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REACTIONS AND KINETICS OF VARIOUS CHLOROETHYLDISTANNOXANES WITH SOME LACTONES

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Summary

Hexaethyldistannoxane and its chloro derivatives when treated with lactones containing four- to seven-membered rings afforded 1/1 adducts with opening of the rings. Kinetic measurements utilizing IR spectroscopic methods gave the following orders of reactivity: (1) ϵ-caprolactone > δ-valerolactone > β-propiolactone > γ-butyrolactone, (2) $Cl_2EtSnOSnEt_2Cl$ > $Et_3SnOSnEt_3$ > $ClEt_2SnOSnEt_3$ > $ClEt_2SnOSnEt_2Cl$; monomeric > dimeric distannoxane, and in non-polar solvent > in polar or basic solvent. These results are discussed in terms of the degree of association of distannoxanes, as well as the acidities and basicities of the lactone, distannoxane and solvent.

Introduction

Ring-opening reactions of β-propiolactone with organometallic compounds of the type $R_nM—X$, such as alkoxides or amides of alkylzinc [1], dialkylaluminium [2], trialkyl-silicon [3], -germanium [4], or -tin [4] have already been reported. In order to elucidate the mechanism of the ring-opening reaction of lactones with organostannyl compounds, we report our results on the kinetics of this reaction of four- to seven-membered lactones of different basicities and reactivities with various chloroethyldistannoxanes having different degrees of association and different acidities and basicities.

Results and discussion

Reaction of lactones with distannoxanes

As is evident from the characteristic change in the IR and NMR spectra (Table 1), ϵ-caprolactone (ϵ-CL) reacted with an equimolar amount of II-0,

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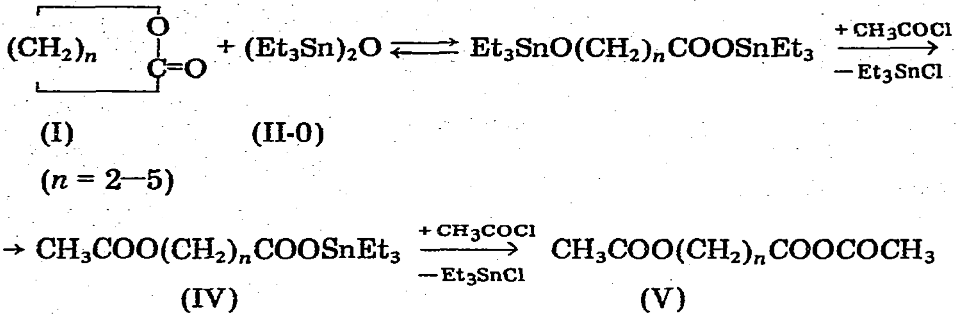
hexaethyldistannoxane within 20 h in carbon tetrachloride at 60° with opening of the lactone ring, to afford the equilibrated mixture of 1/1 adduct (> 90%), hexaethyldistannoxane (< 10%) and ε-CL (< 10%). Attempts to isolate the reaction products by vacuum distillation were unsuccessful; III reverted to the starting materials I and II. However, if III, the ring-opening product was treated with one or two equivalents of acetyl chloride at room temperature, it could be isolated as a mono- or di-acetate by distillation, as shown in eqn.1.



$$(CH_2)_n\text{-O-C(=O)} + (Et_3Sn)_2O \rightleftharpoons Et_3SnO(CH_2)_nCOOSnEt_3 \xrightarrow[-Et_3SnCl]{+CH_3COCl}$$

(I) (II-0)

(n = 2—5) (1)

$$\rightarrow CH_3COO(CH_2)_nCOOSnEt_3 \xrightarrow[-Et_3SnCl]{+CH_3COCl} CH_3COO(CH_2)_nCOOCOCH_3$$

(IV) (V)

Analogous results were obtained in the reaction of hexaethyldistannoxane with δ-valerolactone (δ-VL), γ-butyrolactone (γ-BL) and β-propiolactone (β-PL). The 1/1 adduct of β-PL decomposed during distillation to yield triethylstannyl acrylate among other products. Results of the acylation reactions are given in Tables 1 and 2.

