THE CLEAVAGE BY IODINE OF THE TIN–TIN BOND IN R_6Sn_2 COMPOUNDS. KINETICS AND MECHANISM

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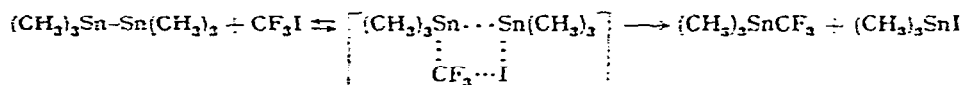
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INTRODUCTION

From a survey of the literature it appears that in studies of S_E processes, organometallic compounds are utilized in order to provide an incipient or free carbanion in the rate-determining process. Generally, such reactions are characterized by multi-center and assisted mechanistic pathways; one would expect nucleophilic assistance to occur where there is a deficiency of electrons near the point of attack, and this is the case in organometallic compounds, in which the metal atom is always electron deficient.

A review by Dessy and Paulik[1] lists reported reactions of organometallic compounds in which a four-center reaction mechanism has been proposed. Among these in the reaction:

$$(CH_3)_3Sn-Sn(CH_3)_3 + CF_3I \rightleftarrows \begin{bmatrix} (CH_3)_3Sn\cdots Sn(CH_3)_3 \\ \vdots \qquad \vdots \\ CF_3\cdots I \end{bmatrix} \longrightarrow (CH_3)_3SnCF_3 + (CH_3)_3SnI$$

the transition state is shown as suggested by Clark and Willis[2] on the basis of stoichiometric data alone. In addition a similar cyclic intermediate was postulated in the reaction between hexaethylditin and ethylene dibromide[3].

Kinetic investigations on the reaction between three ditin compounds and iodine have recently been described. Results on hexaphenylditin in cyclohexane are consistent with a bimolecular addition reaction via a cyclic intermediate[4], while in acetone results on hexamethyl- and hexabutylditin are explained by assuming an electrophilic attack by iodine on one of the tin atom of the ditin compound forming an unsymmetrical intermediate complex[5]. It is well known that the metal–metal bond in ditin compounds is easily broken by halogens in a quantitative reaction[6] of the following type:

$$R_3Sn-SnR_3 + X_2 \longrightarrow 2 R_3SnX$$
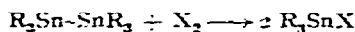
We have now studied kinetically the reaction of ditin compounds with iodine in alcoholic solutions.

Since the reactions are very fast, the technique employed is identical to that used in the case of iodination of tetraorganolead compounds[7].

The purpose of this work has been to study the effect of changing the solvent, to extend the investigation to include other ditin compounds, and thereby to obtain information on the mechanism of the reaction.

EXPERIMENTAL

Chemical and reagents

Hexamethylditin. Trimethyltin bromide was reduced with sodium in liquid ammonia by Kraus and Session's method[8]. The compound obtained was recrystallized from light petroleum (b.p. 60–80°) at —78°; m.p. 23°.

Hexaethylditin and hexapropylditin. These were prepared by the method used for the methyl compound[6]; Et_6Sn_2 b.p. 152–154°/17 mm; Pr_6Sn_2 b.p. 143°/15 mm.

Hexabutylditin. This compound is commercially available from Fluka. The purchased sample was purified by molecular distillation before use.

Trimethyltriphenylditin. This was prepared from triphenyltinsodium and trimethyltin chloride in liquid ammonia by Kraus and Bullard's method[9]; m.p. 104°.

Triethyltriphenylditin. This was prepared by Neumann's method[10] from Ph_3SnH, (30 mmole) and $(Et_3Sn)_2O$ (15 mmole) in dry benzene under a nitrogen atmosphere and at room temperature. The mixed ditin compound is an oil with m.p. 16–17°. It was stored under dry nitrogen in the dark. It was recrystallized from acetonitrile at —40° before use. (Found: C, 51.6; H, 5.08; Sn, 42.9. $C_{24}H_{30}Sn_2$ calcd.: C = 51.85 %, H = 5.44 %, Sn = 42.7 %.)

