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FUNCTIONALLY SUBSTITUTED ORGANOTIN COMPOUNDS

III. (EPOXYALKYL)TIN COMPOUNDS

G. AYREY, J. R. PARSONAGE and R. C. POLLER
Chemistry Department, Queen Elizabeth College, Campden Hill Road, London W8 7AH (Great Britain)
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SUMMARY

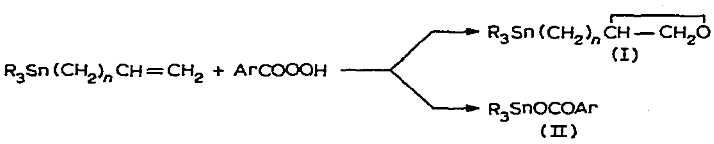
Treatment of vinyltin and 3-butenyltin compounds with perbenzoic acid (or 3-chloroperbenzoic acid) gave (epoxyalkyl)tin derivatives together with the organotin (3-chloro)benzoate. No epoxy derivative could be isolated from the corresponding allyltin compounds. Reduction of tributyl(3,4-epoxybutyl)tin with lithium aluminium hydride gave tributyl(4-hydroxybutyl)tin.

INTRODUCTION

Previous papers in this series[1,2] have dealt with the preparation of compounds containing thioether groups attached to tin. We now report the synthesis of (epoxyalkyl)tin compounds. This class of compound has not been described previously apart from a fragmentary account in the patent literature[3] of the preparation of (epoxyethyl)-triethyltin.

RESULTS AND DISCUSSION

In general, epoxidation of alkenyltrialkyl- or -aryltin compounds using perbenzoic acid or 3-chloroperbenzoic acid gave a mixture of the (epoxyalkyl)tin compound (I) and the trialkyl- or triaryltin carboxylate (II).

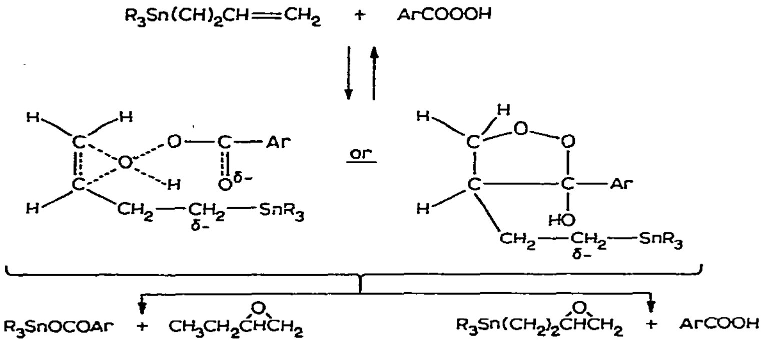


Vinyltin compounds ($n=0$) and 3-butenyltin compounds ($n=2$) gave both products (I) and (II) but only the carboxylates (II) were isolated when allyltin compounds ($n=1$) were treated with peracids. Generally, the reaction products were separated and purified by column chromatography. The products obtained from monoalkenyltin compounds are listed in Table 1.

The commercially available 3-chloroperbenzoic acid was found to be more convenient to use than perbenzoic acid which was prepared from benzoyl peroxide and kept as a solution in chloroform[4]. The solution has only moderate stability and the concentration of perbenzoic acid must be estimated (usually by iodometric titration) immediately before use[4]. The progress of each epoxidation reaction was monitored by withdrawal of aliquots from the reaction mixture and titration of the peracid.

When 3-butenyltriphenyltin was treated with 3-chloroperbenzoic acid at room temperature in a 1/1 mixture of chloroform and benzene, a molar proportion of the peracid was consumed in 2 h. It took between 36 and 48 h for a mole of the peracid to disappear when benzene alone was used as the solvent, but, in this case, the yield of (3,4-epoxybutyl)triphenyltin was increased.

