2,2-Dibutyl-1,3,2-dioxastannolens

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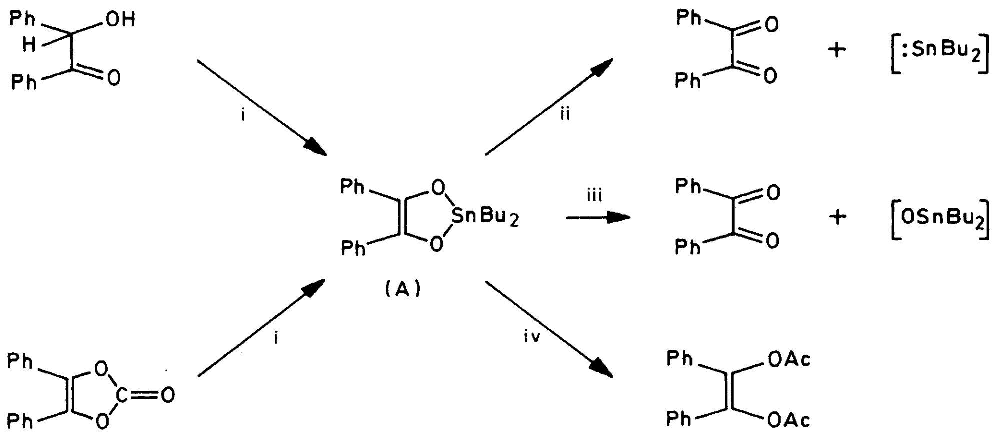
Acyloins or their enediol carbonates (vinylene carbonates) react with dibutyltin oxide or dibutyltin dimethoxide to give 2,2-dibutyl-1,3,2-dioxastannolens [*e.g.* (*A*)].



Reagents: i, Bu_2SnO or $Bu_2Sn(OMe)_2$; ii, heat; iii, O_2; iv, MeCOCl

^{119}Sn N.m.r. and ^{119m}Sn Mössbauer spectra, and molecular weight measurements suggest that, in the solid state or in concentrated solution, the dioxastannolen (A) is associated, but the monomer is present in dilute solution.

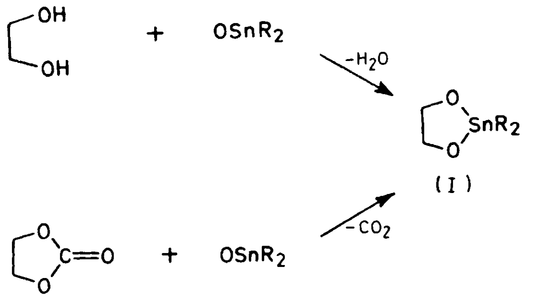
On heating, (A) decomposes into benzil and products which appear to be derived from dibutylstannylene, and it reacts with oxygen to give benzil and products derived from dibutyltin oxide. Acetyl chloride reacts to give *cis*-stilbene diacetate, but less reactive acylating agents (*e.g.* acetic anhydride or benzoyl chloride) give an increasing amount of the *trans*-diester and cyclic anhydrides (*e.g.* phthalic anhydride), and diacid chlorides (*e.g.* phosgene) give cyclic esters.

The organotin alkanolates have been studied extensively;[1] they are frequently prepared from the appropriate organotin chloride, but the trialkyltin alkoxides, in particular, are conveniently obtained by azeotropic dehydration of a mixture of the organotin oxide and alcohol (equation 1) or by heating together the organotin oxide and dialkyl carbonate (equation 2).[2]

$$(R_3Sn)_2O + 2\,R'OH \longrightarrow 2\,R_3SnOR' + H_2O \quad (1)$$

$$(R_3Sn)_2O + (R'O)_2CO \longrightarrow 2\,R_3SnOR' + CO_2 \quad (2)$$

The cyclic dialkyltin derivatives of 1,2-diols can be prepared by the equivalents of reactions (1) and (2) (equation 3),[3] and the products, the 2,2-dialkyl-1,3,2-dioxastannolans (I), have attracted a lot of attention recently because of their application in organic synthesis.[4]



(3)

The organotin enolates are less familiar. Trialkyltin enolates can be prepared from the reaction between trialkyltin alkanolates and enol acetates,[5] or lithium enolates and trialkyltin chlorides,[6] and the n.m.r. spectra show that the products are in metallotropic equilibrium with the keto-form (*e.g.* equation 4). Again, these compounds show promise of being useful in organic synthesis.[6]

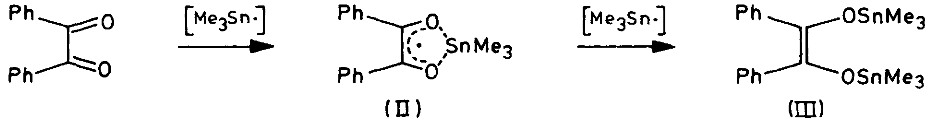
$$\underset{94\%}{CH_2{=}CHOSnBu_3} \rightleftharpoons \underset{6\%}{Bu_3SnCH_2CH{=}O} \quad (4)$$

Very little work has been published on the organotin enediolates. The first report appears to have been that by Schroeder, Neumann, and Hillgärtner;[7] who showed that trimethyltin(III) radicals could be transferred from the bis-stannyl ether of benzopinacol to benzil, to give, *via* the semidione radical (II), the bistrimethyltin enediolate (III), as pale yellow crystals (equations 5 and 6).

