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SYNTHESIS AND STRUCTURE OF 1,1,2,2-TETRAPHENYL-1,2-BIS-(TRIPHENYL-SILANOXY)- AND -GERMANOXY)-DITIN COMPOUNDS

GUALTIERO PLAZZOGNA, VALERIO PERUZZO and GIUSEPPE TAGLIAVINI
Institute of Analytical Chemistry, University of Padua, 35100 Padua (Italy)

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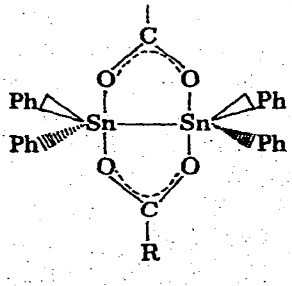
Summary

Compounds of the general formula $Ph_4Sn_2(OOCR)_2$ (R = Et, n-Pr, i-Pr, t-Bu, CH_2Ph) have been prepared. The IR spectra and molecular weights indicate that these compounds exist in solution as monomeric species with a carboxylate group bridging two tin atoms.

The analogous compounds, $Ph_4Sn_2(OOCMPh_3)_2$ (M = C, Si and Ge) also appear to be monomeric in solution. The IR spectra of the silicon and germanium derivatives are consistent with the existence of $(d—p)\pi$ bonding interaction between the silicon or germanium and carbonyl—oxygen atoms.

Introduction

A previous study [1] showed that 1,1,2,2-tetraphenyl-1,2-bis(acyloxy) ditins of the type $Ph_4Sn_2(OOCR)_2$ (R = CH_3, CH_2Cl, $CHCl_2$, CCl_3, CF_3) are monomeric in solution. The carboxylate ligand in these compounds acts as a bridging group between two tin atoms, as in (I).



(I)

A preliminary X-ray investigation [2] has shown that the acetate $Ph_4Sn_2(OOCCH_3)_2$ is a binuclear five-coordinate tin complex, having a slightly distorted trigonal-bipyramidal configuration with two phenyl groups and a tin atom occupying equatorial positions, and oxygen atoms in axial sites, as in (I). Tin-119 *m* Mössbauer spectroscopy [3] has provided additional information concerning the electron density and site symmetry at the tin nucleus for several $Ph_4Sn_2(OOCR)_2$ compounds ($R = CH_3$, CH_2Cl, $CHCl_2$, CCl_3, CF_3, Ph). The observed ρ values ($\rho = \Delta/\delta$) in the range 2.12 - 2.45 satisfy Herber's criterion [4] for pentacoordinate tin in all the compounds examined.

As an extention of previous studies [1] on the behaviour of the carboxylate ligand, we have prepared some other $Ph_4Sn_2(OOCR)_2$ compounds, with R = Et, n-Pr, i-Pr, t-Bu, CH_2Ph, by the method previously described [5]. It thus appeared of interest to prepare the series of compounds $Ph_4Sn_2(OOCMPh_3)_2$ (M = C, Si and Ge), in order to see how the positions of the infrared absorptions are affected by the possibility of interaction between the unshared electrons of the oxygen atom of the carbonyl group and the available *d*-orbitals of silicon and germanium.

Experimental

Materials

Triphenylacetic acid, diphenyltin dichloride, triphenylchlorosilane and triphenylbromogermane were obtained from Schuchardt (München) or Alfa Inorganics, Ventron (USA).

All chemicals and solvents were of reagent grade. IR spectra were recorded on a Perkin—Elmer Model 457 equipped with KBr optics. Molecular weights were determined in chloroform with a Mechrolab Model 302B vapour phase osmometer.

Preparation of $Ph_4Sn_2(OOCR)_2$ compounds

The compounds $Ph_4Sn_2(OOCR)_2$ (R = Et, n-Pr, i-Pr, t-Bu, Ph, Ph—CH_2 and Ph_3C) were prepared by the reaction of diphenyltin dihydride in ether with the appropriate acid according to the method of Sawyer and Kuivila [5]. Analytical and physical data of the compounds are listed in Table 1.

Preparation and characterization of $Ph_4Sn_2(OOCMPh_3)_2$ compounds (M = Si, Ge)

20 ml of an ether solution containing about 5 mmol of diphenyltin dihydride was treated with 1.21 g (4 mmol) of triphenylsilane carboxylic acid prepared as previously reported [9,10]. During 24 h hydrogen was evolved in the expected amount and a crystalline colourless product was formed, to give after filtration, 1.15 g of crude product. Recrystallization from chloroform—petroleum ether (40 - 70°) gave a final product $Ph_4Sn_2(OOCSiPh_3)_2$ (II) melting at 176 - 178°. (Found: C, 64.15; H, 4.25. $C_{62}H_{50}O_4Si_2Sn_2$ calcd.: C, 64.58; H, 4.37%. Mol. wt. found in chloroform, 1080; calcd.: 1151.9.)