Essentially, two mechanisms have been proposed for the reaction between olefins and peracids involving either 3-centered[5] or 5-centered[6] transition states. Recent work on the epoxidation of vinylsilanes[7] appears to favour the former possibility though the nature of the solvent may determine the mechanism[8]. An acceptable mechanism for the epoxidation of alkenyltin compounds must accommodate the fact that specific cleavage of the alkenyl group was a competing reaction with vinyltin and 3-butenyltin compounds and was the sole reaction observed with allyltin compounds. (Separate experiments showed that vinyl and 3-butenyl groups were not cleaved from tin by benzoic acid or by benzoyl peroxide). It seems that, whether there is a 3- or a 5-membered transition state, competition for a proton occurs between the incipient carboxylate anion and the α-carbon atom of the alkenyl group; this carbon atom is known to be particularly sensitive to electrophilic attack in allyltin compounds[9]. This can be illustrated for the butenyltin compounds:



Attempts to form bis(epoxyalkyl)tin compounds were unsuccessful. Reaction between dibutyldivinyltin and excess 3-chloroperbenzoic acid gave dibutyl(epoxyethyl)vinyltin and dibutyltin bis(3-chlorobenzoate). Di-3-butenyldiphenyltin behaved similarly giving 3-butenyl(3,4-epoxybutyl)diphenyltin as the only epoxide.

The stabilities of the (epoxyalkyl)tin compounds varied, thus the (epoxyethyl)-tin compounds decomposed within a few days at room temperature, or very rapidly on warming, to give complex mixtures of product. The (epoxybutyl)tin compounds were unchanged after storage for prolonged periods.

Treatment of tributyl(3,4-epoxybutyl)tin with lithium aluminium hydride gave the expected tributyl(4-hydroxybutyl)tin but attempts to effect a similar conversion

TABLE 1

REACTIONS BETWEEN MONOALKENYLTIN COMPOUNDS AND PERACIDS

Reactants		*Products*	
Alkenyltin	*Peracid*	*(Epoxyalkyl)tin*	*Organotin ester*
$Bu_3SnCH{=}CH_2$	PhCOOOH	$Bu_3Sn\overline{CHCH_2O}$	$Bu_3SnOCOPh$
$Bu_3SnCH{=}CH_2$	3-ClC_6H_4COOOH	$Bu_3Sn\overline{CH_2CH_2O}$	$Bu_3SnOCOC_6H_4Cl$-3
$Bu_3SnCH_2CH{=}CH_2$	PhCOOOH		$Bu_3SnOCOPh$
$Bu_3Sn(CH_2)_2CH{=}CH_2$	PhCOOOH	$Bu_3Sn(CH_2)_2\overline{CHCH_2O}$	$Bu_3SnOCOPh$
$Bu_3Sn(CH_2)_2CH{=}CH_2$	3-ClC_6H_4COOOH	$Bu_3Sn(CH_2)_2\overline{CHCH_2O}$	
$Ph_3Sn(CH_2)_2CH{=}CH_2$	3-ClC_6H_4COOOH	$Ph_3Sn(CH_2)_2\overline{CHCH_2O}$	

with (3,4-epoxybutyl)triphenyltin gave only unchanged starting material. This difference in behaviour is surprising, the triphenyltin derivative is a solid and generally less soluble than the liquid tributyltin compound but these differences in physical properties do not seem adequate to account for the difference in behaviour towards lithium aluminium hydride.

EXPERIMENTAL

Details of the Mössbauer spectrometer have been described elsewhere[10], isomer shifts refer to tin(IV) oxide. NMR spectra were measured using a Perkin–Elmer R10 60 MHz instrument. IR measurements were made with Perkin–Elmer 237 and 325 spectrometers. The reactions were monitored and all products shown to be homogeneous by thin-layer chromatography[1].

Tributylvinyltin[11], dibutyldivinyltin[11], allyltributyltin[12], 3-butenyltributyltin[13] and 3-butenyltriphenyltin[14] were made by published procedures and had boiling points or melting points which were in agreement with values given in the literature.

Di-3-butenyldibutyltin

This compound was prepared in 83% yield by the addition of dibutyltin dichloride to a solution of the Grignard reagent formed from 4-bromo-1-butene in diethyl ether. The product had b.p. 119°/0.7 mmHg; n_D^{25} 1.4878; NMR (neat) $\geq Sn{-}CH_2^aCH_2^bCH^c{=}CH_2^d$, H^b quartet centred at τ 7.70, H^c multiplet τ 3.9–4.5, H^d multiplet τ 4.8–5.4 (H^a masked by butyl protons); IR (liquid film), ν(C=C) 1640 cm^{-1}. (Found: C, 55.7; H, 9.3. $C_{16}H_{32}Sn$ calcd.: C, 56.0; H, 9.4%.)