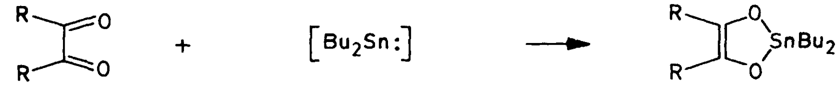
Neumann also showed that the transient dibutyltin(II) obtained from the photolysis of the corresponding cyclic polystannane $(R_2Sn)_n$, would add to biacetyl or benzil to give the 1,3,2-dioxastannolen (IV) (equation 7),[8] and a similar reaction has recently been established with the isolable tin(II) alkoxides (equation 8).[9]

The approach to the organotin enediolates which we have used is the stannylation of enediols or their cyclic carbonates by reactions analogous to those of equations (1) and (2). We

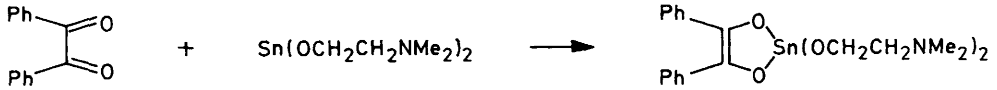
$$\mathrm{Me_3SnOCPh_2CPh_2OSnMe_3} \longrightarrow 2\,[\mathrm{Me_3Sn\cdot}] + 2\ \mathrm{Ph_2C{=}O} \qquad (5)$$



(II) (III) (6)



(R = Me or Ph) (IV) (7)

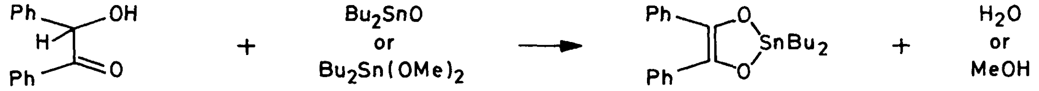


(8)

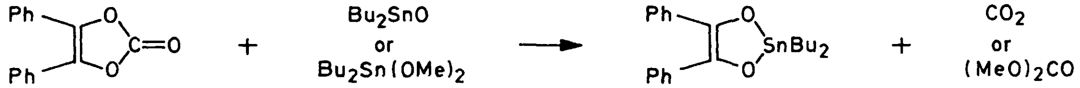
report here the preparation of cyclic and acylic organotin enediolates, particularly 2,2-dibutyl-4,5-diphenyl-1,3,2-dioxastannolen (IV; R = Ph), by the reaction of organotin oxides or the corresponding methoxides with, formally the enediol tautomers of acyloins, or the corresponding vinylene carbonates; a preliminary investigation of the structures and reactions of these products is also described.

Results and Discussion

Preparation of the Organotin Enediolates.—The four routes which we have used for preparing the 1,3,2-dioxastannolens are exemplified in equations (9) and (10).



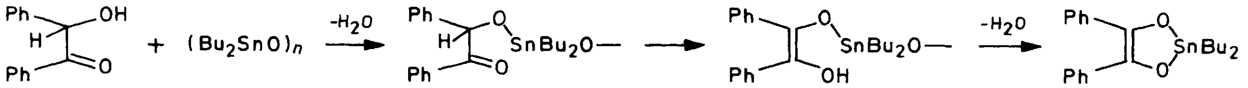
(9a) (9b)



(10a) (10b)

When dibutyltin oxide and benzoin are heated in benzene under a Dean and Stark water separator, the oxide dissolves in *ca.* 1 h as water collects in the trap (equation 9a). Removal of the benzene leaves a viscous orange oil which, from pentane at low temperature, yields the stannolene as an amorphous powder.

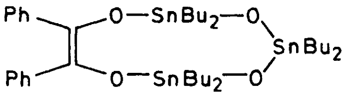
Presumably the reaction involves enolization and then cyclization of the alkoxyltin compound which is formed initially (equation 11).



(11)

The reaction with dibutyltin dimethoxide (equation 9b) proceeds more readily and is complete in 45 min at 40 °C.

When dibutyltin oxide is heated with diphenylvinylene carbonate in benzene, evolution of carbon dioxide begins at 90 °C (equation 10a), and the oxide rapidly dissolves, giving the dioxastannolen together with some of the oligomer (V) containing three Bu_2SnO units.



(V)

The formation of the dioxastannolen probably involves insertion of a Bu_2SnO unit into the acyloxy bond of the carbonate, followed by the familiar decarboxylation[2] of the organotin carbonate (equation 12).

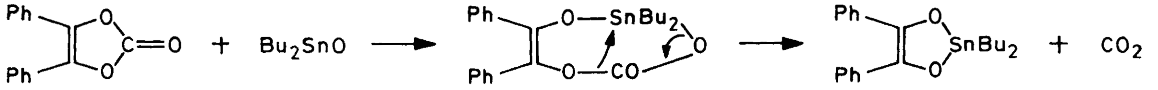
We have shown that the dioxastannolen and dibutyltin oxide are in equilibrium under these condition with higher oligomers such as (V),[10] and, in our reaction, (V) might be formed by incomplete degradation of the polymeric dibutyltin oxide before decarboxylation occurs, or by insertion of dibutyltin oxide units into the initially formed dioxastannolen.

The reaction between dibutyltin dimethoxide and diphenylvinylene carbonate (equation 10b) was carried out at 120—130 °C without a solvent, and gave the dioxastannolene in 86% yield as faint yellow crystals. Ethylene carbonate has been shown to react in the same way to give 2,2-dibutyl-1,3,2-dioxastannolan.[11]

Some benzil was frequently formed in these experiments although they were carried out under nitrogen, and attempts to distil the dioxastannolen under reduced pressure gave only benzil and tetrabutyltin. *p*-Methoxy-substituents enhanced the formation of the dione, and anisoin gave up to 79% yield of anisil when the reaction with dibutyltin oxide was carried out in boiling benzene.

