposed violently at about 65° during distillation. Attempts to obtain tetraperoxides from tetramethoxytin and from tetrakisdiethylaminotin were similarly unsuccessful.

Methoxytriphenyltin in ether was treated with hydrogen peroxide in order to prepare bistriphenyltin peroxide:

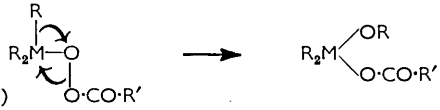
$$\mathrm{2Ph_3Sn{\cdot}OMe + HO{\cdot}OH \longrightarrow Ph_3Sn{\cdot}O{\cdot}O{\cdot}SnPh_3 + 2MeOH} \quad . \; . \; . \; . \; . \; . \quad (5)$$

After about 5 min., heat was evolved: diphenyltin oxide was precipitated and phenol was recovered from the solution.

Thus, in Group IV, peroxides of the structures $Ph_3M{\cdot}O{\cdot}O{\cdot}CR_3$ (M = C, Si,[2] Ge,[5,6] Sn, and Pb [6]) are stable, but the symmetrical peroxides $Ph_3M{\cdot}O{\cdot}O{\cdot}MPh_3$ show an alternating stability: the compounds $Ph_3C{\cdot}O{\cdot}O{\cdot}CPh_3$ and $Ph_3Ge{\cdot}O{\cdot}OGePh_3$ [5] are indefinitely stable at room temperature, whereas $Ph_3Si{\cdot}O{\cdot}O{\cdot}SiPh_3$ decomposes during a few days, and $Ph_3Sn{\cdot}O{\cdot}O{\cdot}SnPh_3$ is too labile to be isolated under the same conditions. The corresponding lead peroxide has not yet been investigated.

t-Alkyl peroxycarboxylates can usually be isolated, but can be caused to undergo a redox rearrangement (reaction 6) with a facility depending on the nature of the groups R and R′.[7] The corresponding silicon [2] and germanium [3] peroxycarboxylates (II; M = Si or Ge) are much more labile and attempts to prepare them have given only the products of rearrangement. A similar rearrangement of trialkyltin peroxycarboxylates would give as the initial products the dialkylalkoxytin carboxylates, which have been claimed only in patents.[8]

(II)



. . . . (6)

When bistriphenyltin oxide was treated with peroxyoctanoic acid, phenol (92%) and the diphenyltin(IV) group (55%) were formed; triphenyltin acetate, triphenyltin hydroxide, and tetraphenyltin did not react under the same conditions. Tributylmethoxytin similarly reduced the peroxy-acid, and the dibutyltin(IV), butoxy-, and octanoyloxy-groups were identified in the products, but tributyltin octanoate was also formed in substantial amounts. Tributyltin octanoate, together with an unidentified compound, was also obtained by treating tributyltin chloride with sodium peroxyoctanoate in methanol. In these last two reactions, the products therefore do not account for all the peroxidic oxygen.

Thus all three classes of tin peroxide described here—the alkylperoxytins, the ditin peroxides, and the acylperoxytins—possess a degree of instability which was not apparent in the corresponding peroxides of carbon, silicon, and germanium. We do not know whether these decomposition reactions are homolytic or heterolytic, or whether more than one mechanism is involved, but two factors might be expected to differentiate the tin peroxides from the others. First, there is not available a stable lower [Sn(II)] oxidation state of the metal, which could be involved in a redox decomposition of the peroxide. A similar picture has been suggested for the redox reaction which occurs between alkyl hydroperoxides and lead(IV) acetate.[9] Secondly, tin is the heaviest element ($Z = 50$) whose peroxides we have studied, and homolysis of the O–O bond might be brought about by a special catalytic effect of the heavy atom.