The same procedure was used to prepare the $Ph_4Sn_2(OOCGePh_3)_2$ compound (III), m.p. 185 - 187°. (Found: C, 59.61; H, 4.10. $C_{62}H_{50}O_4Ge_2Sn_2$ calcd.: C, 59.97; H, 4.03%. Mol. wt. found in chloroform, 1170; calcd.: 1240.6.)

Compounds (II) and (III) show a band at 1110 and 1090 cm^{-1} respectively, corresponding to the "metal-sensitive" C—H out-of-plane bending vibra-

TABLE 1

ANALYTICAL AND PHYSICAL DATA FOR $Ph_4Sn_2(OOCR)_2$ COMPOUNDS

R	M.p. (°C)	Yield (%)	Analysis found (calcd.) (%)		Mol.wt. found[a] (calcd.)
			C	H	
Et	155	75	51.90 (52.06)	4.56 (4.30)	644 (691)
n-Pr	140	70	53.54 (53.30)	4.77 (4.76)	704 (719)
i-Pr	148	78	53.50 (53.30)	4.71 (4.76)	727 (719)
t-Bu	166	62	54.43 (54.50)	5.14 (5.20)	776 (747)
Ph[b]	184	64	58.20 (57.92)	3.71 (3.84)	742 (787)
CH_2—Ph	151	69	59.16 (58.80)	4.21 (4.10)	782 (815)
CPh_3	230	58	68.83 (68.60)	4.61 (4.46)	1070 (1119)

[a] Extrapolated values for C→0 determined in chloroform solution in the concentration range 2.5—20 mg/ml.
[b] This compound has been prepared previously [5].

tions [11,12]. In both spectra a band at 1070 cm^{-1} is also present, and arises from the same deformation with tin as the substituent.

The two compounds were also treated with concentrated aqueous sodium hydroxide. After filtration of a solid residue, which was identified as Ph_2SnO, the filtrate was acidified with HCl and the resulting solution was extracted with ethyl ether. Distillation of the organic layer gave triphenylsilane or triphenylgermane carboxylic acid.

TABLE 2

CARBOXYLATE GROUP FREQUENCIES (cm^{-1}) OBSERVED IN $Ph_4Sn_2(OOCR)_2$ COMPOUNDS IN NUJOL MULLS AND IN CHLOROFORM SOLUTION

R	Medium	$\nu_a(COO)$	$\nu_s(COO)$
Et	Nujol $CHCl_3$	1525 1520	1410 1400
n-Pr	Nujol $CHCl_3$	1525 1520	1405 1405
i-Pr	Nujol $CHCl_3$	1525 1520	1410 1410
t-Bu	Nujol $CHCl_3$	1515 1520	1415 1420
Ph	Nujol $CHCl_3$	1515 1520	1390 1395
CH_2—Ph	Nujol $CHCl_3$	1525 1525	1415 1420
CPh_3	Nujol $CHCl_3$	1535 1535	1355 1355
$SiPh_3$	Nujol $CHCl_3$		
$GePh_3$	Nujol $CHCl_3$		

Results and discussion

The ditin compounds listed in Table 1, and 1,1,2,2-tetraphenyl-1,2-bis(triphenylsilanoxy)ditin (II) and 1,1,2,2-tetraphenyl-1,2-bis(triphenylgermanoxy)-ditin (III) are monomers in chloroform as are the compounds of the type $Ph_4Sn_2(OOCR)_2$ (R = CH_3, CH_2Cl, $CHCl_2$, CCl_3, CF_3) previously studied [1]. The IR spectra of solutions are very similar in all cases to those recorded on Nujol mulls (cf. Table 2): the asymmetric and symmetric COO stretching vibrations do not change their positions, and it seems reasonable to attribute structure (I) to all the compounds.

