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STUDIES ON DIALKYLTIN DIACETATE DERIVATIVES

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Dialkyltin diacetates were described by Cahours[1] in 1860 and their derivatives have been studied by Harada[2-4]. Recently, many researchers have been interested in the structural chemistry of organotin compounds and several brief descriptions on dialkyltin acetate derivatives[3-12] have been reported.

In this paper we will report the preparation and novel properties of a series of dialkyltin diacetates, $R_2Sn(OAc)_2$, and their hydrolyzed derivatives, such as $[(AcO)R_2Sn]_2O$, $(AcO)R_2SnOSnR_2(OH)$ ($R = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9). Since some of these compounds were found to be exceptionally good catalysts for the isocyanate–hydroxyl reaction[13], it is worthwhile to seek structural information concerning these compounds. The structures were deduced by means of molecular weight determination, electric conductivity, IR and PMR measurements.

EXPERIMENTAL

Materials

Dialkyltin oxides were synthesized by the standard method[14]. Acetic anhydride was of commercial grade. All solvents were purified by methods described in the literature[15] for the instrumental measurements.

Dialkyltin diacetates, $R_2Sn(OAc)_2$ ($R = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9)

Dimethyltin oxide (8.2 g, 50 mmole) was dissolved in a slight excess of acetic anhydride (6.2 g, 60 mmole) with heating, and the unreacted anhydride was distilled off under nitrogen. The residual liquid, on vacuum distillation, gave solid dimethyltin diacetate. The other dialkyltin diacetates were prepared in a similar manner. All these compounds are hygroscopic and do not show sharp melting points.

Tetraalkyl-1,3-diacetoxydistannoxanes, $[(AcO)R_2Sn]_2O$ ($R = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9)

The methyl compound was obtained quantitatively by mixing dimethyltin diacetate and a large amount of water. The white, amorphous product was purified by recrystallizations from methanol or chloroform. The other compounds were obtained similarly. They were recrystallized from benzene, toluene or ligroin containing a drop of acetic acid. These compounds were also obtained from the reaction of stoichiometric mixtures of the dialkyltin oxide and acetic acid in a similar solvent.

Tetraalkyl-1-acetoxy-3-hydroxydistannoxanes, $(AcO)R_2SnOSnR_2(OH)$ $(R{=}CH_3, C_2H_5, n\text{-}C_3H_7, n\text{-}C_4H_9$[5]$)$

To a solution of $[(AcO)(C_4H_9)_2Sn]_2O$ (6.0 g, 10 mmole) in acetone (50 ml) was added an equimolar amount of aqueous pyridine (0.1 *N*), and the mixture was refluxed for a short time. The white precipitate, $(AcO)(C_4H_9)_2SnOSn(C_4H_9)_2(OH)$, was recrystallized from benzene (4.9 g, yield 80%). In similar fashion, the n-propyl and ethyl compounds were obtained (yield 80%), but the methyl compound could not be prepared in this manner. Refluxing a mixture of $(CH_3)_2SnO$ (1.65 g, 10 mmole) and $[(AcO)(CH_3)_2Sn]_2O$ (2.15 g, 5 mmole) in ethanol containing a small amount of water, gave a compound which showed characteristic CO_2 and OH vibrational bands. However, this compound seemed to change into a mixture of $[(AcO)(CH_3)_2Sn]_2O$ and $(CH_3)_2SnO$ in a dry atmosphere. Melting points and analytical data are given in Table 1 together with those for the other compounds described above.