The powerful magnetic field of a heavy nucleus increases the probability of a process involving a change in electronic multiplicity. This effect is well established for spectroscopic transitions: for example, 1-chloronaphthalene is yellow in ethyl iodide solution because the iodine atom ($Z = 53$) increases the probability of the otherwise forbidden singlet–triplit transition.[10]

Leffler and his co-workers have made the very interesting suggestion that a nearby heavy atom should in the same way facilitate a bond homolysis if it involves a triplet transition state.[11] There appears as yet to be no unambiguous example of this catalytic

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[5] Rieche and Dahlmann, *Angew. Chem.*, 1959, **71**, 194.

[6] Rieche and Dahlmann, *Monatsh. deut. Akad. Wiss. Berlin*, 1959, **1**, 491.

[7] Davies, " Organic Peroxides," Butterworths Scientific Publns., London, 1961, pp. 144—147.

[8] U.S.P. 2,631,990, 2,684,973.

[9] Hock and Kropf, *Chem. Ber.*, 1958, **91**, 1681.

[10] Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 14; *J. Chem. Phys.*, 1952, **70**, 71.

[11] Leffler, Faulkner, and Petropoulos, *Chem. and Ind.*, 1956, 1238; *J. Amer. Chem. Soc.*, 1958, **80**, 5435; Leffler, " The Reactive Intermediates of Organic Chemistry," Interscience Publ. Inc., New York, 1956, pp. 249—251.

effect. The unusual lability of di-*o*-iodobenzoyl peroxide might be ascribed to the magnetic field effect of the iodine atoms,[11] but alternative, more conventional, explanations cannot be excluded.[12]

If the instability which we observe in the tin peroxides is the first indication in Group IV of this phenomenon, the effect should be much more pronounced in the corresponding peroxides of lead ($Z = 82$), as it increases with the fourth power of the atomic number. As yet, the relevant peroxides have not been investigated to allow this hypothesis to be tested.

EXPERIMENTAL

Analysis.—Peroxidic oxygen was estimated iodometrically,[2,13] and tin gravimetrically as stannic oxide.

Precautions.—All operations involving organotin peroxides were conducted with the exclusion of moisture and behind an explosion screen.

Triethyl-t-butylperoxytin.—t-Butyl hydroperoxide (87% pure; 1·02 g.) in ether (8 c.c.) was added to a solution of sodium methoxide (from sodium, 0·23 g.) in methanol (7 c.c.). Triethyltin bromide (2·82 g.) was then added slowly to the stirred mixture. Sodium bromide (1·00 g., 98%) was precipitated immediately and was filtered off after 1 hr. The filtrate yielded triethyl-t-butylperoxytin (1·03 g.) as a colourless liquid, b. p. 61—62°/0·9 mm. (Found: C, 41·9; H, 9·9; peroxidic O, 10·6; Sn, 38·9. Calc. for $C_{10}H_{24}O_2Sn$: C, 40·7; H, 8·2; peroxidic O, 10·8; Sn, 40·2%). Rieche and Bertz report b. p. 56—57°/12 mm.[4a] and 56—57°/2 mm.;[4b] the first value for the pressure is probably a misprint.

An attempt to catalyse the reaction between the hydroperoxide and triethyltin bromide in cyclohexane with ammonia yielded only triethyldiamminotin.

Tributyl-t-butylperoxytin.—(*a*) *From tributyltin chloride.* t-Butyl hydroperoxide (87% pure; 0·87 g.) in methanol (5 c.c.) was added to a solution of sodium methoxide (from sodium, 0·19 g.) in methanol (5 c.c.) in a short-path still.[14] The solution was stirred, and tributyltin chloride (2·72 g.) in methanol (5 c.c.) was added slowly, precipitating sodium chloride. The mixture was distilled, yielding tributyl-t-butylperoxytin (2·66 g., 84%), b. p. 71—72°/0·001 mm., n_D^{25} 1·4608 (Found: C, 51·7; H, 9·15; peroxidic O, 7·4; Sn, 30·6. Calc. for $C_{16}H_{36}O_2Sn$: C, 50·7; H, 9·6; peroxidic O, 8·4; Sn, 31·3%). After 3 hr. and 20 hr. at 100°, the peroxidic oxygen content fell to 6·5% and 3·8%, respectively. The thermal stability was determined by Dr. J. C. McGowan of Imperial Chemical Industries Limited, Plastics Division: in liquid paraffin at 199·6° the half-life was 69·3 sec., similar to that of t-butyl peroxide. In air, the compound was slowly converted into a viscous liquid, and with water it gave an opaque sticky mass. Triethylamine in ether had no obvious reaction with it.