It is noteworthy that the values of ν_a(COO) and ν_s(COO) stretching vibrations given in Table 2 are only slightly dependent on the nature of the carboxylate R groups. On the contrary, a shift of the two COO stretching vibration bands [ν_a(COO) from 1530 to 1625 cm^{-1} for $Ph_4Sn_2(OOCCH_3)_2$, and ν_s(COO) from 1405 to 1336 cm^{-1} for $Ph_4Sn_2(OOCCF_3)_2$)] [1,13] was observed for the compounds with R = CH_3, CH_2Cl, $CHCl_2$, CCl_3 and CF_3, this was ascribed to the fact that increase in the electron withdrawing power of the R groups strengthens the CO bands, with parallel weakening of the Sn—O bonds [13].

The two compounds $Ph_4Sn_2(OOCMPh_3)_2$ (M = Si and Ge) exhibit unusual behaviour in that the COO absorption bands are absent in the expected region 1700 - 1500 cm^{-1}. Absence of COO absorption bands has previously been reported for the following compounds: *sym*-tetraphenylbis(aroyloxy)ditin [14], *sym*-tetraphenylbis(benzoyloxy)ditin [15] and some other organotin carboxylates [16]. In our case a reasonable explanation may be based on the consideration that in the Ph_3MCOO moiety (M = Si and Ge) $(d—p)\pi$ bonding

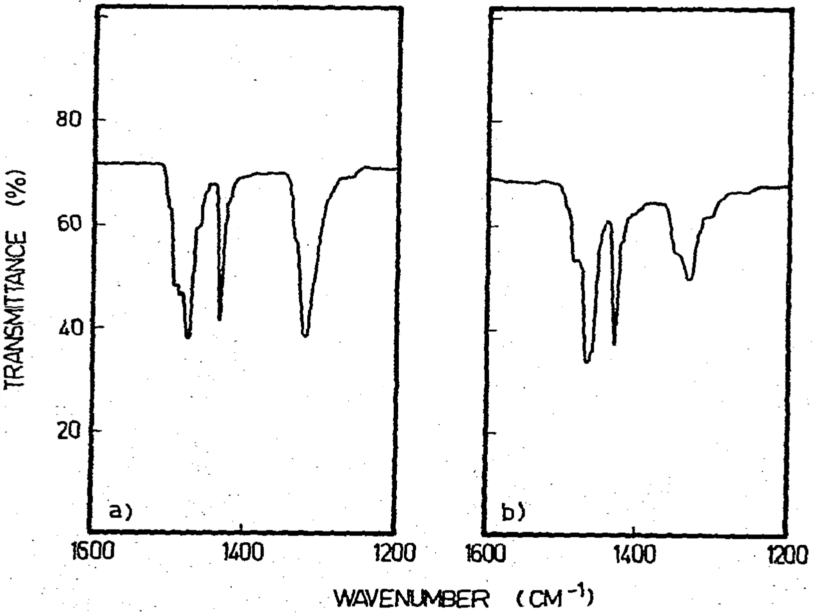


Fig. 1. IR spectra in chloroform solution (20 mg/ml), optics: KBr, 0.1 mm. (a) 1,1,2,2-tetraphenyl-1,2-bis(triphenylsilanoxy)ditin. (b) 1,1,2,2-tetraphenyl-1,2-bis(triphenylgermanoxy)ditin.

occurs involving *p*-orbitals of the COO group and the vacant *d*-orbitals of silicon and germanium [6]. Such interaction is known to cause a shift of the COO vibration bands to lower wavenumbers: a shift of 51 cm^{-1} is observed [17] for the carbonyl stretching frequency on going from trimethylacetic acid (1693 cm^{-1}) to trimethylgermanecarboxylic acid (1642 cm^{-1}). Furthermore, absorption maxima for Ph_3MCOCH_3 (M = Si, Ge) [18] are shifted by 66 and 41 cm^{-1} with respect to that of Ph_3CCOCH_3, which occurs at 1710 cm^{-1}.

In the light of the above considerations, it seems probable that the position of the ν_a(COO) stretching vibration of the compounds (II) and (III) must be shifted to wave numbers about 50 - 65 cm^{-1} less than that for the compounds having M = C. Since the ν_a(COO) bond of $Ph_4Sn_2(OOCCPh_3)_2$ occurs at 1535 cm^{-1} (*cf.* Table 2), the corresponding absorption bands of compounds (II) and (III) should be found in the approximate range 1490 - 1470 cm^{-1}. The poorly resolved IR pattern in this region shown in Fig. 1, may be attributed to overlap of the ν_a(COO) bands of compounds (II) and (III) with ν(CC) bands [19,20].

It is concluded that the IR pattern of the compounds containing silicon and germanium is indicative of the existence of a $(d{-}p)\pi$ bonding between the metal and the carbonyl—oxygen atoms.

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