Tributyl(epoxyethyl)tin

3-Chloroperbenzoic acid (3.50 g, 0.020 mol) in benzene (125 ml) was added to a solution of tributylvinyltin (5.00 g, 0.016 mol) in benzene (125 ml) and the mixture set aside at room temperature for 48 h. The solution was then poured into excess saturated aqueous sodium bicarbonate solution and the mixture stirred for 3 h.

The organic layer was separated and the aqueous phase extracted with three portions (50 ml) of ether, the extracts were combined with the organic layer and the mixture dried over magnesium sulphate. The solvent was removed at room temperature using a rotary evaporator to give a yellow viscous product (2.0 g). Chromatography of this material on silica gel (50 g) using a mixture of 10 volumes benzene and one of chloroform and collecting 20 ml portions of eluate gave the following results (monitored by thin-layer chromatography). (*a*). Fractions 2 and 3 contained tributylvinyltin (0.15 g), n_D^{25} 1.4762 (lit.[11] n_D^{25} 1.4751), infrared spectrum identical with that of the authentic material. (*b*). Fractions 5, 6 and 7 contained tributyl(epoxyethyl)tin (0.60 g), n_D^{25} 1.4837; NMR (CCl_4): epoxide protons gave a multiplet signal at τ 6.0–6.4 alkyl protons multiplet at τ 8.0–9.0; IR (liquid film) showed a band at 850 cm^{-1} characteristic[15] of the epoxide group; the Mössbauer spectrum was a single peak at δ 1.54 mm/s. (Found: C, 50.2; H, 8.9. $C_{14}H_{30}OSn$ calcd.: C, 50.5; H, 9.1%.) (*c*). Fractions 10–13 contained tributyltin 3-chlorobenzoate, m.p. 20°; NMR (CCl_4): aromatic protons τ 2.00, 2.10, 2.60 2.70, alkyl protons, multiplet at τ 8.6–9.2; IR (liquid film): ν(C–Cl) 752 cm^{-1}, $\nu(OCO)_{asym.}$ 1620 cm^{-1}. (Found: Sn, 24.8. $C_{19}H_{31}ClO_2Sn$ calcd.: Sn, 26.6%.)

When perbenzoic acid was used instead of 3-chloroperbenzoic acid essentially the same reaction occurred to give a yellow oil from which was isolated unchanged starting material, tributyl(epoxyethyl)tin and tributyltin benzoate.

Tributyl(3,4-epoxybutyl)tin

A solution of 3-chloroperbenzoic acid (3.00 g, 0.017 mol) in a mixture of equal volumes of benzene and chloroform (500 ml) was set aside at 0° for 1 h and then 3-butenyltributyltin (4.50 g, 0.013 mol) was added. The reaction mixture was kept at room temperature samples being withdrawn at intervals for titrimetric estimation of peracid. After 19 h no peracid remained and the mixture was poured into excess saturated aqueous sodium bicarbonate. The organic layer was separated and the aqueous solution extracted with ether. The organic solutions were combined, dried over magnesium sulphate and the solvent removed at room temperature on a rotary evaporator. The crude viscous product (2.42 g) was added to a chromatography column of silica gel (50 g) and eluted with a mixture of carbon tetrachloride (10 volumes) and benzene (1 volume) collecting 20 ml fractions. Fractions 2, 3 and 4 gave unchanged 3-butenyltributyltin (0.60 g), n_D^{25} 1.4800 (lit.[13] n_D^{25} 1.4792). Fractions 5–15 contained tributyl(3,4-epoxybutyl)tin (1.80 g), n_D^{25} 1.4822; NMR (neat) multiplet due to epoxide protons at τ 7.2–7.9; IR (liquid film) ν(C–H, epoxide) 3040 cm^{-1}, band at 845 cm^{-1} characteristic[15] of an epoxide; Mössbauer spectrum was a singlet at δ 1.33 mm/s. (Found: C, 53.2; H, 9.4; O, 5.2. $C_{16}H_{34}OSn$ calcd.: C, 53.2; H, 9.5; O, 4.4%.)

In a similar experiment using perbenzoic acid it was shown that the reaction was complete within 2 h. Chromatography of the crude product gave unchanged 3-butenyltributyltin, tributyl(3,4-epoxybutyl)tin and tributyltin benzoate.