To determine the effect of temperature, the reaction between 1,2-bis(*p*-methoxyphenyl)vinylene carbonate and dibutyltin dimethoxide was monitored by n.m.r. In chloroform at 37 °C, a trace of anisil could be detected after 20 h, but this did not increase to more than *ca.* 7% during 21 days as the signals of the carbonate were progressively replaced by those of the organotin enediolate. When the same reaction was carried out at 78 °C in deuteriobenzene, the ratio of the dione and enediolate was *ca.* 1 : 1.

The most likely source of the dione appears to be the thermal decomposition of the dioxastannolen to give a transi-

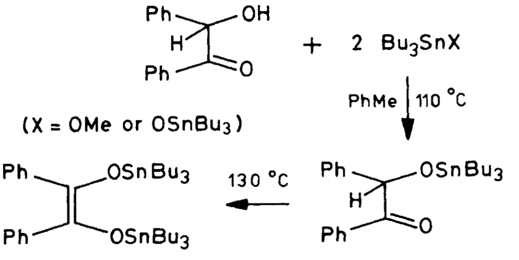


(12)

ent dialkylstannylene, which forms a cyclic oligomer which in turn could give tetrabutyltin by thermal rearrangement; this would be the reverse of reaction (7), though there the stannylene was generated photolytically and may be in a different spin state.

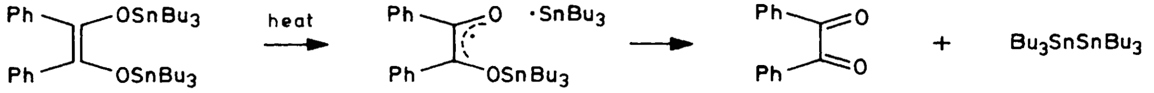
This type of decomposition was not important with acetoin, which reacted with dibutyltin oxide in benzene to give 2,2-dibutyl-4,5-dimethyl-1,3,2-dioxastannolen in good yield.

The preparation of the bistributyltin enediolates was studied briefly for comparison with the dialkyltin analogues. We have shown previously that azeotropic dehydration of a mixture of acetoin and bistributyltin oxide in benzene or toluene gives the monotributyltin derivative.[12] Under the same conditions, benzoin reacts with bistributyltin oxide or with tributyltin methoxide to give the monotributyltin derivative (VI), and Neumann[7] established a similar reaction between benzoin and trimethyltin diethylamide in benzene; but if benzoin is heated with bistributyltin oxide or tributyltin methoxide at 130 °C without solvent, the bistributyltin enediolate (VII), probably with the *cis*-structure, can be isolated as a distillable liquid (equation 13).



(VII) (VI) (13)

Some benzil and hexabutylditin are formed alongside compound (VII), suggesting that a process involving the $R_3Sn^{\cdot}$ radical may occur (equation 14) which is analogous to that which was proposed above, involving $R_2Sn\colon$ from the dibutyltin enediolate (equation 15).



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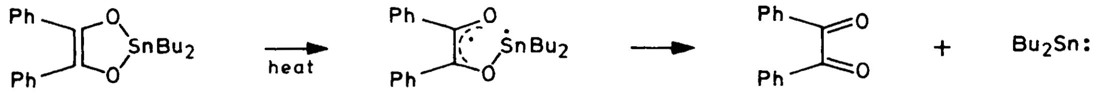
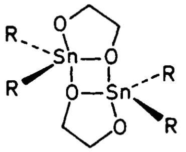


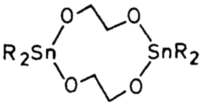
(15)

Structures of the Dioxastannolens.—The structures of the dioxastannolens are best discussed in comparison with the familiar corresponding saturated dioxastannolans. Molecular-weight measurements show that these dioxastannolans are dimeric in non-polar solvents.[3,13] This has been interpreted in terms of two associated five-membered rings containing 5-co-ordinate tin (VIII) or of ten-membered rings containing 4-c -ordinate tin (IX)[11,4k-n] but a recent *X*-ray diffraction study of a carbohydrate-derived dioxastannolan showed that, in the crystal, the former model is correct.[4f] In agreement with this, the Mössbauer quadrupole coupling in three dioxastannolans lay within the range 2.77—2.85 mm s^{-1}, appropriate for a trigonal bipyramidal *cis*-R_2SnX_3.[14]

In the liquid state, ^{119}Sn n.m.r. spectroscopy can be used to



(VIII)



(IX)

analyse the structures. As the neat liquids, dibutyltin dialkoxides, $Bu_2Sn(OR)_2$ show δ (^{119}Sn) from −150 to −165 when R is small (*e.g.* Me, Et, Pr, Bu), but δ *ca.* −34 when R is bulky (*e.g.* Bu^t or Pe^t). The large negative (upfield) shifts move to lower field as the liquids are diluted with carbon tetrachloride, but the smaller shifts are concentration-independent. It is concluded that the low-field chemical shifts indicate monomeric species with 4-co-ordinate tin, and the high-field shifts, which are concentration-dependent, indicate associated species with 5- or possibly 6-co-ordinate tin.[14]

Three dibutyldioxastannolans showed δ($CDCl_3$) −155 to −189 p.p.m. which would be compatible with the dimeric structure (VIII).[14]

Our 2,2-diphenyl-1,3,2-dioxastannolen in chloroform showed (by vapour pressure osmometry), a molecular weight of 450 at 1.4×10^{-2}M and 504 at 1.4×10^{-1}M, against a monomolecular formula weight of 443. The ^{119}Sn n.m.r. spectrum showed δ *ca.* −216, appropriate for a co-ordination number greater than 4, and this was confirmed by the Mössbauer spectrum of the solid (δ 1.46, ΔE_q 3.55 mm s^{-1}).