Symmetrical dichlorotetraethyldistannoxane (II-2) when treated with β-PL in carbon tetrachloride (20 h at 60°) afforded a ring-opening product which exhibited a carbonyl stretching band of the $COOSnEt_2Cl$ group at 1575 cm^{-1}; this compound was converted to Va, the diacetate, in 76% yield by treating it with excess acetyl chloride at room temperature.

Chloropentaethyldistannoxane (II-1) exists as a dimer in solution, and when treated with β-PL or ε-CL in carbon tetrachloride (20 h at 50—70°) gives a reaction mixture showing a weak ν(CO) band at 1630 cm^{-1} and a strong ν(CO) band at 1575 cm^{-1} (Fig.1). Because the strong ν(CO) band observed at the position of lower wave number is ascribable to the $COOSnEt_2Cl$ group, the main course of the ring-opening reaction involving β-PL or ε-CL seems to proceed via

TABLE 1

REACTION OF HEXAETHYLDISTANNOXANE WITH VARIOUS LACTONES

Lactone used	Reaction condns.[a]		Conversion (%)	NMR[b]				IR (cm^{-1})	
	Temp. (°C)	Time (h)		τ(Sn—Et)[c]	$\tau(CH_2)$[d]	$\tau(CH_2CO)$[d]	τ(other)	ν(C=O)	ν(C—O)
β-PL	60	20	100	∿8.8	6.23	7.70		1650	1070
γ-BL	80	30	95	∿8.8	6.32	7.68	∿8.2	1648	1071
δ-VL	60	20	95	∿8.8	6.36	7.55	∿8.5	1649	1070
ε-CL	60	20	90	∿8.8	6.43	7.78	∿8.6	1650	1070

[a] Equimolar reaction (10 mmol) in carbon tetrachloride (4 ml). [b] τ-Value in carbon tetrachloride. [c] Multiplet. [d] Triplet (J 6.0 Hz).

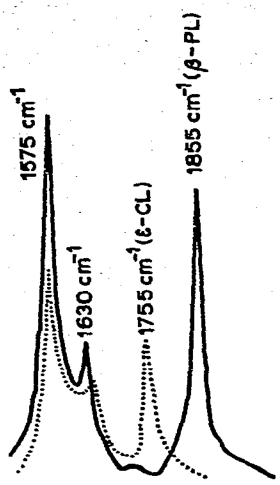
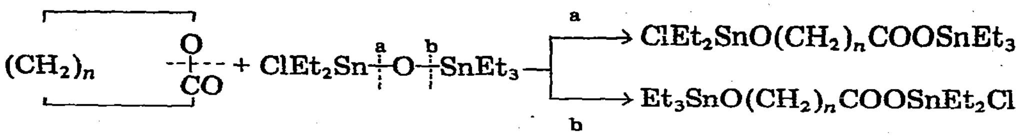


Fig.1. IR spectra of the reaction mixtures of chloropentaethyldistannoxane with β-PL (solid line) and with ε-CL (dotted line).

insertion (path b) of the lactone species into the $Et_3Sn—O$ bond. It is assumed that the two lactone rings open with acyl—oxygen bond fission.

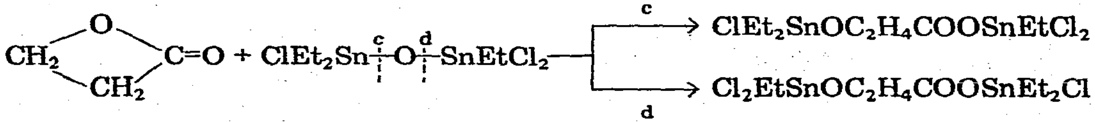


(2)

(n = 2,5) (II-1)

The reaction mixture was also treated with excess acetyl chloride and was subsequently distilled to yield Va.

