THE REACTIONS OF TETRAVINYLTIN WITH CARBOXYLIC ACIDS: PROPERTIES OF TIN(IV) TETRACARBOXYLATES

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Although lead(IV) tetracarboxylates are well-known, those of tin(IV) have been little studied; tin(IV) tetraacetate has been prepared from tin(IV) iodide and acetic anhydride[1] and the tetraisobutyrate from stannic chloride and silver isobutyrate[2], but in neither case have any chemical or structural properties been reported. The reactions of organotin compounds R_4Sn with organic acids HX have been shown to give only the mono- or disubstituted derivatives R_3SnX, R_2SnX_2 in poor yield (R = alkyl) for a wide range of acids[3]. However, quantitative cleavage of all organic groups from organoboron compounds R_3B has been achieved[4] by heating with an anhydrous carboxylic acid, for a wide range of organic groups R, and we report here the application of this method to tetravinyltin, when the reaction

$$Sn(CH{=}CH_2)_4 + 4RCO_2H \longrightarrow Sn(O_2CR)_4 + 4C_2H_4$$

is virtually quantitative, and gives the tin tetracarboxylate directly in a pure state when the carboxylic acid is sufficiently volatile.

EXPERIMENTAL AND RESULTS

Tetravinyltin was prepared by reaction of tin(IV) chloride with vinyl magnesium bromide in tetrahydrofuran, and purified by fractionation in a vacuum line. The carboxylic acids were dried by treating with phosphorus(V) oxide *in vacuo*. Transfers of tetravinyltin and sufficiently volatile carboxylic acids were all made in the vacuum line, and the amounts of tetravinyltin used were determined by direct weighing. Reactions were carried out in sealed tubes at 110° for periods up to 40 h. In a typical experiment, tetravinyltin (3.26 mmol) and excess propionic acid were heated at 110° for 33 h; the only volatile product was ethylene (13.10 mmol). After removal of excess acid, the product was obtained as colourless needle-shaped crystals, very sensitive to hydrolysis. Hydrolysis with water at 100° for 2 h in a sealed tube gave tin(IV) oxide and propionic acid which were, respectively, weighed and titrated, to give Sn/HO_2CEt = 1/4.00. Results for other acids are shown in Table 1, with the m.p. of the product where this could be isolated from excess acid.

The product of the tetravinyltin/stearic acid reaction was sufficiently resistant to hydrolysis to permit recrystallisation from benzene. (Found: C, 67.4; H, 11.2; Sn, 9.6. $C_{72}H_{140}O_8Sn$ calcd.: C, 69.1; H, 11.2; Sn, 9.5 %.) Shorter reaction times, or lower reaction temperatures, normally gave incomplete reaction and no intermediate

TABLE 1

TIN(IV) TETRACARBOXYLATES PREPARED

R (in HO_2CR)	*$Sn(CH{=}CH_2)_4$ used (mmol)*	*C_2H_4 evolved (mmol)*	*Ratio. C_2H_4/Sn*	*Time (h)*	*M.p. of product (°C)*
H	0.69	2.65	3.84	20	250
Me	0.66	2.61	3.95	18	255–256[a]
Et	3.26	13.10	4.01	33	146
iso-Bu	1.35	5.23	3.88	30	116[a]
n-Bu	1.97	7.94	4.03	36	—
n-$C_{11}H_{23}$	1.22	4.71	3.88	20	—
n-$C_{17}H_{35}$	1.57	6.24	3.98	15	65–66

[a] M.p. agrees with that previously reported[1,2].

products, except with formic acid, where reaction at room temperature gave a C_2H_4/Sn ratio of 2.02 and a solid product insensitive to hydrolysis, which sublimed at 180° but did not melt below 300°, and which analysed for divinyltin(IV) diformate. (Found: C, 27.3; H, 3.0; Sn, 44.9. $C_6H_8O_4Sn$ calcd.: C, 27.4; H, 3.0; Sn, 45.2 %.)