Molecular weight and electric conductivity

Molecular weights of hygroscopic dialkyltin diacetates were determined

TABLE 1

ANALYSES OF DIALKYLTIN DIACETATES AND THEIR DERIVATIVES

Compound	*M.p. (°C) found (reported)*	*% Sn found (calcd.)*	*% C found (calcd.)*	*% H found (calcd.)*
$R_2Sn(OAc)_2$				
$R{=}CH_3$[a]	*ca.* 67	44.35	27.48	4.54
		(44.48)	(27.01)	(4.53)
C_2H_5[b]	*ca.* 44	40.19		
		(40.05)		
$n\text{-}C_3H_7$[c]	*ca.* 36	36.78		
		(36.75)		
$n\text{-}C_4H_9$[d]	*ca.* 8	33.81		
		(33.82)		
$[(AcO)R_2Sn]_2O$				
$R{=}CH_3$	236	54.89	22.36	4.16
	(240)[9]	(55.00)	(22.26)	(4.20)
C_2H_5	105–106	48.56	29.82	5.38
		(48.67)	(29.55)	(5.37)
$n\text{-}C_3H_7$	111–113	43.71	35.02	6.17
		(43.65)	(35.32)	(6.30)
$n\text{-}C_4H_9$	58–60	39.62	40.49	7.12
	(58–60)[6]	(39.57)	(40.04)	(7.06)
$(AcO)R_2SnOSnR_2(OH)$				
$R{=}C_2H_5$	*ca.* 200[e]	53.40		
		(53.28)		
$n\text{-}C_3H_7$	206–208	47.45	32.55	6.36
		(47.31)	(33.02)	(6.40)
$n\text{-}C_4H_9$	129	42.50	38.71	7.15
	(129)[12]	(42.55)	(38.73)	(7.23)

[a] B.p. 93–94°/5 mm. [b] B.p. 97°/5 mm. [c] B.p. 115°/5 mm (Lit.[14] 81–83°/1 mm). [d] B.p. 130°/5 mm (Lit.[14] 142–145°/10 mm). [e] Partially decomposes.

cryoscopically in benzene under dry nitrogen. A Mechrolab vapor pressure osmometer was used for the other compounds dissolved in chloroform or benzene at 25°. The results are shown in Fig. 1. An appreciable electric conductivity was not observed for $[(AcO)(CH_3)_2Sn]_2O$ or $[(AcO)(C_4H_9)_2Sn]_2O$ in chloroform (0.05 *M*).

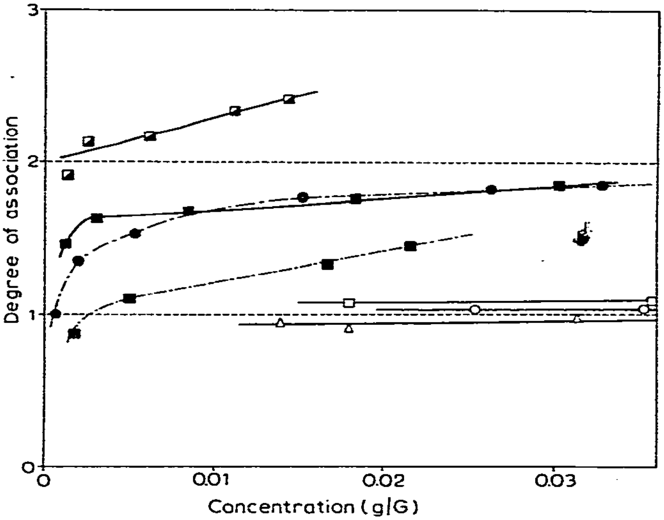


Fig. 1. Degree of association of dialkyltin diacetates and their derivatives. ○ $(CH_3)_2Sn(OAc)_2$, △ $(C_3H_7)_2Sn(OAc)_2$, □ $(C_4H_9)_2Sn(OAc)_2$ ● $[(AcO)(CH_3)_2Sn]_2O$. ■ $[(AcO)(C_4H_9)_2Sn]_2O$, ◪ $(AcO)(C_4H_9)_2SnOSn(C_4H_9)_2(OH)$, ——— in benzene, - — - — in chloroform.

Infrared spectra

The infrared absorption spectra were recorded using a Hitachi EPI-2G and a Hitachi EPI-L spectrophotometer, both equipped with gratings covering the range 4000 cm^{-1} to 250 cm^{-1}. They were recorded as mulls in nujol and hexachlorobutadiene, or in liquid films. Solution spectra in benzene, cyclohexane, carbon tetrachloride or chloroform at various concentrations were also obtained. Results are given in Fig. 2 and 3, and Table 3, 4 and 5 with tentative assignments.

TABLE 2

TIN PROTON COUPLING CONSTANTS AND PROTON CHEMICAL SHIFTS AT 20° FOR $(CH_3)_2Sn(OAc)_2$ AND $[(AcO)(CH_3)_2Sn]_2O$

Compounds	$J(^{117}Sn\text{-}CH_3)$ *(cps)*	$J(^{119}Sn\text{-}CH_3)$ *(cps)*	$\tau(Sn\text{-}CH_3)$ *(ppm)*[a]	$\tau(CH_3COO)$ *(ppm)*[a]
$(CH_3)_2Sn(OAc)_2$[b]	78.9	82.5	9.09	7.99
$[(AcO)(CH_3)_2Sn]_2O$[c]	83.2	86.8	9.20	8.05
	86.3	89.0	9.18	

[a] Tetramethylsilane τ 10.0 ppm. [b] 20% CCl_4. [c] 9% $CHCl_3$.