When equimolar amounts of β-PL and 1,1,1'-trichlorotriethyldistannoxane (II-3) were heated in carbon tetrachloride (5 h at 50°), the resulting reaction mixture exhibited two ν(CO) bands at 1450 and 1575 cm^{-1}, whose wave numbers coincided with those of $Cl_2EtSnOCOCH_3$ and $ClEt_2SnOCOCH_3$, respectively. Since these bands are of approximately the same intensity, it seems reasonable to assume that the rates of reactions c and d are nearly the same.



(II-3) (3)

Investigation of the kinetics of the ring-opening reactions

During the reaction of hexaethyldistannoxane with a lactone in carbon tetrachloride at 60°, the ν(CO) band of III the ring-opening product increased with decrease of the ν(CO) band of the lactone, and since no other ν(CO) band appeared (except in the reaction of β-PL at temperatures above 80° when some of the β-PL was polymerized), the apparent first-order rate constants could be

TABLE 2

ACETYLATION PRODUCTS OF REACTION MIXTURES OF HEXAETHYLDISTANNOXANE WITH LACTONES

No.	Acetylated product, CH_3COO-$(CH_2)_nCOOX$	B.p. (°C/mm)	M.p. (°C)	Yield (%)	Analysis found (calcd.) (%)			NMR (τ ppm)					IR (cm^{-1})		
					C	H	Sn	SnEt	CH_2—O^a	CH_2—CO^a	CH_3—CO	Other	ν(COOSn)	ν(CO) (ester)	ν(CO) (anhyd.)
	n, X														
IVa	2 $SnEt_3$	101—103 /0.3	58—59	59	38.87 (39.12)	6.48 (6.58)	35.18 (35.22)	∿8.8	5.84	7.51	8.02		1660	1750	
IVb	3 $SnEt_3$	105—108 /0.4	71—72	64	41.25 (41.06)	6.89 (6.89)	33.83 (33.85)	∿8.8	5.89	7.64	7.96	∿8.2	1650	1750	
IVc	4 $SnEt_3$	110—119 /0.2	46—47	71	42.47 (42.77)	7.09 (7.09)	32.57 (32.51)	∿8.8	5.91	7.69	7.98	∿8.3	1650	1745	
IVd	5 $SnEt_3$	115—123 /0.2	49—50	63	44.01 (44.36)	7.50 (7.45)	31.32 (31.31)	∿8.8	6.05	7.82	8.07	∿8.6	1650	1740	
Va	2 $COCH_3$	72—73 /0.3		69	48.11 (48.27)	5.77 (5.79)			5.78	7.25	8.03,8.82[b]			1755	1830
Vb	3 $COCH_3$	73—76 /0.3		41	50.89 (51.06)	6.33 (6.43)			5.88	7.51	7.98,8.80	∿8.2		1750	1830
Vc	4 $COCH_3$	75—79 /0.3		48	53.38 (53.46)	6.82 (6.98)			5.92	7.51	8.03,7.82	∿8.3		1750	1825
Vd	5 $COCH_3$	104—115 /0.4		71	55.51 (55.54)	7.37 (7.46)			6.09	7.57	8.06,7.83	∿8.5		1745	1830

[a] Triplet (*J* 6.0 Hz). [b] Two singlets assignable to ester— and anhydride—acetyl groups.