Cryoscopic molecular weight determinations in benzene, for the tetraacetate and tetrapropionate, showed a fall over the first 30 min, after mixing solute and solvent, to values close to those expected for the monomers, and thereafter remaining constant. Thus, for the tetraacetate the mol. wt. values were, successively, 595, 395, 372, and finally 365 (mol. wt. for $Sn(O_2CCH_3)_4$ is 355). These observations suggested association in the solid, breaking down in solution. The infrared spectra of the same two solid carboxylates showed absorptions, assigned to carbonyl stretching, at 1262 and 1704 cm^{-1} which increased in intensity when the carboxylates were dissolved in carbon tetrachloride; but two additional peaks at 1440 and 1560 cm^{-1}, in the spectra of the solids, disappeared completely in solution. With the tetrastearate, these two peaks decreased but did not disappear in solution. The solid divinyltin(IV) diformate showed four carbonyl absorptions at 1368, 1382, 1590 and 1600 cm^{-1}; it was insoluble in benzene and carbon tetrachloride.

A study of the chemical properties of tin(IV) tetrapropionate showed no evidence of adduct formation with trimethylamine at 0° or at −78°. With dimethylamine, about 6 moles were taken up by 1 mol of the tetrapropionate at temperatures below −10°, but above this temperature some dimethylamine was evolved together with N,N-dimethylpropionamide and water. Rapid fractionation permitted separation and measurement of the latter products before they reacted, and in a typical reaction at room temperature 1.68 mmol tin tetrapropionate reacted with 6.75 mmol dimethylamine to yield 3.28 mmol water and 3.31 mmol dimethylpropionamide; the residual solid (0.598 g) on hydrolysis gave 1.68 mmol tin and 3.33 mmol dimethylamine. The reaction:

$$Sn(O_2CEt)_4 + 4Me_2NH \longrightarrow 2H_2O + 2EtCONMe_2 + (Me_2N)_2Sn(O_2CEt)_2$$

accounts satisfactorily for these data, and 0.598 g of residual solid corresponds to 1.69 mmol of bis(dimethylamino)tin(IV) dipropionate. Changes in reaction time or amount of dimethylamine added caused no change in the reaction ratios given above.

The product, a crystalline solid, had no definite m.p. and was sensitive to hydrolysis, evolving dimethylamine with cold water. The infrared spectrum of the solid showed peaks at 1402 and 1558 cm^{-1}; in solution in carbon tetrachloride these shifted to ~ 1260 and 1704 (broad band) cm^{-1} respectively. Additional peaks at 812, 883 and 1015 cm^{-1}, observed for both solid and solution, were assigned to $Sn–NMe_2$ vibrations[5].

Tin(IV) tetrapropionate was found to dissolve in liquid hydrogen chloride; at —78°, 3.63 mmol of the tetrapropionate retained 21.68 mmol of hydrogen chloride, but between —20° and +20° 10.93 mmol hydrogen chloride were evolved together with 10.64 mmol propionic acid. The solid reaction product then remaining gave on hydrolysis 3.64 mmol tin (as SnO_2) and an acid solution containing 14.33 mmol acid and 10.75 mmol chloride. These data suggest the reaction at —78°:

$$Sn(O_2CEt)_4 + 6HCl \longrightarrow Cl_3Sn(O_2CEt) + 3[EtCO_2H_2]^+Cl^-$$

and above —20°:

$$3[EtCO_2H_2]^+Cl^- \longrightarrow 3EtCO_2H + 3HCl$$

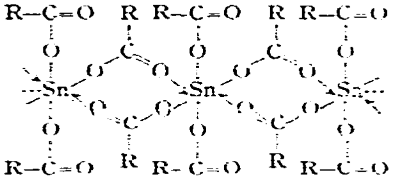
The solid product appeared as dark brown crystals of indefinite m.p. The reaction ratios quoted above were highly reproducible, supporting formulation as a definite compound Cl_3SnO_2CEt, but this was not studied further.