Hexaphenylditin. To triphenyltin chloride suspended in liquid ammonia was added, with stirring, an excess of sodium. The ammonia was allowed to evaporate and the product was extracted with cold chloroform. Ethanol was added to the chloroform solution to precipitate out the hexaphenylditin; m.p. 231°.

Hexa-p-tolylditin. Tetra-p-tolyltin was prepared by Lesbre and Rouet's technique[11]. A mixture of tin tetrachloride (0.1 mole) and p-tolyl chloride (0.4 mole) was slowly added, under a dry nitrogen atmosphere, to a sodium suspension (0.8 mole) in boiling toluene, external heating being suspended at the start of the reaction. The mixture was refluxed for 7 h, then the hot solution was filtered and allowed to cool in the dark. On cooling, powdery crystals of tetra-p-tolyltin separated. By recrystallization from ethyl acetate, crystals were obtained with m.p. 234–236°. Yield 24.4 g.

Tri-p-tolyltin bromide was prepared from 11.4 g of tetra-p-tolyltin and 3.51 g of tin tetrabromide. The mixture was heated for 3 h at 205–215°, then for 3 h at 180°. Finally the heating proceeded for 1.5 h at 150–160°. The solid reaction products were extracted with ether (Soxhlet), and the solvent was distilled under vacuum. The crude tri-p-tolyltin bromide was recrystallized from acetone; m.p. 98°. Yield 7.2 g. The final product, hexa-p-tolylditin, was obtained by refluxing tri-p-tolyltin bromide and metallic sodium[6] in dry xylene; m.p. 253–254°. (Found: C, 64.0; H, 5.1; Sn, 30.5. $C_{42}H_{42}Sn_2$ calcd.: C, 64.3; H, 5.4; Sn, 30.3 %.)

Solvent purification

Methanol was purified by Lund and Bjerrum's method, by means of magnesium activated with iodine. Absolute ethanol (99.2 vol. %) was refluxed over freshly

calcined calcium oxide and was then fractionally distilled. Propanol was dried with metallic sodium and fractionally distilled[12].

"Spectroscopic grade" RP 2-propanol from C. Erba (Milano, Italy) was used. Benzene, sodium iodide, lithium nitrate were R.P., C. Erba reagents. Dry lithium perchlorate and sodium perchlorate were prepared from lithium and sodium carbonates and perchloric acid. The salts were dried in an oven under vacuum first at 130° and then at 200°. Alcoholic solutions of liquid ditin compounds of approximately $10^{-3} M$ were prepared before use. Their molarity was checked by coulometric titration with silver ion or bromine[13-15]. Solutions of solid ditin compounds were prepared by dissolving a known weighed amount of the sample in alcohols. Before preparing the solutions, the solvent was degassed with dry nitrogen and the solutions were kept under nitrogen atmosphere and stored in the dark. Under these conditions no decomposition was observed: the solutions tested after a week showed no change from the initial molarity.

Kinetic method

The reaction $R_6Sn_2 + I_2 \rightarrow 2\ R_3SnI$ (1) can only be followed by fast reaction techniques. In alcoholic solutions, however, the system is complicated by the formation of $R_3Sn^+I_3^-$, and it is best to follow the above reaction in the presence of a known amount of iodide ion $(10^{-2}—2 \times 10^{-1} M)$. This makes the reaction slower and simplifies handling of the complication caused by formation of the I_3^- complex. Under these conditions the equilibrium $I_3^- \rightleftarrows I^- + I_2$ (2) must be taken into account, and the most convenient method of following reaction (1) is by determining the change in the concentration of I_3^- with time. This may be to done by a spectrophotometric method or alternatively by an electrochemical method with amperometric indication of the I_3^-/I^- reversible redox system. The latter method has been employed in this work. The cell and apparatus have been described in previous papers[13-15], and are the same as those used for analytical work. In Fig. 1 a typical plot obtained by this method is shown. For a kinetic run the alcoholic iodide solution was previously degassed with dry nitrogen and heated until the temperature had reached the desired value. An appropriate amount of iodine was then generated electrolytically at constant current and for a known time, after which the indicator current due to the redox system I_3^-/I^- stabilizes itself at a definitive value noted by the galvanometer on the photographic paper. This value is represented by the horizontal line in the upper part of Fig. 1.