TABLE 3

RELEVANT INFRARED FREQUENCIES OF $R_2Sn(OAc)_2$
Positions of bands in cm^{-1}

$R=CH_3$		$R=C_2H_5$		$R=n\text{-}C_3H_7$		$R=n\text{-}C_4H_9$		*Assignments*
Crystal. film	*C_6H_{12} 7% soln.*	*Neat liquid*	*C_6H_{12} 5% soln.*	*Neat liquid*	*C_6H_{12} 5% soln.*	*Neat liquid*	*C_6H_{12} 5% soln.*	
1600 s 1560 s	1607 s	1600 s 1570 s	1607 s	1605 s 1570 s	1609 s	1605 s 1570 s	1609 s	CO_2 asym. str.
1438 sh	1433 sh 1405 sh	1422 sh	1425 sh 1400 sh	1432 sh	1425 sh 1400 sh	1425 s	1425 sh 1400 sh	CO_2 sym. str.[a]
1374 s	1380 s	1376 s	1378 s	1378 s	1377 s	1380 s	1377 s	
1334 s	1331 s	1330 s	1331 s	1332 s	1330 s	1333 m	1333 s	CH_3 deform.[a]
698 s	698 s	679 s 667 s	697 s 685 s	693 s 666 s	695 s	690 s	694 s	CO_2 scissor.
619 m	622 m	622 m	622 m	622 m	622 m	623 m	622 m	CO_2 out-of-plane bend.
571 m	574 m	542 m	542 m					SnC_2 antisym. str.
526 m	528 m	501 m	501 w					SnC_2 sym. str.
492 w	493 w	492 sh	492 w	492 w	491 w	491 w	490 w	CO_2 rock. (in plane)
304 s 280 sh	305 s	302 s 280 sh	304 s	303 s 281 sh	304 s	302 s	303 s	SnO str.

[a] The assignments were tentatively carried out considering the intensities.

TABLE 4

RELEVANT INFRARED VIBRATIONAL FREQUENCIES OF $[(AcO)R_2Sn]_2O$
Positions of bands in cm^{-1}

$R=CH_3$		$R=C_2H_5$		$R=n\text{-}C_3H_7$		$R=n\text{-}C_4H_9$			Assignments
Solid state	$CHCl_3$ 9% *soln.*	*Solid state*	$CHCl_3$ 5% *soln.*	*Solid state*	$CHCl_3$ 5% *soln.*	*Solid state*	C_6H_{12} 5% *soln.*	$CHCl_3$ 5% *soln.*	
	1630 s	1643 s	1627 s	1630 s	1627 s	1637 s	1639 s	1628 s	CO_2 asym. str.
	1605 m		1601 s		1601 s			1605 s	
1560 s	1562 s	1562 s	1564 s	1570 s	1564 s	1570 s	1571 s	1565 s	
1418 s	1426 s	1421 s	1421 s	1428 s	1422 s	1420 s	1422 s	1425 s	CO_2 sym. str. and CH_3 deform.
1398 sh	1378 s	1370 s	1379 s	1372 s	1378 s	1376 s	1373 s	1378 s	
1334 m	1319 s	1301 s	1332 s	1312 s	1328 s	1307 s	1306 s	1320 s	
666 s	[a]	684 s	[a]	675 s	[a]	671 s	675 s	[a]	CO_2 scissor.
656 s	[a]	668 s	[a]		[a]			[a]	
623 sh	645 s	645 s	630 s	640 s	[a]	652 s	641 s		SnO str. and CO_2 out-of-plane bend
610 s		613 m		625 sh	625 s	635 s	621 sh	621 s	
579 m	575 s								SnC_2 str.
	560 sh		560 w		558 w			558 m, br	SnO (monomer?)
530 s	525 m	542 w	543 m						SnC_2 str.
505 s	505 s	495 s	490 s	482 s	488 s	475 s	485 s	485 s	SnO ring[b] and CO_2 rock.
493 sh	481 sh	476 s							
300 s	278 s	300 s	295 s	311 s	313 s	292 s	292 s	292 s	SnO
				265 w			280 sh	280 sh	

[a] Not examined. [b] The assignment was made tentatively, because the positions and the shapes are similar to those of the SnO ring vibrations of $[XYSn(acac)(OCH_3)]_2$[30].