(*b*) *From tributyltin cyanide.* t-Butyl hydroperoxide (93% pure; 0·85 g.) in cyclohexane (20 c.c.) was added to a solution of tributyltin cyanide [15] (2·50 g.) in cyclohexane (130 c.c.) at 65°. There was no obvious change even after 30 min. at 60—75°. The addition of dried polystyrenesulphonic acid (*ca.* 1 g.) initiated slow evolution of gas at 50°. The mixture was kept at 75° until no more gas was given off: the supernatant liquid was decanted and the solvent removed, leaving a white paste (Found: peroxidic O, 5·2%) which showed the presence of a CN group (2160 cm.$^{-1}$) in the infrared spectrum. This paste in cyclohexane (50 c.c.) was treated with a large excess of t-butyl hydroperoxide (15 c.c.) in the presence of the sulphonic acid (1 g.) at 50°, whereupon more gas was evolved. The solution yielded tributyl-t-butylperoxytin, b. p. $<$100°(bath)/0·001 mm., n_D^{26} 1·4628 (Found: C, 50·4; H, 9·6; N, 0·0; peroxidic O, 7·9%). The infrared spectrum was identical with that of the specimen obtained from tributyltin chloride and showed the absence of the CN group.

(*c*) *From tributyltin hydride.* Tributyltin hydride, b. p. 73·5—76·5°/0·55—0·60 mm. (Found: C, 49·4; H, 9·9. Calc. for $C_{12}H_{28}Sn$: C, 49·5; H, 9·7%) was prepared by reducing tributyltin chloride with lithium aluminium hydride.[16] Its infrared spectrum showed the intense band at

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[12] Martin and Bentrude, *Chem. and Ind.*, 1959, 192; Davies, ref. 7, p. 139; Leffler and Wilson, *J. Org. Chem.*, 1960, **25**, 424.

[13] Kokatnur and Jelling, *J. Amer. Chem. Soc.*, 1941, **63**, 1432.

[14] Davies and Moodie, *J.*, 1958, 2372.

[15] Luijten and van der Kerk, "Investigations in the Field of Organotin Chemistry," Tin Research Institute, Greenford, 1955.

[16] Noltes and van der Kerk, "Functionally Substituted Organotin Compounds," Tin Research Institute, Greenford, 1958.

1830 cm.$^{-1}$ associated with the SnH vibration;[17] this band was not affected when the hydride on the cell plates was exposed to dry air, and no band in the region of 3300 cm.$^{-1}$ which could be ascribed to an OH group appeared.

Preliminary experiments showed that an excess of t-butyl hydroperoxide was reduced quantitatively by the hydride without evolving hydrogen and leaving a relatively involatile peroxide.

Tributyltin hydride (2·19 g.) was added to a solution of t-butyl hydroperoxide (93% pure; 1·55 g., 2·12 mol.) in decalin (20 c.c.) in the short-path still. The solution became slightly turbid after a few seconds, and opalescent after 3—4 min., the internal temperature having risen to 35°. Distillation yielded t-butyl hydroperoxide (0·23 mol.) and then tributyl-t-butylperoxytin (1·9 g., 45%), b. p. $<100°$(bath)/0·001 mm., n_D^{25} 1·4642, with an infrared spectrum identical with that of the previous specimens (Found: C, 51·3; H, 9·7; peroxidic O, 7·95%).