Practically all the iodine generated is in the form of I_3^-, since the equilibrium constant of (2) is approximately 10^{-5} and $[I^-] = 0.2\ M$. The initial value of the indicator current, is therefore related to the concentration of the species I_3^-. The organo compound solution (1 or 2 ml) was then injected into the cell, and the kinetic curve corresponding to the decrease of I_3^- by interaction of the R_6Sn_2 compound was obtained. It was assumed that the experimental rate equation must be of the form

$$v = k_{obs} [R_6Sn_2]^m [I_3^-]^n \tag{3}$$

and the order of the reaction was determined by the method of integration and by the differential method[16]. It was found that $m = n = 1$. The resulting k_{obs} values are in excellent agreement with the integrated second-order equation:

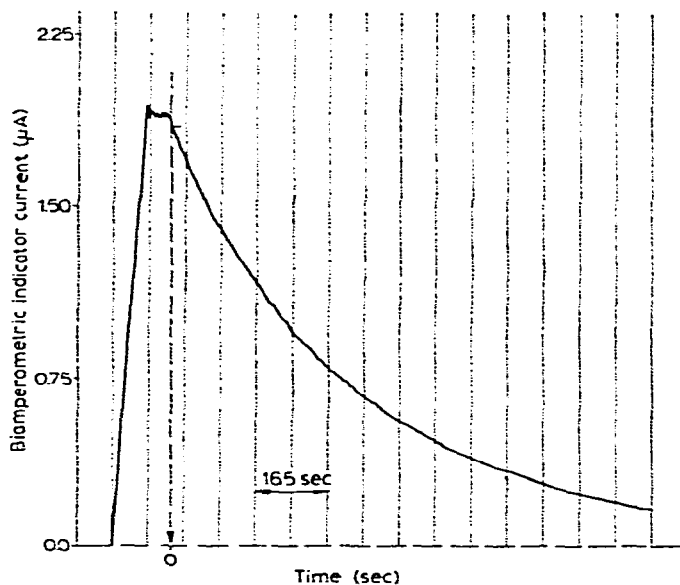$$k_{obs} = \frac{2.303}{t(a-b)} \log \frac{b\,(a-x)}{a\,(b-x)}$$

Fig. 1. Example of a kinetic plot as obtained for reaction $Bu_6Sn_2 + I_2$ in Methanol–0.2 M NaI at 17° (cf. Table 1).

in which $a = [R_6Sn_2]_0$, $b = [I_3^-]_0$. As an example Table 1 lists the figures obtained for one run, the kinetic plot of which is given in fig. 1.

TABLE 1

REACTION $Bu_6Sn_2 + I_2$ IN METHANOL: 0.2 M NaI

$a = [Bu_6Sn_2]_0 = 2.3342 \times 10^{-5}$; $b = [I_3^-]_0 = 0.7124 \times 10^{-5}$.

Time t (sec)	$\dfrac{2.303}{t(a-b)} \times 10^3$	$(b-x)$ $\times 10^5$	x $\times 10^5$	$(a-x)$ $\times 10^5$	$k_{obs}{}^a$ ($l \cdot mole^{-1} \cdot sec^{-1}$)
247.2	0.5744	0.4058	0.3065	2.0276	105
329.6	0.4308	0.3341	0.3783	1.9559	108
412.0	0.3447	0.2820	0.4304	1.9038	108
494.4	0.2872	0.2348	0.4776	1.8566	109
576.8	0.2462	0.1992	0.5132	1.8221	109

^{a} Average value 107 ± 2.

The initial concentrations of organoditin compounds and iodine were usually in the range 10^{-5} to 10^{-4} M, depending upon the rate of the reaction. The ratio a/b was equal to 2–3. The reproducibility of k_{obs} was 2 %.