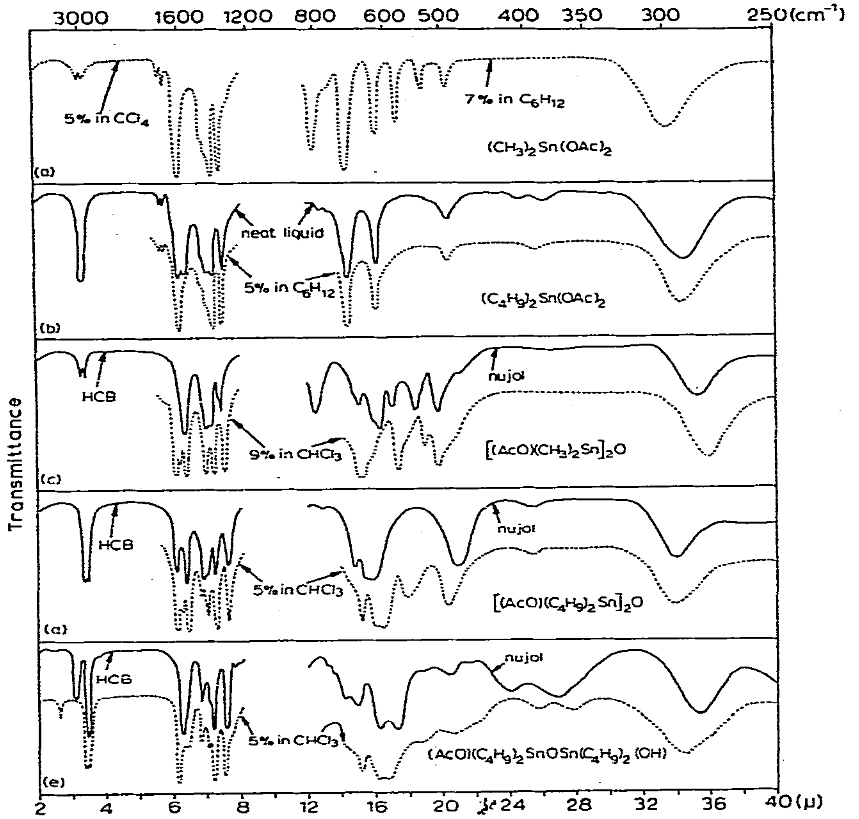


Fig. 2. The typical infrared spectra of dialkyltin diacetates and their derivatives. ——— solid or neat liquid, ----- solution.

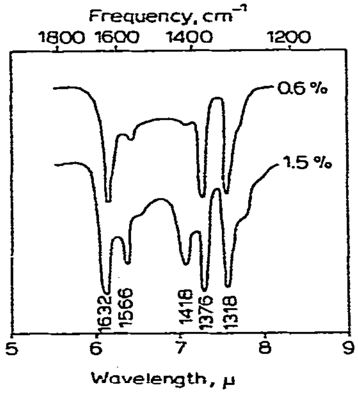


Fig. 3. The change of the relative intensities of CO_2 vibrational bands for $(AcO)(C_4H_9)_2SnOSn(C_4H_9)_2(OH)$ in benzene.

PMR spectra

PMR spectra were recorded for dimethyltin derivatives in chloroform at various temperatures (−50° to +50°) using a JNM-3H-60 spectrometer, and the results are listed in Table 2.