TABLE 3

EFFECTS OF INITIAL CONCENTRATIONS ON THE REACTION RATES OF $(Et_3Sn)_2O$ WITH ϵ-CL IN CARBON TETRACHLORIDE AT 60.0°

Initial concentrations (M)		$10^5 k_1$ (s^{-1})
$(Et_3Sn)_2O$	ϵ-CL	
0.050	0.025	8.05
0.050	0.050	8.20
0.050	0.100	8.14
0.050	0.200	8.32
0.025	0.050	4.21
0.100	0.050	16.18
0.150	0.050	22.92

estimated from the increase in the intensity of the ν(CO) band of III to give a straight line in the range between 0 and 65% conversion; the initial first-order constant (k_1) was calculated at various initial concentrations of ϵ-CL and hexaethyldistannoxane. From the results in Table 3, we obtained an approximation to the second-order rate equation (eqn.4).

$$\frac{-d[\epsilon\text{-CL}]}{dt} = \frac{+d[\text{III}]}{dt} = k_1 \cdot [\epsilon\text{-CL}] = k_2 \cdot [\epsilon\text{-CL}] \cdot [\text{II}] \qquad (4)$$

Several different lactones were treated at constant initial concentration of hexaethyldistannoxane (0.05 M) in carbon tetrachloride in order to estimate the apparent first-order rate constants (Table 4). In the alkaline hydrolysis the rate order (k_b) was reported to be: β-PL $\gg$ δ-VL > ϵ-CL > γ-BL [5] which is in contrast to our result (ϵ-CL > δ-VL > β-PL $\gg$ γ-BL). The apparent activation energies and entropy values shown in Table 4 seem to be rather low. Coordination of ϵ-CL to hexaethyldistannoxane was not observed in basic solvents, such as tetrahydrofuran but is noticeable in dilute hexane solution where free and coordinated ν(CO) bands of ϵ-CL appeared at 1747 and 1728 cm^{-1}, respectively. Shifts [$\Delta\nu$(CO) in Table 4] of the carbonyl bands of lactones due to their coordination to a strong Lewis acid, 1,1,1'-trichlorotriethyldistannoxane (II-3), were also observed. The greatest shift occurred for the mixture of the more basic lactone

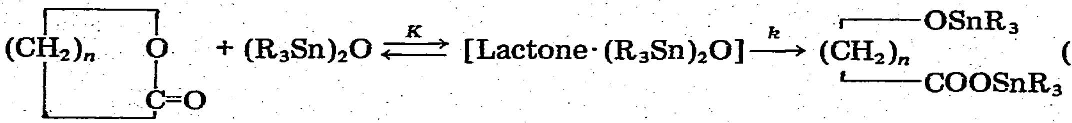
TABLE 4

REACTION RATE CONSTANTS, $10^5 \times k_1$ (s^{-1}), OF $(Et_3Sn)_2O$ WITH VARIOUS LACTONES IN CARBON TETRACHLORIDE

Lactone	pK_b[a]	k_b[b]	$\Delta\nu$(C=O) (cm^{-1})[c]	Rate const. $10^5 \times k_1$ (s^{-1})				$E_{act.}$ (kcal·mol^{-1})	ΔS (cal·mol^{-1}·K^{-1})
				60°	70°	85°	100°		
β-PL	10.06	> 140	8	3.75	6.72	12.5	26.3	12.0	−22
γ-BL	6.12	0.6	27	0.42	0.89	1.98	4.77	14.5	−17
δ-VL	5.10	22	44	5.76	8.82	14.7	21.2	9.5	−23
ϵ-CL	5.30	1	41	8.20	13.8	23.0	60.1	12.5	−16

[a] Ref.7. [b] Ref.5. [c] The shift of the carbonyl stretching band of each lactone in the mixture with 1,1,1'-trichlorotriethylstannoxane, II-3.

with lower pK_b value [7]. The rate of the reaction of ϵ-CL with II was faster in non-polar or weakly basic solvents than in polar or stronger basic solvents as shown in Table 5. Therefore, it is tentatively assumed that coordination of the lactone to hexaethyldistannoxane preceeds the ring-opening reaction.



$$\begin{matrix}(CH_2)_n & O \\ & C{=}O\end{matrix} + (R_3Sn)_2O \overset{K}{\rightleftharpoons} [\text{Lactone}\cdot(R_3Sn)_2O] \xrightarrow{k} (CH_2)_n\begin{matrix}-OSnR_3\\-COOSnR_3\end{matrix} \qquad (5)$$

The equilibrium constant K of the coordination reaction will be small and it will be affected by the basicity of lactones and solvents or by the acidity of distannoxanes. Now we discuss the reaction rates of various distannoxanes with lactones shown in Table 6 and Fig.2.