RESULTS AND DISCUSSION

Effect of varying iodide concentration on k_{obs}

Table 2 shows the k_{obs} values, as determined in methanol at 17° for three ditin compounds, *i.e.*, hexamethyl-, hexaethyl- and hexabutyl-, at different iodide con-

TABLE 2

EFFECT OF VARYING $[I^-]$ ON k_{obs} IN METHANOL AT $17°$

Compound	Concn. NaI (mole/l)	Concn. NaClO$_4$ (mole/l)	k_{obs} (l·mole^{-1}·sec^{-1})	$k_{obs}[I^-]$
$(CH_3)_3Sn–Sn(CH_3)_3$	0.1944	0	162 ± 1	31.5
	0.0985	0.0985	315 ± 4	31.0
	0.0704	0.1267	448 ± 20	31.5
	0.0563	0.1408	536 ± 15	30.2
	0.0422	0.1549	756 ± 10	31.9
$(C_2H_5)_3Sn–Sn(C_2H_5)_3$	0.1944	0	255 ± 6	49.6
	0.0986	0.0986	502 ± 6	49.5
	0.0704	0.1267	695 ± 6	49.0
	0.0563	0.1408	875 ± 10	49.2
$(C_4H_9)_3Sn–Sn(C_4H_9)_3$	0.1944	0	107 ± 2	20.8
	0.0985	0.0986	213 ± 5	21.0
	0.0704	0.1267	291 ± 7	20.5
	0.0555	0.1388	376 ± 7	20.9

centrations. In all runs the total salt concentration was kept constant by adding an appropriate amount of sodium perchlorate.

As shown in the last column of Table 2, the product $k_{obs}[I^-]$ is fairly constant; if k_{obs} is plotted against $1/[I^-]$, straight lines with zero intercept on the axes are obtained.

By taking into account the kinetic equation $v = k_2[R_6Sn_2]\cdot[I_2]$ and the equilibrium constant $K = [I_2][I^-]/[I_3^-]$ the experimental equation becomes

$$\frac{d[I_3^-]}{dt} = k_2K\cdot\frac{[R_6Sn_2][I_3^-]}{[I^-]} \qquad \text{and hence} \qquad k_{obs} = \frac{k_2K}{[I^-]}$$

This last equation is consistent with the above results; since K is known, k_2 may be evaluated.

Effect of added salts

The effect of added salts on the rate of iodination of two of the ditin compounds was determined by dissolving calculated amounts of salt (NaClO$_4$ or LiClO$_4$) in the methanol–0.1 M NaI reaction solvent. Experiments were carried out with hexamethyl- and hexaethylditin and the results are shown in Table 2. It is evident that the addition of a salt has a positive effect on the reaction rate, with the increase in rate being roughly proportional to the amount of sodium perchlorate or lithium perchlorate which is added.

By comparing the two first rows of Table 3 it is noted that the rate of increase (per cent) in k_{obs} is different for the same amounts of sodium perchlorate in the case of the two compounds under consideration (38 % for Me$_6$Sn$_2$ and 22 % for Et$_6$Sn$_2$). It is concluded that the addition of salts affects not only the activity coefficients of the equilibrium (2), but also the specific rate of the reaction.

The large increases in k_{obs} for hexaethylditin which result from the addition of

TABLE 3

SALT EFFECT

Compound	Concn. NaI (mole/l)	Concn. NaClO₄ (mole/l)	Concn. LiClO₄ (mole/l)	Concn. total salt (mole/l)	k_{obs} (l·mole⁻¹·sec⁻¹)	Increase in k_{obs} %
(CH₃)₃Sn–Sn(CH₃)₃						
In methanol at 17°	0.1	0	—	0.1	258	0
	0.1	0.042	—	0.142	290	12.5
	0.1	0.098	—	0.198	315	22.0
	0.1	0.197	—	0.297	359	38.0
(C₂H₅)₃Sn–Sn(C₂H₅)₃						
In methanol at 17°	0.1	0	—	0.1	464	0
	0.1	0.042	—	0.142	485	4.5
	0.1	0.098	—	0.198	502	8.0
	0.1	0.197	—	0.297	564	22.0
(C₂H₅)₃Sn–Sn(C₂H₅)₃						
In methanol at 17°	0.1	—	0	0.1	464	0
	0.1	—	0.112	0.212	480	3.5
	0.1	—	0.197	0.297	530	14
	0.1	—	0.563	0.663	584	26
(C₆H₅)₃Sn–Sn(C₆H₅)₃						
In ethanol at 22°	0.0133	—	0	0.0133	7.5	0
	0.0133	—	0.0266	0.040	8	6.6
	0.0133	—	0.1866	0.1996	11	47.0

TABLE 4

REACTION RATE CONSTANTS

Temp. $32°$; Ionic strength 0.2.