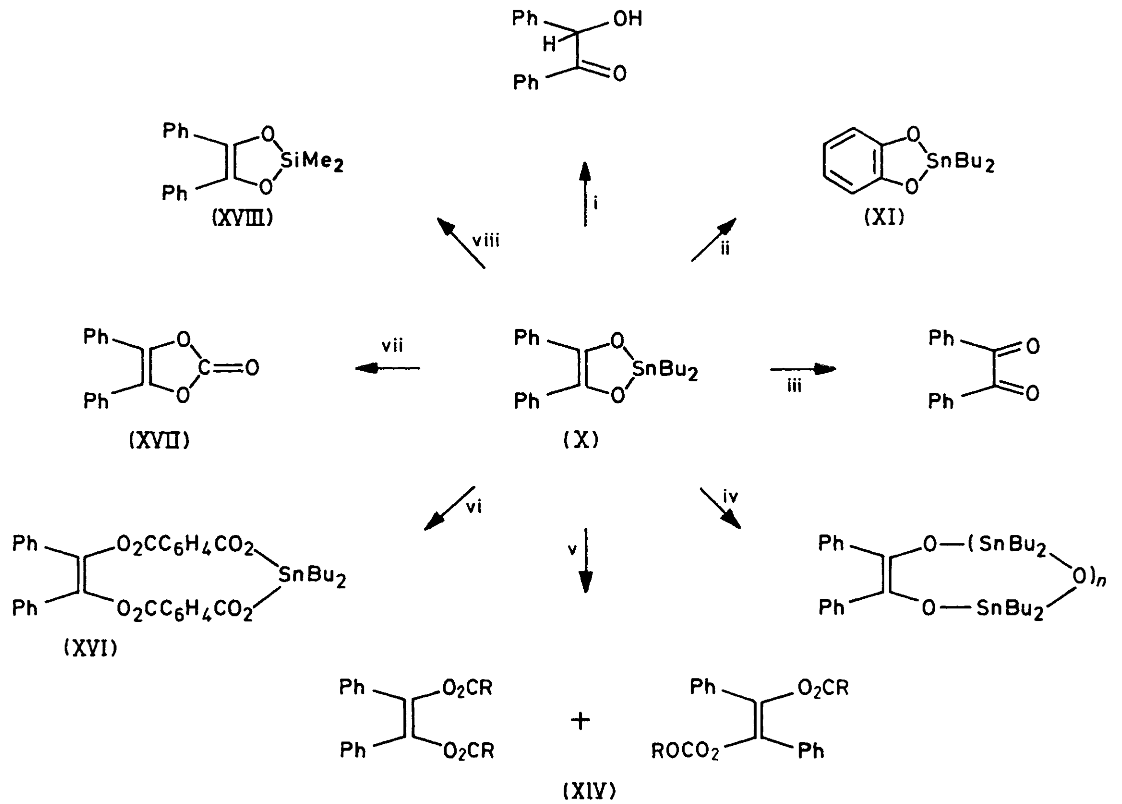
The best interpretation of these data appears to be that, in the crystal, the dioxastannolen is associated so that the co-ordination number of the tin is 5 or 6. In concentrated solution, the molecules are associated into at least dimers, but in more dilute solution, dissociation occurs to give monomeric dioxastannolen units.

Reactions of the Organotin Enediolates.—The principal reactions of 2,2-diphenyl-1,3,2-dioxastannolen (X) which we have studied are shown in the Scheme.

Whereas the bistributyltin derivative of benzoin, (VII), is readily hydrolysed in air, the cyclic dibutyltin derivative (X) is stable towards neutral water and methanol, but it is hydrolysed by dilute hydrochloric acid to give benzoin, and reacts readily with catechol to give benzoin and the catecholate (XI).

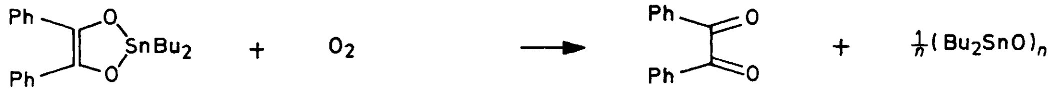
Bromine is known to oxidise a 1,3,2-dioxastannolan to the corresponding acyloin;[4c] presumably, the HBr formed by oxidation of the first HCOSn group then brings about rapid acidolysis of the second O–Sn bond. Under the same mild conditions, bromine oxidises the dioxastannolen to benzil.

The oxidation with dioxygen is less expected: a sample of (X), on exposure to air for a few hours, was converted into benzil and the enediolate (V), derived from benzoin and three dibutyltin oxide units. The reaction probably proceeds



Scheme. *Reagents:* i, H_3O^+; ii, *o*-$C_6H_4(OH)_2$; iii, Br_2 or O_2; iv, Bu_2SnO; v, RCOCl or $(RCO)_2O$; vi, *o*-$C_6H_4(CO)_2O$; vii, $COCl_2$; viii, Me_2SiCl_2

by initial autoxidation of the dioxastannolen to give benzil and a reactive low oligomer of dibutyltin oxide (equation 16), which then inserts into the unchanged dioxastannolen as we have described,[10] to give the telomer (V) (equation 17).