TABLE 5

RELEVANT INFRARED VIBRATIONAL FREQUENCIES OF $(AcO)R_2SnOSnR_2(OH)$
Positions of bands in cm^{-1}

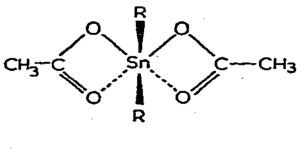
$R=C_2H_5$		*$R=n\text{-}C_3H_7$*		*$R=n\text{-}C_4H_9$*		*Assignments*
Solid state	*$CHCl_3$ 5% soln*	*Solid state*	*$CHCl_3$ 5% soln.*	*Solid state*	*$CHCl_3$ 5% soln.*	
3340 s	3670 w	3260 s	3670 w	3320 s	3660 m	OH str.
1610 s	1618 s	1600 s	1620 s	1605 s	1620 s	CO_2 asym. str.
	1565 w		1566 w		1570 w	
1421 w	1418 w		1414 w	1418 m	1416 sh	CO_2 sym. str. and CH_3 deform.
1386 s	1380 s	1388 s	1380 s	1385 s	1380 s	
1331 s	1325 s	1333 m	1325 m	1330 s	1327 s	
673 s		669 s		670 s		CO_2 scissor.
618 s	615 s	618 s	615 s	620 s	615 s	SnO and CO_2 out-of-plane bend.
589 s	595 s	580 s	595 s	585 s	597 s	
534 s	535 s		535 w, br	519 w	545 m, br	SnC_2 str. and SnO
495 m	492 m, br	488 w	482 m, br	488 w	483 m, br	CO_2 rock.
425 m	385 w	426 m	386 w	423 m	385 w	SnO and C–C–C bend.
378 m	360 w	377 m	360 w	373 m	360 w	
300 m	302 m	310 m	314 m	287 m	293 m	SnO

RESULTS AND DISCUSSION

Dialkyltin diacetates

The typical infrared spectra for these compounds are shown in Fig. 2(a) and (b). The positions of relevant absorption bands and their assignments made by referring to the spectra of sodium acetate[16] and the corresponding trialkyltin acetates[10,18], are listed in Table 3. The methyl and ethyl compounds in solution clearly showed two bands due to the SnC_2 antisymmetric and symmetric stretching vibrations, indicating that the C–Sn–C skeleton of these compounds may not be linear. The values of tin–proton coupling constants for the methyl compound listed in Table 2 suggests this conclusion, as discussed in the preceding communication[17]. Since dialkyltin diacetates are monomeric in benzene (Fig. 1), CO_2 vibrational bands appeared at the regions 1600–1610 cm^{-1} and 1370–1380 cm^{-1} could be attributed to a non-symmetrically chelated configuration of dialkyltin diacetates (I)[17].

In neat liquid or crystalline film, however, an additional band at about



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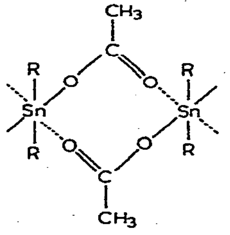
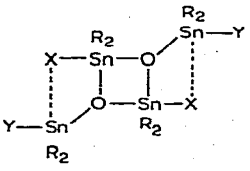


II



III

1565 cm^{-1}, and an increase in intensity of the bands at 1400–1440 cm^{-1}, were observed. The positions of these bands are almost the same as those of CO_2 vibrational bands of trialkyltin acetates in the solid state (1565–1572 cm^{-1} and 1408–1412 cm^{-1} respectively)[10,18], where acetoxy groups were found to form the bridge between two tin atoms by IR spectra[18] on X-ray analyses[19]. Hence, appearance of the additional CO_2 bands may indicate that there are bridging acetoxy groups (II) to some extent in the liquid or crystalline film.

A strong absorption band found at about 300 cm^{-1} for these compounds will be associated to Sn–O(Ac) stretching vibrations, considering that the SnO vibration band of trialkyltin carboxylates has been found[20,21] at 280–350 cm^{-1}.

General configuration of distannoxane

The structure of tetraalkyl-1,3-disubstituted distannoxanes[22] $XR_2SnOSnR_2Y$ (X, Y = electro-negative groups) have been suggested by the results of some physicochemical mearurements to have a dimeric configuration (III)[23,24,11]. If the substituents X (or Y) are coordinating groups [X = OH, Y = halogen[24], NCS[25], NO_3[26]; X, Y = NCS[25]; X, Y = $OSi(CH_3)_3$[27]], there are additional weak intramolecular coordinations.