Tributyldecahydro-9-naphthylperoxytin.—Solutions of decahydro-9-naphthyl hydroperoxide (1·79 g.) and of tributylmethoxytin[18] (3·28 g.) in ether (40 c.c. in all) were mixed. The solvent was removed at reduced pressure, leaving a liquid which set to a glass at $-80°$; it was soluble in light petroleum but could not be obtained crystalline when the solution was cooled. The product, which could not be distilled at 70°(bath)/0·01 mm., was filtered from a small amount of solid to give *tributyldecahydro-9-naphthylperoxytin* as an oil, $n_D^{19·5}$ 1·4952 (Found: C, 57·6; H, 9·6; peroxidic O, 6·8. $C_{22}H_{44}O_2Sn$ requires C, 57·5; H, 9·7; peroxidic O, 7·0%).

In a similar reaction, 1-methyl-1-phenylethyl hydroperoxide gave tributyl-(1-methyl-1-phenylethylperoxy)tin which distilled very slowly with some decomposition at 110—120°(bath)/0·01 mm. (Found: peroxidic O, 5·8. $C_{21}H_{38}O_2Sn$ requires peroxidic O, 7·25%).

Decahydro-9-naphthylperoxytriphenyltin.—Decahydro-9-naphthyl hydroperoxide (1·55 g.) and methoxytriphenyltin[14] (3·47 g.) in ether (25 c.c. in all) gave a white solid when the solvent was removed. This was recrystallised from light petroleum (b. p. 60—80°), giving *decahydro-9-naphthylperoxytriphenyltin,* m. p. (sealed tube) 102—105° (Found: C, 66·1; H, 6·5; peroxidic O, 6·1. $C_{28}H_{32}O_2Sn$ requires C, 64·8; H, 6·2; peroxidic O, 6·2%).

Dibutyldi-t-butylperoxytin.—Dibutyltin dichloride (3·81 g.) in methanol (12 c.c.) was added slowly to a stirred solution of sodium methoxide (from sodium, 0·57 g.) in methanol (10 c.c.) in the short-path still. Sodium chloride was immediately precipitated. t-Butyl hydroperoxide (87% pure; 2·48 g.) in methanol (2 c.c.) was added, and the solvent was removed under reduced pressure, leaving a white paste. Distillation of the residue slowly yielded *dibutyldi-t-butylperoxytin* (1·10 g.), b. p. 100°(bath)/$<$0·001 mm., n_D^{25} 1·4652 (Found: C, 46·9; H, 9·5; peroxidic O, 12·9; Sn, 28·7. $C_{16}H_{36}O_4Sn$ requires C, 46·7; H 8·8; peroxidic O, 15·6; Sn, 28·9%). It was hydrolysed rapidly in the air giving a white, infusible, non-peroxidic solid.

Attempts to Prepare Triperoxytin Compounds.—(*a*) Butyltin trichloride (1 mol.) in methanol was added slowly to t-butyl hydroperoxide (4 mol.) and sodium methoxide (3 mol.) in methanol. Sodium chloride was immediately precipitated; titration showed that no loss of peroxide had occurred. Volatile material was removed into a cold trap which collected more than the 1 mol. excess of hydroperoxide; the residue was an oil which contained about half of the theoretical amount of peroxide.

(*b*) A similar reaction with 1-methyl-1-phenylethyl hydroperoxide gave an oil which was recrystallised from pentane at $-80°$ (Found: C, 65·4; H, 7·7; peroxidic O, 15·8. Calc. for $C_{31}H_{42}O_6Sn$: C, 59·2; H, 6·7; peroxidic O, 15·3. Calc. for the hydroperoxide, $C_9H_{12}O_2$: C, 71·0; H, 7·9; peroxidic O, 21·0%). The product was probably partially hydrolysed butyltri-(1-methyl-1-phenylethylperoxy)tin, and the infrared spectrum showed the presence of a hydroxyl group.