The properties of the distannoxanes used are given in Table 7; the degrees of association are taken from the literature except the value of chloropentaethyldistannoxane which was measured by ourselves. Basicities of distannoxanes were estimated by the deuterochloroform method [10] in carbon tetrachloride and the acidities of distannoxanes were compared in terms of the carbonyl stretching band shift, $\Delta\nu$(CO), of ϵ-CL in carbon tetrachloride.

Because hexaethyldistannoxane has the highest basicity and nucleophilicity to the sp^2-carbonyl carbon atom, it gave the fastest rate of ring-opening with the lactones. The trichlorinated distannoxane, $ClEt_2SnOSnEtCl_2$, is the strongest acid and probably the weakest base among the distannoxanes used, but the rate of its reaction with ϵ-CL was the fastest measured.

Compared with the reaction with a "basic" distannoxane, $Et_3SnOSnEt_3$, the reactions with an "acidic" distannoxane, $ClEt_2SnOSnEtCl_2$, with basic lactones, δ-VL and ϵ-CL, were accelerated, while that with the less basic lactone, β-PL, was retarded. These results can be explained if the ring-opening of lactones is assisted by coordination with the distannoxane moiety. This follows from the observation that coordination of the carbonyl group to 1,1,1'-trichlorotriethyldistannoxane (II-3) is strong in the case of δ-VL or ϵ-CL, but very weak for β-PL, as shown by $\Delta\nu$(CO) in Table 4.

As becomes clear from Fig.2, the dimeric distannoxanes $ClEt_3SnOSnEt_3$ and $ClEt_2SnOSnEt_2Cl$ reacted more slowly than the monomeric species $Et_3SnOSnEt_3$ and $Cl_2Et_2SnOSnEt_2Cl$. Because of the low reactivity of $ClEt_2SnOSnEt_2Cl$ which prevented us from determining the kinetic order of its reaction by IR spectroscopic methods, the kinetic order of the reaction of chloropentaethyl-

TABLE 5

SOLVENT EFFECTS ON THE REACTION RATES OF ϵ-CL WITH THE DISTANNOXANE $(XEt_2Sn)_2O$

Solvent	Dielectric constant (ϵ)	pK_b^6	$10^5 \times k_1$ (s^{-1})	
			X = Et	X = Cl
n-Hexane	1.89	> 12	12.3	12.5
Carbon tetrachloride	2.24	12.1	8.20	1.49
Chloroform	4.81		1.82	1.11
Tetrahydrofuran	7.39	4.9	1.65	1.03
1,2-Dichloroethane	10.39		0.81	0.32

TABLE 6

APPARENT REACTION RATE OF VARIOUS DISTANNOXANES WITH SOME LACTONES IN CARBON TETRACHLORIDE AT 60.0°

Distannoxane	Lactone	$10^5 \times k_1$ (s^{-1})	Final conversion (%)
$Et_3SnOSnEt_3$	β-PL	3.75	> 90
	δ-VL	5.10	> 90
	ε-CL	8.20	> 90
$ClEt_2SnOSnEt_3$	β-PL	1.99	> 90
	δ-VL	3.48	59
	ε-CL	3.70	65
$ClEt_2SnOSnEt_2Cl$	β-PL	0.40	> 90
	δ-VL	1.13	16
	ε-CL	1.49	67
$ClEt_2SnOSnEtCl_2$	β-PL	1.83	> 90
	δ-VL	7.23	> 90
	ε-CL	10.7	> 90