(3,4-Epoxybutyl)triphenyltin

In a similar manner to that described above 3-butenyltriphenyltin (1.00 g) was oxidised with 3-chloroperbenzoic acid (0.70 g) using benzene as solvent and a reaction time of 48 h to give as sole product (3,4-epoxybutyl)triphenyltin (0.80 g) no chromatographic purification being necessary. The product had m.p. 78–82°, NMR (CCl_4)

multiplet signal from epoxide protons τ 7.2–7.9; IR (Nujol mull) characteristic[15] epoxide band at 820 cm^{-1}. (Found: C, 62.9; H, 5.4; O, 3.2. $C_{22}H_{22}OSn$ calcd.: C, 62.7; H, 5.3; O, 3.8%.)

Reaction between allyltin compounds and peracids

In a similar manner to that already described allyltributyltin (3.00 g) was allowed to react with a solution of perbenzoic acid (1.22 g) in chloroform for 2 h 40 min. Chromatography of the crude product showed that the principal component was tributyltin benzoate (1.50 g), n_D^{25} 1.5143 (lit.[16] n_D^{20} 1.5157), confirmed by NMR, IR and Mössbauer spectra. Small amounts of the starting material were obtained from the column but no epoxycompounds could be isolated.

Reactions between dialkenyltin compounds and 3-chloroperbenzoic acid

Dibutyldivinyltin (5.00 g, 0.017 mol) was oxidised for 48 h with 3-chloroperbenzoic acid (8.00 g, 0.047 mol) in benzene and the crude product submitted to chromatographic separation as described previously. The first product (fractions 4 and 5) eluted from the column was dibutyl(epoxyethyl)vinyltin (0.50 g), n_D^{25} 1.4769; NMR (CCl_4): epoxide protons show a multiplet at τ 6.0–6.4; the vinyl protons show complex absorption centred at $\tau \approx 4.0$. (Found: C, 47.7; H, 8.6. $C_{12}H_{24}OSn$ calcd.: C, 47.6; H, 8.0%.) The second product (fractions 8–12) was dibutyltin bis(3-chlorobenzoate) (0.41 g), m.p. 35–40°, NMR (CCl_4): aromatic protons at τ 1.90, 1.93, 2.60, 2.70. (Found: C, 49.2; H, 5.5. $C_{22}H_{26}Cl_2O_4Sn$ calcd.: C, 48.6; H, 4.8%.)

In a similar manner the crude product from the oxidation of di-3-butenyldiphenyltin (1.20 g, 0.0031 mol) with 3-chloroperbenzoic acid (1.65 g, 0.0096 mol) was separated into its constituents by column chromatography. The first compound to be eluted from the column was unchanged di-3-butenyldiphenyltin (0.70 g) having infrared and NMR spectra identical with those of authentic material. The next compound eluted was 3-butenyl(3,4-epoxybutyl)diphenyltin (0.10 g); IR (liquid film) showed characteristic[15] epoxide absorption at 820 cm^{-1} and the ν(C=C) band at 1640 cm^{-1}; NMR (CCl_4): complex multiplet due to epoxide protons τ 7.4–7.8, signal from aromatic protons at τ 2.7. (Found: C, 60.4; H, 6.25. $C_{20}H_{24}OSn$ calcd.: C, 60.2; H, 6.1%.)

Tributyl(4-hydroxybutyl)tin

Tributyl(3,4-epoxybutyl)tin (0.40 g, 0.0011 mol) was added to a suspension of lithium aluminium hydride (0.04 g, 0.0011 mol) in light petroleum (b.p. 30–40°, 2 ml) and the mixture allowed to stand at room temperature for 30 min. After pouring into water the organic components were extracted with ether, the extract dried over magnesium sulphate and the solvent removed on a rotary evaporator. This gave, as a colourless liquid, tributyl(4-hydroxybutyl)tin (0.40 g), n_D^{25} 1.4824; IR (liquid film): ν(OH) 3320 cm^{-1} (broad); NMR (neat): signal at τ 6.37 due to one OH proton, Mössbauer spectrum showed a single peak at δ 1.33 mm/s. (Found: C, 52.8; H, 9.9; mol. wt. osmometrically in benzene, 362. $C_{16}H_{36}OSn$ calcd.: C, 52.9; H, 10.0%; mol. wt., 363.)

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