(*c*) Butyltin trihydride[16] and t-butyl hydroperoxide reacted violently at room temperature evolving clouds of a dark grey smoke. In decalin at $-23°$ the reaction was still vigorous and each molecule of the hydride reduced three of the hydroperoxide. When the volatile material was removed, a white solid remained which had a negligible peroxide content.

In contrast, no reaction was apparent when the hydride and t-butyl peroxide were mixed.

Attempts to Prepare Tetraperoxytin Compounds.—(*a*) Tin tetrachloride (1·73 g.) in benzene (5 c.c.) was added slowly to a stirred mixture of t-butyl hydroperoxide (87% pure; 3·03 g.) and sodium methoxide (from sodium, 0·61 g.) in methanol (20 c.c.) under anhydrous conditions.

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[17] Mathis-Noël, Lesbre, and Sérée de Roch, *Compt. rend.*, 1956, **243**, **257**.

[18] Alleston and Davies, *J.*, 1962, 2050.

Finely divided sodium chloride separated immediately and was allowed to settle. The supernatant liquid was decanted into a short-path still and the solvent was removed under reduced pressure, leaving a cream paste. At $<0\cdot001$ mm., a sudden violent but not explosive decomposition occurred when the temperature was raised to 62° (bath), giving a voluminous, flossy, rather sticky solid. A small amount of a colourless liquid, which was probably slightly impure tetra-t-butylperoxytin, was collected in the receiver (Found, in the distillate; peroxidic O, 24·4; in the residue, 14·0. Calc. for $C_{16}H_{36}O_8Sn$: peroxidic O, 26·9%). In a second experiment a similar decomposition occurred at 72°(bath)/$<0\cdot001$ mm. but no distillate was collected.

(*b*) A similar reaction was carried out with decahydro-9-naphthyl hydroperoxide in the hope that the product, tetrakis(decahydro-9-naphthylperoxy)tin, might be crystalline. The sodium chloride and volatile material were removed, leaving a white solid; this was recrystallised from pentane, when, despite precautions to avoid hydrolysis, the hydroperoxide was recovered, m. p. and mixed m. p. 95·5—96° (Found: peroxidic O, 18·5. Calc. for $C_{10}H_{18}O_2$: peroxidic O, 18·8%).

(*c*) Tetrakisdimethylaminotin [19] in pentane was treated with t-butyl hydroperoxide (6 mol.) in pentane at room temperature. No reaction was apparent, but analysis showed that 1·5 mol. of peroxide had been reduced. Under reduced pressure, 1·95 mol. of hydroperoxide were collected in a cold trap, leaving a small amount of an opaque viscous yellow oil (Found: peroxidic O, 11·7%).

(*d*) A suspension of tetramethoxytin in pentane was prepared by treating tetrakisdiethylaminotin with methanol. t-Butyl hydroperoxide (6 mol.) was added; the solid dissolved, giving a yellow solution. Volatile material was removed under reduced pressure into a cold trap, leaving a viscous brown oil (0·40 g.) (Found: peroxidic O, 15·1, 15·7%). The cold trap contained 3·56 mol. of t-butyl-hydroperoxide, showing that there had been an overall loss of 0·61 mol. of peroxide.

Reaction between Methoxytriphenyltin and Hydrogen Peroxide.—Anhydrous 0·250M-ethereal hydrogen peroxide (20·63 c.c.) was added to a stirred solution of methoxytriphenyltin (3·93 g., 2 mol.) in ether (20 c.c.). After 5 min., the solution became warm; it deposited a cream precipitate during 1 hr. The solid (1·52 g.) was centrifuged off and was shown to be impure diphenyltin oxide, m. p. >280° (Found: C, 47·5; H, 3·5. Calc. for $C_{12}H_{10}OSn$: C, 49·9; H, 3·5%). Its infrared spectrum was identical with that of an authentic specimen. With warm hydrochloric acid it gave diphenyltin dichloride which was identified as its 2,2′-bipyridyl derivative,[18] m. p. and mixed m. p. 242—244°.