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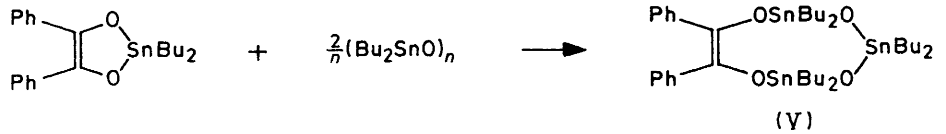


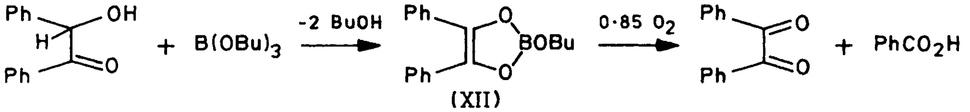
(V)

(17)

The mechanism of this oxidation is not obvious, but it appears not to be restricted to tin compounds. Benzoin reacts with tributyl borate at 100 °C to give 2-butoxy-4,5-diphenyl-1,3,2-dioxaborolen (XII), which absorbed oxygen, at a rate not affected by quinol, to give benzil and benzoic acid together with a trace of benzoic anhydride (equation 18).[15]

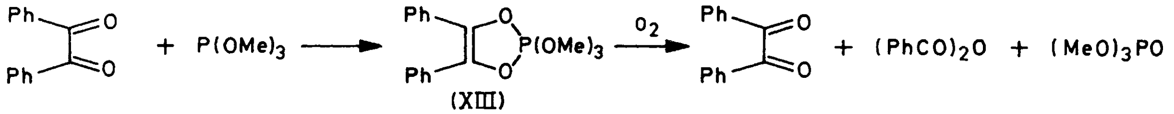
Similarly, 2,2,2-trimethoxy-4,5-diphenyl-1,3,2-dioxaphospholen (XIII), formed from the reaction between benzil and trimethyl phosphite, absorbs oxygen during a few days at room temperature to give benzil (*ca.* 67%), benzoic anhydride (*ca.* 30%), and trimethyl phosphate (*ca.* 94%) (equation 19).[16]

Many of the applications of the dioxastannolans in organic synthesis involve regiospecific monoacylation. With the dioxastannolens, one can envisage monoacylation, with the possibility of retention or exchange of the original positions of the carbonyl and hydroxy-groups, or diacylation.



(XII)

(18)

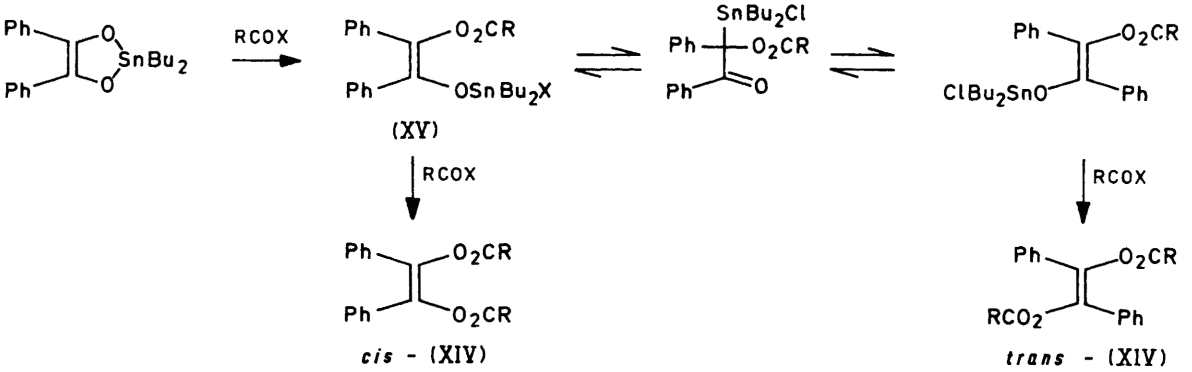


(XIII)

(19)

The dioxastannolen (X) reacted exothermically with one molar equivalent of acetyl chloride to give benzoin acetate. With two molar equivalents of acetyl chloride it gave only the *cis*-diacetate (*cis*-XIV; R = Me) [as did also the endiolate (VII) confirming its *cis*-structure], but with acetic anhydride, the *trans*-diacetate (*trans*-XIV; R = Me) was also formed in *ca.* 10% yield. Benzoyl chloride is less reactive than acetyl chloride; in the presence of two molar equivalents at 0 °C, only benzoin benzoate was formed, while at 70 °C, only *trans*-stilbene dibenzoate (*trans*-XIV; R = Ph) was obtained, m.p. 185 °C. Wakeshima and Kijima[9] reported that 2,2-bis(2-dimethylaminoethoxy)-4,5-diphenyl-1,3,2-dioxastannolen (see equation 8) reacted at 40 °C to give the *cis*-dibenzoate, m.p. 156—158 °C.

This stereoselectivity can be understood in terms of competitive acylation and metallotropic isomerisation of the initial monoacyl derivative (XV) (equation 20).



(20)

A very reactive acylating agent such as acetyl chloride can capture (XV) to give the *cis*-stilbene diester, but, with a less reactive reagent such as acetic anhydride or benzoyl chloride, the *cis*-monoester has time to rearrange to the *trans*-monoester before further acylation now gives preferentially the *trans*-diester.

Such an isomerisation should not be possible with the initial monoester from a cyclic anhydride, and phthalic anhydride reacted with the dioxastannolen (X) to give the cyclic dibutyltin derivative of the di(hydrogen phthalate) of *cis*-stilbene (XVI).