TABLE 7

CHARACTERISTICS OF DISTANNOXANES

Distannoxane	$Et_3SnOSnEt_3$	$ClEt_2SnOSnEt_3$	$ClEt_2SnOSnEt_2Cl$	$Cl_2EtSnOSnEt_2Cl$
Assocn. No.	1[8]	2	2[8]	1[9]
Basicity [ν(C—D)cm^{-1}]	72	0	0	0
Acidity [ν(C=O)cm^{-1}]	< 5	∿0	∿0	41

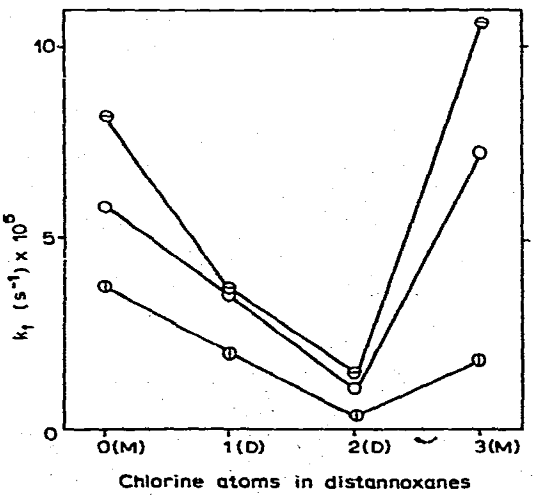


Fig.2. Reaction rate constants of chloroethyldistannoxanes with β-PL (⦶), δ-VL (○), and ε-CL (⊖); M = monomeric and D = dimeric distannoxanes.

TABLE 8

EFFECTS OF INITIAL CONCENTRATIONS ON REACTION RATES OF $(ClEt_2Sn)_2O$ WITH ε-CL

Initial concentration (*M*)		$10^5 \times k_1$ (s^{-1})
ε-CL	$(ClEt_2Sn)_2O$	
0.025	0.050	3.81
0.050	0.050	3.70
0.100	0.050	3.83
0.050	0.025	2.39
0.050	0.100	5.42
0.050	0.150	7.05

distannoxane with ε-CL was studied. The results are given in Table 8 and they support the kinetic equation 6.

$$\frac{-d[\epsilon\text{-CL}]}{dt} = \frac{+d[\text{III}]}{dt} = k_1\,[\epsilon\text{-CL}] = k_{\frac{3}{2}} \cdot [\epsilon\text{-CL}] \cdot [\text{II}]^{\frac{1}{2}} \qquad (6)$$

On the basis of eqn.6, the equilibrium reaction 7 may be explained.

$$[ClEt_2SnOSnEt_3]_2 \overset{K_0}{\rightleftharpoons} 2\,ClEt_2SnOSnEt_3 \qquad (7)$$

In this case, it is to be expected that the apparent rate constant is very small because the distannoxane exists in the form of the inactive dimer in solution and the available concentration of reactive monomer is very low. The strong effect of the basic solvent on the reaction rate of 1,1′-dichlorotetraethyldistannoxane with ε-CL was also observed and is shown in Table 5.

It has already been mentioned that the reaction of lactone with distannoxane is essentially reversible, except in the case of β-PL which reacts irreversibly due to its great ring-strain. The monomeric distannoxanes, II-0 and II-3, reacted almost completely with the lactones to form the corresponding 1/1 adducts (III) with more than 90% conversion. However, conversion of the lactones in the reaction of the dimeric distannoxanes, II-1 and II-2, converged to 16-67% (Table 6), and even if the reaction temperature was raised to 100°, higher conversions were never observed.

Monomeric distannoxane (II-3) reacted rapidly giving high conversion in a short time. After longer reaction times at higher temperature, e.g. longer than 60 minutes at temperatures above 80°, lactone appeared to be regenerated (according to the IR spectra) probably because the distannoxane, II-3, would have undergone a disproportionation reaction which affects the equilibrium constant *K*. Because of these troublesome phenomena, a detailed discussion of the reaction involving II-3 was not attempted.