Compound	Methanol			Ethanol			1-Propanol
	k_{obs} (l·mole⁻¹·sec⁻¹)	Concn. NaI (mole/l)	k_{obs} [I⁻]	k_{obs} (l·mole⁻¹·sec⁻¹)	Concn. NaI (mole/l)	k_{obs} [I⁻]	k_{obs} (l·mole⁻¹·sec⁻¹)
Me₆Sn₂	491	0.2	98.2	217	0.2	43.4	150
Et₆Sn₂	759	0.2	151.8	227	0.2	45.4	250
Pr₆Sn₂	295	0.2	59.0	62	0.2	12.4	78
Bu₆Sn₂	306	0.2	61.2	94	0.2	18.8	85
Me₃Sn–SnPh₃	132	0.01	1.32	38	0.01	0.38	43
Et₃Sn–SnPh₃	156	0.01	1.56	40	0.01	0.40	45
Ph₆Sn₂	1.7	0.01	0.017	0.94	0.01	0.0094	0.75
(p-MeC₆H₄)₆Sn₂							

TABLE 5

CALCULATED RATE CONSTANTS AND RELATIVE RATE

Temp. $25°$; Ionic strength 0.2.

Compound	Methanol			Ethanol		
	k_{obs} (l·mole⁻¹·sec⁻¹)	$k_2 \times 10^{-5}$ (l·mole⁻¹·sec⁻¹)	Relative rate	k_{obs} (l·mole⁻¹·sec⁻¹)	$k_2 \times 10^{-5}$ (l·mole⁻¹·sec⁻¹)	Relative rate
Me₆Sn₂	282	8.7	7250	142	9.5	6300
Et₆Sn₂	471	14.5	12000	141	9.4	6300
Pr₆Sn₂	178	5.5	4600	40	2.7	1800
Bu₆Sn₂	192	5.9	4900	55	3.7	2460
Me₃Sn–SnPh₃	80	0.123	100	20	0.0700	50
Ph₆Sn₂	0.78	0.0012	1	0.45	0.0015	1

sodium perchlorate instead of lithium perchlorate, may be due to the fact that lithium salts are more dissociated than sodium salts in alcohols[17]; hence the formation of undissociated species LiI and LiI₃ is reduced.

Effect of varying R group and solvent

Table 4 shows the reaction rate constants, k_{obs}, as determined for the selected ditin compounds reacting with iodine in alcohol–NaI solvent, at the iodide concentration and temperature indicated.

In this Table are also reported the figures related to hexaphenyl-, and hexa-*p*-tolylditin, as obtained in a mixture of ethanol–benzene (50:50 vol.) in view of the great insolubility of the latter compound in alcohols.

From the values of $k_{obs} \times [I⁻]$ it is apparent that the nature of the R groups has a marked effect upon the rate of reaction, this effect depending also on the solvent used. Only in the case of 2-propanol did the three substrates hexamethyl-, hexapropyl- and hexabutylditin show approximately the same reactivity.

The rates of reaction can be divided roughly into three groups, slow, fast and medium, with the aryl compounds falling into the slow group, the alkyl into the fast group and the two mixed ditin compounds into the medium group.

cn. l le/l) kobs [I⁻]	2-Propanol			Benzene–Ethanol (50:50 vol.)			Compound
	kobs (l·mole⁻¹·sec⁻¹)	Concn. NaI (mole/l)	kobs [I⁻]	kobs (l·mole⁻¹·sec⁻¹)	concn. NaI (mole/l)	kobs [I⁻]	
30	95	0.2	19				Me_6Sn_2
50	150	0.2	30				Et_6Sn_2
15.6	100	0.2	20				Pr_6Sn_2
17	80	0.2	16				Bu_6Sn_2
0.43							$Me_3Sn–SnPh_3$
0.45							$Et_3Sn–SnPh_3$
0.0075				0.48	0.01	0.0048	Ph_6Sn_2
				0.28	0.01	0.0028	$(p\text{-}MeC_6H_4)_6Sn_2$