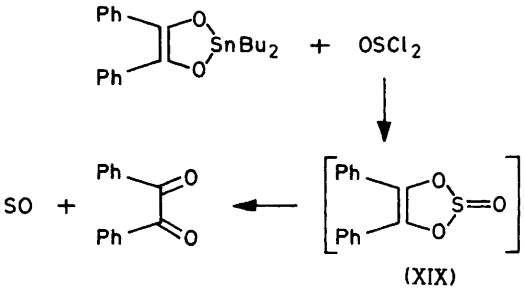
Diacid chlorides, $ClCO(CH_2)_nCOCl$ should similarly give cyclic *cis*-products, and Shanzer has reported the reaction with dioxastannolans to give cyclic esters.[4n] In the same way, our dioxastannolen (X) reacted with phosgene to give the *cis*-vinylene carbonate (XVII), and with succinyl dichloride to give the monomeric cyclic succinate. It is interesting that Shanzer has shown that higher diacid dichlorides $ClCO(CH_2)_nCOCl$ ($n \geqslant 3$) react with dioxastannolans to give, not dilactones, but tetralactones as though the stannolans reacted through the ten-membered ringd imers (VII).[4n] We have confirmed that 2,2-dibutyl-1,3,2-dioxastannolen reacts with succinyl dichloride to give the tetralactone, but the dioxastannolen (X) gave the dilactone. This emphasises the reduced tendency of the stannolen to behave as a dimer in solution.

Similar reactions can be envisaged with inorganic dichlorides to give other types of heterodioxolens.

Dimethyldichlorosilane reacted with the dioxastannolen (X) exothermically; the n.m.r. spectrum indicated that the dioxasilolen (XVIII) was formed, but the pure compound could not be isolated.* The difficulty in obtaining the pure compound may be related to ther eaction which is observed when the dioxastannolen (X) is treated with thionyl chloride, which gave not the sulphite (XIX), but benzil and, presumably, sulphur monoxide (equation 21). Fieser and Okumura[18] showed that benzoin reacted with thionyl chloride to give benzil and sulphur monoxide (together with some PhCOCHClPh), and they produced evidence showing that the sulphite (XIX) was involved as an intermediate.

A further characteristic reaction of organotin alkanolates is their addition to heterocumulenes such as isocyanates [*e.g.* equation (22)], isothiocyanates, carbon dioxide, and carbodiimides,[1] and Shanzer has extended these reactions to the preparation of cyclic carbamates from dioxastannolans and diisocyanates.

However, the dioxastannolen (X) did not react with methyl, phenyl, or 1-naphthyl isocyanate, or with phenyl isothiocyanate, even under reflux in toluene or in the presence of tetrabutylammonium bromide as a potential catalyst. In this respect, the vinyloxytin compounds resemble the phenoxytin compounds:[19] the addition reactions are dominated by the nucleophilic power of the oxygen bonded to tin for the nitrogen of the heterocumulene, and this is reduced by the presence of the electron-attracting phenyl of vinyl group.



(21)

$$Bu_2Sn(OMe)_2 + PhNCO \xrightarrow[\text{exothermic}]{20\,^{\circ}\mathrm{C}} Bu_2Sn(NPhCO_2Me)_2 \quad (22)$$

Conclusion

This work has provided a convenient route to the organotin derivatives of the enediolates, particularly the dioxastannolens, which, by reaction with suitable metallic dihalides, can provide a route to the enediolates of other metals. The reaction of the dioxastannolens with reactive acylating agents to give stereospecifically the *cis*-vinylene acylates may be synthetically useful, and the dioxastannolens may also find applications in cycloaddition reactions.

The properties of the dioxastannolens focus attention on two unusual reactions which may be important in a wider

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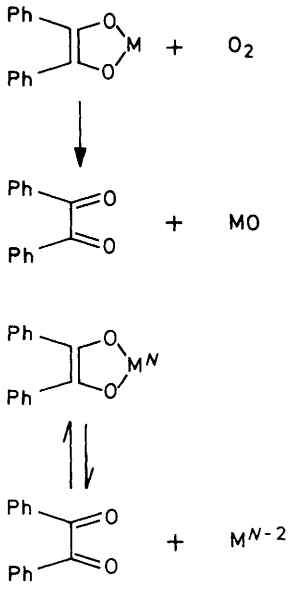
* The bistrialkylsilyl derivatives of enediols are familiar as intermediates in the acyloin condensation,[17] but the dialkylsilyl derivatives do not appear to have been described.

context. The first is the sensitivity of the dioxastannolens to oxygen, which is paralleled in the boron, phosphorus, and sulphur analogues (equation 23).



(23)

(24)

The second is the oxidative addition–reductive elimination process of equation (24), which is recognised also for compounds of phosphorus and of sulphur.

We hope now to study these reactions in more detail.

Experimental

2,2-*Dibutyl*-4,5-*diphenyl*-1,3,2-*dioxastannolen* (IV; R = Ph).—(i) *From benzoin and dibutyltin oxide*. Dibutyltin oxide (2.0 g) was heated under reflux with a solution of benzoin (1.7 g) in benzene (50 cm^3) under nitrogen under a Dean and Stark separator. During 1 h the oxide dissolved and water collected in the trap. The benzene was distilled off leaving compound (IV; R = Ph), a viscous red oil, which was recovered from pentane at −50 °C as an amorphous powder (2.9 g, 81%), m.p. 89—90 °C (Found: C, 60.0; H, 6.15. $C_{22}H_{28}O_2Sn$ requires C, 59.6; H, 6.32%); δ ($CDCl_3$) 0.7—1.9 (18 H, m, Bu), 7.2—7.7 and 7.9—8.1 (10 H, m, Ph); $\nu_{max.}$ 1 650 (C=C) and 670 cm^{-1} (SnOC). Other physical data are given in the text. The residual oil (0.85 g) consisted of benzil together with oligomers such as (V).

(ii) *From benzoin and dibutyltin dimethoxide*. Dibutyltin dimethoxide (3.2 g) and benzoin (2.3 g) in benzene (50 cm^3) were kept at 40 °C for 45 min. The solvent was removed leaving an oil; the i.r. and n.m.r. spectra were identical with that of the dioxastannolen (IV; R = Ph) obtained above, and showed the absence of carbonyl and methoxy-groups.