Experimental

General

All m.p.'s and b.p.'s are uncorrected. Analyses were performed by Toagosei Chemical Co., Ltd. IR spectra were recorded on Nippon Bunko Model

403-G and IR-S spectrometers. NMR spectra were obtained with TMS as an internal standard on a Japan Electron Optics C-60HL or Minimer JNM-HM 60 spectrometers. Molecular weights were measured using a Mekrolab vapor pressure osmometer with benzene as solvent. All reactions and measurements were performed in anhydrous carbon tetrachloride maintaining a dry nitrogen atmosphere, unless otherwise noted.

The distannoxanes, II-0, II-2, and II-3, were prepared according to published methods [8,10]. The distannoxane II-1 was prepared by the reaction of equimolar amounts (10 mmol) of Et_3SnCl and Et_2SnO in benzene (30 ml). The crude product was washed with diethyl ether and recrystallized from carbon tetrachloride. Yield 35%, white solid, m.p. 209-211°. (Anal. found: Cl, 8.11%, mol. wt. 864.8. $C_{10}H_{25}ClOSn_2$ (monomer) calcd.: Cl, 8.17%, mol. wt. 434.) Commercially available lactones were dried over calcium hydride powder and distilled. The solvents used were dried over phosphorus pentoxide and distilled before use.

Reaction of hexaethyldistannoxane with lactone

Equimolar amounts (10.0 mmol) of the distannoxane, II-0, were treated with the corresponding lactone in carbon tetrachloride, usually for 20 h at 60° Detailed reaction conditions are described in Table 1, and IR measurements show that the lactones were almost completely consumed under these reaction conditions. Distillation of the reaction mixtures gave lactones, except β-PL, in higher than 85% yields. Upon distillation of the adduct from β-PL having only a ν(CO) band (ascribed to $COOSnEt_3$), β-PL was not recovered and triethylstannyl acrylate and other decomposition products were detected by NMR measurement.

Acetylation of the ring-opening products

The 1/1 adducts were treated with equimolar or two molar equivalents of acetyl chloride in carbon tetrachloride or in n-hexane at room temperature, followed by distillation to yield mon- or di-acetyl derivatives. Their respective yields and properties are shown in Table 2.

Kinetic measurement by IR spectroscopic methods

A standard example is as follows. To the magnetically stirred solution of distannoxane (0.0500 *M*) in carbon tetrachloride in a stoppered flask set in a thermostat (± 0.05°) a given amount (0.050 *M*) of lactone was added by means of a syringe. The intensities of the ν(CO) bands in the lactones and the 1/1 adducts, samples of which were taken from the flask by a syringe, were measured using a JASCO IR-S spectrometer at 30 minutes intervals. The residual concentration of lactones or the concentration of the 1/1 adducts formed was estimated by applying the Lambert—Beer equation and generally apparent first-order rate constants were calculated.

Estimation of acidity and basicity of distannoxanes

Ten molar equivalents of the distannoxanes, II-0 and II-3, and one of deuterochloroform were mixed in carbon tetrachloride, (30% soln.) and the shift, Δν(C—D) of the C—D stretching band at 2252 cm^{-1} was determined as a measure of the basicity of distannoxanes. Due to the very low solubility of the distannoxanes (II-2) and (II-3) no shift of ν(CO) at 0.01 *M* concentrations of both distannoxane and deuterochloroform was observed. The data are summarized in Table 7.

To estimate the acidity of the distannoxanes the shift of the ν(CO) band of ϵ-CL in an equimolar mixture of ϵ-CL and distannoxane in carbon tetrachloride was measured. This is described in Table 7.

The shifts of the ν(CO) band in mixtures of the lactones and excess amounts (ten molar equivalents) of 1,1,1'-trichlorotriethyldistannoxane in carbon tetrachloride (30%) were measured by a 403-G IR spectrometer. This was carried out to establish that coordination of the lactone to the distannoxane occurs and to re-estimate the basicities of the lactones.

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