Tetraalkyl-1,3-diacetoxydistannoxanes, $[(AcO)R_2Sn]_2O$

The butyl compound of this series was reported to be monomeric by Zemlyanskii *et al.*[6], but Alleston *et al.*[11] described it essentially as a dimer. As shown in Fig. 1, the butyl compound is almost dimeric at moderate concentrations in benzene, and its molecular weight decreases with dilution. This tendency was much clearer in chloroform. The methyl compound is hardly soluble in benzene but showed similar behavior in chloroform. This results from dissociation of a dimeric molecule to monomers and not from ionic dissociation of acetoxy groups, because an appreciable electric conductivity could not be observed in chloroform.

$$[(AcO)R_2SnOSnR_2(OAc)]_2 \rightleftarrows 2\ (AcO)R_2SnOSnR_2(OAc)$$

It has been pointed out by Zemlyanskii *et al.*[6], that the butyl compound showed the two kinds of CO_2 vibrational bands and they assumed these to originate from crystal effects. The infrared spectrum of this compound in cyclohexane or benzene, however, also showed these two kinds of CO_2 bands (Table 4). The same results were obtained for all the compounds of this series except the methyl compound which showed only one CO_2 band in the solid state [Table 4, Fig. 2(c)]. Therefore, it is clear that the splitting of the CO_2 bands is essentially due to the dimeric configuration, and not to the crystal effect. The exceptional behavior of the methyl compound in the solid state may be explained by the relatively small methyl groups which easily allow intermolecular acetoxy bridges as in the case of dialkyltin diacetates.

In the chloroform solution an additional CO_2 asymmetric stretching band appeared at 1600–1605 cm^{-1} for each compound. A spectral change was also reflected in the region of the skeletal SnO vibrations: In addition to the strong broad bands at 610–650 cm^{-1} (ref. 25) and 470–510 cm^{-1} (ref. 30), which are characteristic of the dimers, a broad band appeared at about 560 cm^{-1} in chloroform solution. Taking account of the molecular weight, these additional bands may be attributable to monomers.

PMR spectra of the methyl compound at 20° in 9% chloroform, where almost all species of the solute are dimeric, showed one sharp signal at τ 8.05 ppm assigned to methyl protons of acetoxy groups, and two almost overlapped signals at τ 9.18 and 9.20 ppm which are assigned to the methyl protons attached to tin (Table 2). Essentially the same spectra were observed from $-50°$ to $+50°$. It is remarkable that the chemical shifts of the two kinds of Sn-CH_3 are not so different as those of tetramethyl-1,3-bis(trimethylsiloxy)distannoxane ($\Delta\tau = 0.1$ ppm)[28]. The fact that we could not find two kinds of CH_3COO in the PMR spectra agrees with the result of Davies *et al.* for trialkyltin carboxylates[29].

Tetraalkyl-1-acetoxy-3-hydroxydistannoxanes, (AcO)R_2SnOSnR_2(OH)

The positions and the shapes of the OH stretching band and the SnO bands[25] at about 600 cm^{-1} of these compounds shown in Table 5 and Fig. 2(e) are indicative of the dimeric configuration (III) as was indicated in $XR_2SnOSnR_2(OH)$ (X = halogen)[24].

The only CO_2 asymmetric stretching band in the solid state splits into two bands in solution. In the case of the butyl compound, the molecular weight in benzene (Fig. 1) and the relative intensity of the infrared bands (Fig. 3) at 1566 and 1418 cm^{-1}, which might be associated with the bridging acetoxy groups, increase with increasing concentrations. Since the position of the OH band at 3660 cm^{-1} did not show an appreciable change in these conditions, it is considered that the association of the dimers may occur through acetoxy bridges.

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SUMMARY

A series of dialkyltin diacetates and their derivatives, $R_2Sn(OAc)_2$, $[(AcO)R_2Sn]_2O$ and $(AcO)R_2SnOSnR_2(OH)$ ($R = CH_3, C_2H_5$, n-C_3H_7, n-C_4H_9), have been prepared. Dialkyltin diacetates are monomeric in benzene, having a nonsymmetrically chelated octahedral configuration; bridging of acetoxy groups seems to occur in the neat liquid or in the crystalline state. The compounds $[(AcO)R_2Sn]_2O$ are dimeric at moderate concentrations and dissociate to monomers in dilute benzene and chloroform solutions. This change is reflected in changes of the CO_2 and SnO infrared bands. The dimeric methyl compound showed two tin–methyl proton chemical shifts with a small difference. Molecular weight of $(AcO)(C_4H_9)_2SnOSn(C_4H_9)_2(OH)$ increases with concentration from that of dimer. This seems to be caused by the bridging of the acetoxy groups among dimers.

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