DISCUSSION

Two studies of the cleavage reactions of compounds $R_2Sn(CH{=}CH_2)_2$ (R = alkyl or phenyl) have both indicated that the vinyl group is more easily cleaved from tin than any alkyl group, but less easily than phenyl[6]. However, reaction of tetraphenyltin with the carboxylic acids used in the present work, and under the same conditions, gave no more than 70 % cleavage even after prolonged heating; hence vinyl is more readily cleaved *completely* than is phenyl. Moreover, not all carboxylic acids can effect complete cleavage; thus, trifluoroacetic acid only removes three vinyl groups from tetravinyltin[7], and in the present work, although formic acid effects complete cleavage at 110°, at ordinary temperature only two vinyl groups are removed. These facts suggest that acids of high strength are less effective for complete cleavage. If a commonly postulated cleavage mechanism requiring electrophilic attack at the α-carbon atom and nucleophilic attack at the tin atom is assumed, then initial attack will be favoured by any factors, which impart a polarity in the sense $Sn^{\delta+}–C^{\delta-}$ to the tin–carbon bond, and by high acid strength. But as attached groups R are successively removed from R_4Sn and replaced by carboxylate groups, the electron-attracting nature of the latter will then render further cleavage more difficult. Hence carboxylate groups corresponding to acids of high strength must retard complete substitution. It is then surprising that with, (say) three carboxylate groups already attached, the remaining tin–vinyl bond is so readily cleaved; it must be supposed that the electron density at the α-carbon atoms is initially high, and is not reduced to the point of unreactivity. In compounds R_3SnR' where R′ is a phenyl or substituted phenyl group, the existence of $p_\pi–d_\pi$ bonding between the tin and α-carbon atoms has been demonstrated[8]; this may therefore be important in reducing attack on tin–

phenyl bonds in partly carboxylated phenyltin(IV) compounds, but is apparently less important for corresponding vinyltin carboxylates.

In trialkyltin carboxylates, a shift of the carbonyl stretching frequencies from 1410 and 1570 cm^{-1} in the solids to 1300 and 1650 cm^{-1} in the dissolved state has been ascribed to a change from bridging to non-bridging (ester) carboxylate groups[9]. The changes in the infrared spectra of the tin tetracarboxylates on solution, and the rapid decrease of the molecular weights to values near to those of the monomers, are consistent with the presence of both bridging and non-bridging groups in the solid, bridging virtually disappearing in solution. Since the solid tetracarboxylates have definite melting points, definite units rather than co-ordination polymers of indefinite size appear to be present. Of the four carboxylate groups directly attached to any one tin atom, it is not possible to say with certainty how many are bridging and how many ester-like, but there is some evidence to suggest an average of two groups of each kind for each tin atom. The peaks attributed to carbonyl stretching in the spectrum of divinyltin diformate are very similar to those found in dimethyltin diformate, where only bridging formate groups are present[11]; and both compounds are not easily hydrolysed and are insoluble in non-polar solvents, in contrast to the tetraformate. Trimethyltin acetate is also insensitive to hydrolysis and insoluble in non-polar solvents. It therefore seems likely that in compounds $R_{4-n}Sn\ (O_2CR)_n$, bridging-only carboxylate groups are present up to $n = 2$; above this value, non-bridging groups are present and impart sensitivity to hydrolysis and solubility in non-polar solvents. Hence a structure



for the tetracarboxylates seems plausible, with 6-co-ordinate tin. Support for this structure comes from the reaction of the solid tetrapropionate with dimethylamine. Here, initial attack by the latter at the carbonyl carbon atom of an attached carboxylate group seems likely (since dimethylpropionamide is a reaction product) but attack stops when two carboxylate groups have been replaced, the solid product retains the bridging propionate groups, and initial hydrolysis releases dimethylamine. These observations are explained if attack occurs only at the two non-bridging carboxylate groups, which are replaced by terminal dimethylamino groups.

SUMMARY

Complete cleavage of tetravinyltin is achieved by heating with anhydrous carboxylic acids; the products, tin(IV) tetracarboxylates, contain both bridging and ester carboxylate groups in the solid state but are essentially monomeric in solution. Reaction of the tetrapropionate with dimethylamine gives the compound $(Me_2N)_2$-$Sn(O_2CEt)_2$ and with hydrogen chloride $Cl_3Sn(O_2CEt)$ is formed.

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