'ropanol			2-Propanol			Compound
nole⁻¹·sec⁻¹)	$k_2 \times 10^{-5}$ (l·mole⁻¹·sec⁻¹)	Relative rate	kobs (l·mole⁻¹·sec⁻¹)	$k_2 \times 10^{-5}$ (l·mole⁻¹·sec⁻¹)	Relative rate	Compound
·	5.8	5300	50	2.5	2300	Me_6Sn_2
·	7.5	6800	85	4.25	3800	Et_6Sn_2
·	2.3	2100	55	2.75	2500	Pr_6Sn_2
·	2.5	2300	42	2.10	1900	Bu_6Sn_2
	0.0625	56				$Me_3Sn–SnPh_3$
.44	0.0011	1			1	Ph_6Sn_2

It is interesting to note that the slow and medium groups contain those substrates possessing π-electrons. The slower rate of reaction seems reasonable with respect to the increased stabilization of the tin–tin bond by the interaction between phenyl π-electrons and d-orbital of tin[4,18]. The order of reactivity of iodination of ditin compounds in the examined solvents is approximately as follows:

$$Me_6Sn_2 < Et_6Sn_2 > Pr_6Sn_2 = Bu_6Sn_2 \gg Me_3SnSnPh_3 = Et_3SnSnPh_3 > Ph_6Sn_2 >$$
$$p\text{-}Tolyl_6Sn_2$$
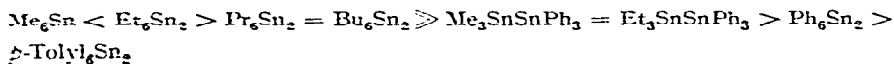
In Table 5 are reported the k_{obs} values obtained at 25°. The k_2 values, as obtained from the known equilibrium constant K for three solvents (methanol $K = 6 \times 10^{-5}$; ethanol $K = 3 \times 10^{-5}$ and 1-propanol $K = 4 \times 10^{-5}$)[7,19] are also listed. The relative rates are also reported.

With 2-propanol as solvent, the calculated values involve the approximation that K for this solvent is roughly the same as those observed for the other alcohols.

Table 6 lists the calculated thermodynamic data: ΔH_{obs} represents the activation energy, as derived from an Arrhenius plot of log k_{obs} vs. $1/T$.

Since only the ΔH enthalpic value of the equilibrium (2) (8 kcal/mole)[19] in

methanol is known the activation energy, $\Delta H^{\neq}$, has been derived from $\Delta H^{\neq} = \Delta H_{obs} - \Delta H$ and the $\Delta S^{\neq}$ values at $25°$ have been calculated therefrom.

TABLE 6

CALCULATED THERMODYNAMIC QUANTITIES

Compounds	Methanol		
	ΔH_{obs} (kcal/mole)	$\Delta H^{\neq}$ (kcal/mole)	$\Delta S^{\neq}$ ($25°$) (e.u.)
Me_6Sn_2	13	5	-14.5
Et_6Sn_2	12	4	-17
Pr_6Sn_2	13	5	-15.5
Bu_6Sn_2	13	5	-15
$Me_3Sn-SnPh_3$	13	5	-23
Ph_6Sn_2	18	10	-15

Mechanism

The main factors which might be expected to influence the reactivities of $R_3Sn-SnR_3$ compounds are (a) the varying strength of the Sn–Sn bond in relation to the surrounding R's groups, (b) the accessibility of d-orbitals in the valency shell of the tin atom, and (c) steric, polar and solvation effects.

From the experimental data it is clearly evident that, under the experimental conditions employed in this investigation, the iodination of ditin compounds is not dependent upon a concerted attack by both I^+ and I^- parts of the iodine molecule. In fact, no assistance is provided by iodide and triiodide ions in these solvents. This seems fully consistent with the view that nucleophilic assistance in organometal reactions can be observed only when the solvents employed do not coordinate with, and therefore mitigate the effect of[1,20]. On the other hand the iodine molecule must be considered as coordinated with the solvent to form the complex $I_2 \cdot O(H)R^{21}$. With regard to observed salt effect, this is better explained by assuming a polar transition state than a cyclic four-center one, and hence it may be concluded that the intermediate:

$$\begin{bmatrix} -Sn \cdots Sn- \\ \vdots \quad\quad \vdots \\ I \cdots I \end{bmatrix}$$ must be rejected.