(iii) *From* 1,2-*diphenylvinylene carbonate and dibutyltin oxide*. The carbonate (0.95 g) and dibutyltin oxide (0.99 g) were heated together in toluene (30 cm^3) under nitrogen and under reflux. Carbon dioxide began to be evolved at 90 °C, and the dibutyltin oxide dissolved within 5 min at 110 °C. The solution was heated under reflux for 1 h, then the toluene was distilled off. The residual oil was dissolved in pentane, and, at −10 °C, 1,2-diphenylvinylene carbonate (100 mg), the dioxastannolen (IV; R = Ph), m.p. 86—88 °C (180 mg), and the oligomer (V), m.p. *ca.* 140 °C (290 mg), were recovered.

(iv) *From* 1,2-*diphenylvinylene carbonate and dibutyltin dimethoxide*. Dibutyltin dimethoxide (0.77 g) and the carbonate (0.62 g) were heated under nitrogen at 120—130 °C for 90 min. Dimethyl carbonate was distilled off leaving a yellow oil, which was recovered from pentane as pale yellow crystals, m.p. 89—90 °C. An attempt to distil the dioxastannolen gave, at 82—86 °C/0.5 mmHg, tetrabutyltin (55%), then a yellow oil (15%) which solidified to give benzil; a dark grey residue was left in the flask.

Reaction of Dianisylvinylene Carbonate with Dibutyltin Dimethoxide.—The carbonate (0.56 g)[20] and dibutyltin dimethoxide (0.55 g) were heated together at 130 ± 5 °C for 90 min; dimethyl carbonate was distilled off leaving a yellow oil from which anisil, m.p. 130—132 °C (79%), was recovered.

The carbonate (50 mg) and dialkoxide (50 mg) in $CDCl_3$ (1 cm^3) were sealed in an n.m.r. tube, and the progress of the reaction at 37 °C was monitored by the signals of the methoxy-groups. During 3 weeks, the singlet for dimethyl carbonate (δ 3.78) developed, and the tin enediolate (63%; δ 3.80) and anisil (7%; δ 3.84) were formed.

2,2-*Dibutyl*-4,5-*dimethyl*-1,3,2-*dioxastannolen* (IV; R = Me).—Azeotropic dehydration of dibutyltin oxide (7.0 g) and monomeric acetoin (2.4 g) in benzene (50 cm^3) for 1 h gave the dioxastannolen as an oil, which was recovered from pentane as an amorphous powder (4.1 g, 47%), m.p. 80 °C; $\nu_{max.}$ 670 cm^{-1} (SnOC) (Found: C, 46.6; H, 7.5. $C_{12}H_{24}O_2Sn$ requires C, 45.2; H, 7.6%).

1,2-*Bis*(*tributylstannyloxy*)-1,2-*diphenylethene* (VII).—(i) *From benzoin and tributyltin methoxide*. The methoxide (2.15 g) and benzoin (0.71 g) were kept at 130—135 °C for 90 min, giving a yellow oil which was distilled into the following three fractions: (a) hexabutylditin, b.p. 100—115 °C/0.05 mmHg, identified by its n.m.r. spectrum and its reaction with bromine; (b) 1,2-bis(tributylstannyloxy)-1,2-diphenylethene (VII) (1.08 g, 41%), b.p. 144—148 °C/0.05 mmHg, identical with the sample described below; and (c) benzil, b.p. 150 °C/0.05 mmHg.

Azeotropic dehydration of bistributyltin oxide (10 mmol) and benzoin (20 mmol) in toluene for 90 min gave the monotributyltin derivative as an oil, δ (CCl_4) 0.7—1.7 (18 H, Bu), 6.0 [1 H, s, C*H*(OH)], 6.0—7.5 (5 H, Ph), and 7.7—8.0 (5 H, Ph). Under the same conditions, acetoin gave the monotributyltin derivative, b.p. 84 °C/0.01 mmHg as described in ref. 12.

Reaction of 2,2-*Dibutyl*-4,5-*diphenyl*-1,3,2-*dioxastannolen* (IV; R = Ph) *with Catechol*.—The dioxastannolen [from benzoin (2.29 g) and dibutyltin oxide (2.69 g)] was heated under reflux in benzene (50 cm^3) with catechol (0.85 g) for 2 h. The dibutyltin derivative of catechol (11.55 g, 59%) separated as a white powder, m.p. 272—274 °C, identical with authentic material. Benzoin (0.84 g, 37%) was recovered from the filtrate.

Oxidation of 2,2-*Dibutyl*-4,5-*diphenyl*-1,3,2-*dioxastannolen* (IV; R = Ph) *with Bromine*.—The dioxastannolen [from benzoin (2.42 g) and dibutyltin oxide (2.64 g)] in benzene (50 cm^3) was treated slowly with a solution of bromine (250 μl) in dichloromethane. The colour of the bromine was discharged as an exothermic reaction took place. After 2 h, the solvent was removed yielding an oil which was recrystallised from hexane to give benzil (1.65 g, 78%) as yellow needles, together with a residual oil consisting largely of Bu_2SnBr_2 (i.r. spectrum).

Autoxidation of 2,2-*Dibutyl*-4,5-*diphenyl*-1,3,2-*dioxastannolen* (IV; R = Ph).—A sample of the dioxastannolen (10.0 g), prepared by azeotropic dehydration of dibutyltin oxide and benzoin in benzene (100 cm^3) under nitrogen, was divided into two equal parts. One was worked up immediately, giving the tin enediolate and 80 mg of benzil. The second fraction was stirred in an open flask for 5 h in the dark at room temperature, then kept in contact with air overnight. The solvent was then removed giving benzil (1.1 g) and the oligomeric cyclo-oxastannonan (V) (2.3 g), and a final fraction of an oil consisting of the more soluble oligomers $\overline{PhC{=}CPh(OSnBu)_nO}$, $n = 1$ and 2.