The ethereal supernatant solution was evaporated at reduced pressure, leaving a cream solid which smelled of phenol. It was steam-distilled, yielding phenol (tribromo-derivative, m. p. and mixed m. p. 93°). The solid residue (1·79 g.) from the steam-distillation was apparently diphenyltin oxide, m. p. >280°.

Reaction between Trialkyltin(IV) *Compounds and Peroxyoctanoic acid.*—(*a*) *Bistriphenyltin oxide.* Bistriphenyltin oxide (5·00 g.) in dry ether (150 c.c.) was treated with peroxyoctanoic acid (85% pure; 2·65 g., 2 mol.) in ether (30 c.c.), yielding a slight white precipitate (0·16 g.) After 3 hr. the supernatant liquid was shaken with aqueous sodium hydroxide yielding diphenyltin oxide (2·21 g., 55%) and phenol (1·21 g., 92%), b. p. 180° (tribromo-derivative, m. p. 92—93°).

Bistriphenyltin oxide was treated with peroxyoctanoic acid (9 mol.) in anhydrous methanol; after 45 min. titration showed that 5·14 mol. of the peroxy-acid had been reduced. Similar experiments with triphenyltin acetate, triphenyltin hydroxide, and tetraphenyltin showed no significant reaction during 2 days.

(*b*) *Tributylmethoxytin.* Peroxyoctanoic acid (1·60 g.) in ether (20 c.c.) was added dropwise to a stirred solution of tributylmethoxytin (3·21 g.) in ether (15 c.c.). Volatile material was removed under reduced pressure into a trap at −196° and was shown by gas–liquid chromatography to contain butanol. The residue, an almost non-peroxidic mixture of needles and viscous liquid, was soluble in pentane and apparently inert to water. The liquid from a part of the mixture was absorbed into filter paper, leaving tributyltin octanoate,[18] m. p. and mixed m. p. 53—55°. The remainder of the mixture was dissolved in ethanol and treated with a small amount of concentrated hydrochloric acid (which does not dealkylate tributyltin compounds under these conditions) and then with bipyridyl, yielding dibutyl-2,2′-bipyridyltin dichloride, m. p. and mixed m. p. 179—179·5°.

[19] Thomas, *Canad. J. Chem.*, 1961, **39**, 1386.

(*c*) *Tributyltin chloride.* Peroxyoctanoic acid (91% pure, 2·77 g.) in methanol (8 c.c.) was added very slowly to a solution of sodium methoxide (from sodium, 0·36 g.) in methanol (5 c.c.); the temperature of the mixture rose to *ca.* 30°, and sodium peroxyoctanoate separated as a voluminous white precipitate. The stirred suspension was treated with tributyltin chloride (5·14 g.) in methanol (3 c.c.). After 75 min., sodium chloride (0·84 g., 91%) was removed. The filtrate was evaporated, yielding a white paste which was distilled at 110—185°(bath)/0·01—0·035 mm., giving a mixture of a colourless liquid and crystals. Redistillation of the solid gave impure tributyltin octanoate, b. p. 105°(bath)/0·005 mm., m. p. 52—54°, with an infrared spectrum identical with that of authentic material (Found: C, 51·2, 53·8; H, 8·8, 9·3. Calc. for $C_{20}H_{42}O_2Sn$: C, 55·4; H, 9·8%). Redistillation of the liquid gave an unidentified colourless product, b. p. 70—84°(bath)/0·005 mm. [Found: C, 47·6, 47·6; H, 8·8, 8·6; Sn (ash), 2·7%, " negligible." If it is accepted that only carbon, hydrogen, and oxygen are present, this corresponds to an unlikely formula such as $C_{13}H_{28}O_9$ which requires C, 47·6; H, 8·6; O, 43·9%]. The infrared spectrum showed no evidence of a hydroxyl group, but had a broad absorption band at about 1590 cm.$^{-1}$ corresponding to the C=O stretching vibration.

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William Ramsay and Ralph Foster Laboratories,
University College,
Gower Street, London, W.C.1.

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