If one assumes that the reaction rates are dependent on the solvation state of the iodine molecule (K_S' values (mole fraction units at $25°$) for the equilibrium $I_2 + ROH \rightleftharpoons I_2ROH$ are 4.65, 4.00, 6.25, for methanol, ethanol[21] and 1-propanol[22] respectively), the observed fall in the reactivity for each substrate from methanol, ethanol, 1-propanol to 2-propanol can be justified. In addition, the change in reactivity from solvent to solvent as described above could be dependent on the variation of iodine electrophilic strength due to the increased nucleophilicity of the alcohols used.
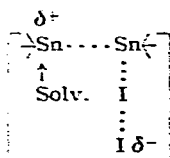
These effects would be expected if the reaction is a simple S_E2 type electrophilic substitution at the tin center.

Generally, as expected for an electrophilic substitution, electron-releasing groups facilitate and electron-drawing groups hinder the reaction[23]. The data obtained for hexaphenyl- ($K_{obs} \times [I^-]$) and hexa-p-tolylditin (cf. Table 4) compounds are

significant and it seems likely that the mechanism of the reaction is not consistent with an S_E2 process alone. On the other hand, the fall in the reactivity of mixed ditin compounds in respect to hexaalkylditin, as well as the similar reactivity observed for trimethyltriphenyl- and triethyltriphenylditin do not agree with a simple process of electrophilic substitution.

In fact electrophilic attack by iodine would preferentially occur at the tin atom bearing the alkyl groups, and the reactivity of these compounds would be the same, or nearly so, as for the observed in the corresponding hexaalkyl compounds.

We conclude that an intermediate of the type:

$$\begin{array}{c} \delta^+ \\ \left[{\scriptstyle\searrow}Sn\cdots\cdots Sn{\scriptstyle\swarrow} \right] \\ \uparrow \quad\quad \vdots \\ \text{Solv.} \quad I \\ \vdots \\ I\,\delta^- \end{array}$$

involving pre rate-determining nucleophilic assistance at a tin center by the solvent provides a more likely explanation of experimental findings. In fact since two centers of the ditin molecule are involved in such a process, the order of reactivity in each solvent, as well as the rate reduction in passing from methanol to n-propanol as described, could be dependent on the balance of steric and polar effects due to the R groups attached to tin, and on the various nucleophilic strengths of the solvents used.

Nucleophilic assistance by the solvent involves a step in which a tin atom is subject to high negative charge

$$\begin{array}{c} \delta^- \\ {\scriptstyle\searrow}Sn\!-\!Sn{\scriptstyle\swarrow} \\ \vdots \\ \delta^+Solv. \end{array}$$
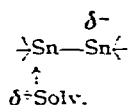
The calculated thermodynamic quantities $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are consistent with a transition state in which solvation is important.

From a comparison of $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and k_2 values for the iodination of hexaphenyl-ditin in cyclohexane and methanol (Table 7) it is concluded that four-center transition states may occur in different solvents. In cyclohexane nucleophilic assistance must be

TABLE 7

COMPARISON OF DATA ON THE HEXAPHENYLDITIN IODINATION

Solvent	k_2 ($l \cdot mole^{-1} \cdot sec^{-1}$)	$\Delta H_{\ddagger}$ ($kcal/mole$)	$\Delta S_{\ddagger}$ (e.u.)	Temp. (°C)	Reference
Cyclohexane	740	14	0	27	4
Methanol	120	10	−15	25	this work

due to the nucleophilic part of iodine molecule and an S_E2 cyclic transition state results, while in nucleophilic solvents such as alcohols the assistance due to the solvent appears in an acyclic four-center transition state.

On the other hand Boue *et al.*[5] explain their results on the iodination of hexabutylditin in acetone, in terms of nucleophilic assistance by Bu_2SnO. In our opinion, however, a better explanation of their results takes into account nucleophilic assistance by iodide ion, which should be possible in an aprotic polar solvent such as acetone.

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SUMMARY

The rates of cleavage of selected ditin compounds by iodine have been measured in alcoholic solvents. Possible mechanisms for the cleavage are discussed. It is concluded that an acyclic four-center intermediate, formed after attachment of solvent in a fast preliminary step, provides the best explanation of the experimental results.

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