Acylation of Organotin Endiolates.—(i) Heat was evolved when acetyl chloride (1.5 g, 19 mmol) was added to a toluene solution of 2,2-dibutyl-4,5-diphenyl-1,3,2-dioxastannolen (IV; R = Ph) (3.75 g, 8.5 mmol). After 30 min, the toluene was distilled off yielding *cis*-1,2-diphenyl-1,2-diacetoxyethene as needles from methanol (1.1 g), m.p. 117—118 °C, $\delta(CDCl_3)$ 2.20 (6 H, s, Me), 7.32 (10 H, s, Ph), identical with an authentic sample prepared by reductive acetylation of benzil with acetic anhydride, hydrochloric acid, and zinc.[21]

(ii) Under the same conditions, acetic anhydride gave in 62% yield a mixture of the *cis*-diacetate (90%) and *trans*-diacetate (10%), $\delta(CDCl_3)$ 2.08 (6 H, s, Me), 7.3—7.7 (10 H, m, Ph).

(iii) A mixture of the dioxastannolen (3 g, 7 mmol) in toluene (30 cm³) and benzoyl chloride (2.0 g, 14 mmol) in ether (25 cm³) was kept overnight at room temperature. Next day, benzoyl chloride was recovered together with benzoin benzoate (5.1 g, 89%), m.p. 123—124 °C (lit.,[22] m.p. 124 °C).

(iv) A solution of the dioxastannolen (1.3 g, 3.0 mmol) and phthalic anhydride (0.9 g, 4.5 mmol) in benzene (40 cm³) was kept for 1 h at 55 °C. The solvent was distilled off and the residual solid was recrystallised from pentane yielding benzil, dibutyltin phthalate (m.p. 202—204 °C; identical with the authentic material prepared from dibutyltin oxide and phthalic anhydride), and the cyclic diphthalate (XVI) (0.3 g), m.p. 125—127 °C, $\nu_{max.}$ 1 710 cm⁻¹ (C=C); $\delta(CDCl_3)$ 0.7—2.0 (18 H, m, Bu), 7.0—8.2 (18 H, C_6H_4 and Ph) (Found: C, 62.7; H, 4.4. $C_{38}H_{38}O_8Sn$ requires C, 61.7; H, 4.9%).

(v) The dioxastannolen [from benzoin (2.4 g) and dibutyltin oxide (2.5 g)] in benzene (50 cm³) was treated with phosgene (0.9 g) in toluene (5 cm³). After 1 h at room temperature, the solvents were distilled off giving an oil which yielded, from light petroleum, large crystals of 1,2-diphenylvinylene carbonate (2.0 g, 84%), m.p. and mixed m.p. 74—75 °C.

(vi) An exothermic reaction occurred when acetyl chloride was added to a solution of *cis*-1,2-bis(tributylstannyloxy)-1,2-diphenylethene (100 mg) in $CDCl_3$. The n.m.r. spectrum showed δ 2.20 (6 H, s, Me), 7.32 (10 H, s, Ph), characteristic of the *cis*-diacetate.

(vii) Succinyl dichloride (1.8 g) in benzene (10 cm³) was added to a solution of the dioxastannolen (X) [from dibutyltin oxide (4.4 g) and benzoin (3.7 g)] in benzene (50 cm³) under nitrogen and left overnight. The solvent was then removed leaving an oil which was recrystallised from pentane and then from carbon tetrachloride-light petroleum, yielding 1,2-*diphenylvinylene succinate* (2.5 g), sintering 70 °C, m.p. 85 °C, which was unstable in air; *M* (in $CHCl_3$, by vapour pressure osmometry) 318; $C_{18}H_{14}O_4$ requires 294; $\delta(CDCl_3)$ 2.82 (4 H, s, CH_2), 7.15—7.80 (10 H, Ph); *m/e* 294 (26%, *M*), 250 (12, $M - CO_2$), 212 (21, PhCOCOPh), 165 [22, PhC(OH)-$OCOCH_3$], 122 (19, $PhCO_2H$), 105 (100, PhCO), and 77 (75, Ph).

Reaction with Dichlorodimethylsilane.—The enediolate (X) (3.30 g) in toluene (15 cm³) was treated, with stirring, with dichlorodimethylsilane (0.96 g) in toluene (10 cm³) at 0 °C. The mixture was allowed to warm to room temperature after 20 min, and a solution of bipyridyl (1.16 g) in benzene (10 cm³) was added. The complex [Bu_2SnCl_2, bipy] separated, and was filtered off (2.80 g, 82%), m.p. 178—179 °C. Volatile material was removed from the filtrate, leaving the dioxasilolen (XVIII), which could not be distilled, δ (CCl_4) 0.18 (6 H, s, Me_2), 7.98 and 7.48 (10 H, Ph_2); $\nu_{max.}$ 1 650 cm⁻¹ (C=C str.). After brief exposure to air, a strong band was apparent at 3 450 cm⁻¹ (OH str.).

Reaction with Thionyl Chloride.—The dioxastannolen (X) was prepared from dibutyltin oxide (3.5 g) and benzoin (3.0 g); thionyl chloride (1.6 g) in benzene (15 cm³) was then added at 0—5 °C, and the mixture was kept at room temperature overnight. The solvent was removed, yielding benzil (2.65 g, 89%).

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